

Optimization of Pollutants Removal from Textile Wastewater by Electrocoagulation through RSM

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Abstract

This study concerns with electrochemical technique known electrocoagulation used to treat a high polluted effluent whereby sacrificial anodes corrode to release active coagulant precursors into the solution. Response Surface Methodology (RSM) was applied in the development of modeling, statistical analyzing, and interpreting the resulted treatment data of textile wastewater by electrocoagulation, besides response, residual, probability, surface and contour plots. A central composite design has been used for the simultaneous study of the effects of operation time and the current density on electrocoagulation responses. The effectiveness of the considered design parameters was well examined to find the optimum experiments with less lack of fit. Models to perform simulated regressions with one response gives the best fitted equation of second-order functions of two factor variables that has been obtained to find optimum removals. The optimum conditions for predicted maximum COD, TSS and Turbidity removals were found to be (56.54 min. and 20mA/cm²), (53.13 min. and 20 mA/cm²) and (54.74 min. and 20 mA/cm²), respectively.

Keywords: Electrocoagulation (EC), RSM, CCD, Model, ANOVA, Optimization.

الخلاصة

هذه الدراسة تتضمن استخدام الطريقة المسماة التخثير الكهروكيميائي وهي تقنية كهروكيميائية تستعمل لمعالجة المياه الصناعية المتدفقة ذات المستويات العاليه من التلوث باستخدام أقطاب تضحية من الحديد تتأكل لإنتاج مادة مخثرة نشيطة ترتبط مع الملوثات لترسيبها. تم تطبيق منهج الاستجابة السطحية لتحليل نتائج معالجة المياه الملوثة الناتجة من الصناعة النسيجية باستخدام منظومة مختبرية تعمل بطريقة الوجبات ولعدد من الملوثات مثل المواد الصلبة العالقة الكلية، متطلب الكيمياء للأوكسجين، والكلور. من خلال منهج الاستجابة السطحية استخدم تصميم التوليف المركزي لتحديد نوع وعدد التجارب المطلوبة التي تعطي أفضل موديل رياضي لنسبة الأزالة لكل ملوث بدلالة متغيرين هما كثافة التيار وزمن التشغيل، وبالتالي تم تحديد الظروف التشغيلية المثلى لأعلى معدل أزالة لكل ملوث.

الكلمات المفتاحية: الكهربي (EC)، نموذج، ANOVA، الامثل.

1. Introduction

Water has traditionally been our most available resource and one that has been generally taken for granted. That is quickly changing. The availability of water, its cost and the treatment of wastewater are growing areas of concern. Textile industry is one of the largest industrial of wastewaters, which uses massive amounts of water in the production process. Textile wastewater is well known with its high COD, strong color, bulky TSS, variable pH, salt content and sometimes, heavy metal. The textile industry generally has difficulty in meeting wastewater discharge limits, due to its high and various pollutants percent. Therefore, the treatment systems combined with physical, biological and chemical methods become inefficient for the effective treatment (Chen et al., 2005). However, with regulations becoming increasingly stringent, industrial users are searching for more advanced methods to solve their wastewater treatment problems. When feasible in the facility design, the electrochemical process may be joined with other processes to provide a substantial water reuse capability (Chithra et al., 2008).

In recent years, electrocoagulation process (EC) has received increasing attention concerning its potential for destruction and removal of organic and non-organic pollutants in wastewater, and could eliminate adding expensive chemicals to the wastewater and would subsequently generate less solid waste, thus saving on disposal costs (Mollah et al. 2001). Response surface methodology (RSM) which is a technique for designing experiment helps researchers to build models, evaluate the effect of several factors and achieve optimum conditions for desirable responses (Khuri and Cornell, 1996). (RSM) was employed to investigate the effects of pH and

current density on the removal of cadmium, copper and zinc in artificial wastewater with high COD by electrocoagulation technique (Suárez and Agudelo, 2011). Six iron electrodes were used in 2 liters reactor with agitation. A regulated AC/DC power supply was used to maintain a constant voltage/current. Vepsäläinen et al., 2009, investigated the removal of natural organic matter (NOM) from surface water by electrocoagulation (EC) using (RSM). Factors used in the empirical model were electric charge per liter, initial pH and temperature. Relevant square and interaction terms of factors were studied. Based on analysis of variance (ANOVA), the model fitted well with dissolved organic carbon (DOC) reduction, aluminum dissolving and pH changes.

Arslen-Alton et al., 2009, concluded that the central composite design was used to optimize CI Acid Blue 193 treatment by electrocoagulation. They explained that central composite design is capable of achieving maximum color, COD and TOC removals by manipulating the pH, current density and treatment time by means of a response surface quadratic model. In the same manner, Ölmez, 2009, studied hexavalent chromium removal with stainless steel electrodes with electrocoagulation by (RSM), and concluded that complete treatment could be accomplished.

The production of biodiesel through a transesterification method produces a large amount of wastewater that contains high levels of chemical oxygen demand (COD) and oil and grease (O&G), currently, flotation is the conventional primary treatment for O&G removal prior to biological treatments. Chavalparit and Ongwandee, 2009, studied EC process, which was adopted to treat the biodiesel wastewater. The initial pH, applied voltage and reaction time on the EC process for the removal of COD, O&G and suspended solids (SS) were investigated using one factor at a time experiment. Furthermore, the Box-Behnken design, an experimental design for (RSM), was used to create a set of 15 experimental runs needed for optimizing of the operating conditions. Quadratic regression models with estimated coefficients were developed to describe the pollutant removals.

İLHAN et al., 2009, conducted experiments with several operational conditions for the removal of organics pollutants from leachate using (RSM). They determined the effects of EC process on the removals of COD, BOD and TOC pollutants. Experimental results showed that EC process is not only applicable to the treatment of biodegradable organics but also all other organics. The optimum operational conditions for the removal of organic pollutants were predicted and optimized models were developed to estimate the organic removal rate.

Aleboye et al., 2008, described the removal of C.I. Acid Red 14 azo dye by electrocoagulation batch process using (RSM). They found a treatment condition obtained within an electrocoagulation batch reaction under a 23 full factorial central composite face center design, where a second-order regression model was used. Bhatti et al., 2009, determined the performance for treatment of Cr (VI) from simulated wastewater using Al-Al electrodes. They concluded that electrocoagulation could reduce Cr (VI) by 90.4% at a specific condition using (RSM). The results for optimization were compared using coefficients of determination.

Ghafari, et al., 2009, investigated the treatment of stabilized leachate from (PBL) site using poly-aluminum chloride (PAC) and alum in coagulation-flocculation process. The removal efficiencies for COD, turbidity, color and TSS obtained were compared with those obtained using alum as conventional coagulant and a central composite design (CCD) and (RSM) were applied to optimize the operating variables viz. coagulant and pH. Quadratic models developed for four responses studied indicate the optimum conditions to PAC dosage. Trinh et al., 2010, demonstrates an experimental design using (RSM) that was applied as an alternative to conventional methods for the optimization of coagulation tests. A central composite design was

used to build a model for evaluating and optimizing the coagulation process. Mathematical model equations were derived by computer simulation programming with a least squares method. In these equations, the removal efficiencies of turbidity and total organic carbon (TOC) were expressed as second-order functions of two factors, such as alum dose and pH.

In the present study, a previously experimental data of textile wastewater plant located in Al-Hilla-Iraq, obtained by electrocoagulation with carbon steel electrodes was applied by response surface methodology (RSM) to accomplish relationships between the removals of COD, TSS and Turbidity as responses and the operating conditions affecting the EC process (operation time and current density) as factor variables at ambient temperature of 25°C and initial pH of 4.52. In addition, the methodology was utilized to predict the optimum values for these operating variables in order to obtain the maximum values of pollutant removal.

2. Materials and Methods

2.1 Apparatus

The electrocoagulator cell used was 1500 ml glass reactor with upper Teflon cover contains four glands for electrodes fixation and equipped with magnetic stirrer without temperature control. The total operation time was established of 60 minute using DC power supply of 30 V and a current controlled via rheostat. A set of current densities of 4, 8, 10, 12, 16 and 20 mA/cm² were tested at ambient temperature of 25°C and initial pH of 4.52. Pollutant removal percent was examined using two factor variables: current density mA/cm² and EC operation time (min.). The experimental set up was previously mentioned with a schematic diagram, (Ajjam and Ghanim, 2012).

2.2 Experimental Procedure

In each run, 1 liter of textile wastewater sample was used to treat by electrocoagulation process. Two electrodes of iron with surface area of 20 cm² were utilized. The gap between the anode and the cathode was kept at 5 cm. Controlled direct current was supplied by a DC power supply (ATTEN DC power supply type APR 3002A of 0-30V). The current was kept invariant in each test by a rheostat (Wheatstone Type 2755-Japan) and measured by an ammeter (Aswar DT830D, China). The solution in the reactor was stirred by a magnetic plate stirrer with teflon bar at a rotating velocity of 500 rpm (HP-3000). In all experiments, the impeller speed was fixed at 500 rpm to avoid mass transfer limitations on the process. Then a current density was applied for various time periods (ranging from 5 to 60 min.). Treated wastewater samples were collected after settling for 60 min. to estimate the effect of EC treatment on removals of COD, TSS and Turbidity (Moh Faiqun et al., 2007). In each experimental run, after settling, about 50 ml supernatant sample was collected for laboratory analysis (Ajjam and Ghanim, 2012).

2.3 Analytical Methods

Turbidity of the solutions were measured by mean of Turbidimeter (HACH 2100P). Chemical Oxygen Demand COD was measured following titration method according to the Standard Methods for Examination of Water and Wastewater (APHA, American Public Health Association 2000). Total suspended solids TSS was also measured by standard method 2540D (APHA, American Public Health Association 2000). The calculation of COD, TSS and Turbidity removals after electrocoagulation treatment were performed using the following formula (Carneiro, P.A., 2003):

$$\%C_R = [(C_o - C)/C_o] \times 100 \quad (1)$$

Where C_R is contaminant removal, C_o and C are concentrations of wastewater before and after electrocoagulation.

2.4 Data Analysis

The treatment of high strength textile wastewater located in Al-Hilla-Iraq using a batchwise mode by electrocoagulation was developed and optimized following the response surface methodology (RSM). The response surface methodology was applied to optimize the most two important operating variables; current density and operation time that have a significant influence on the EC process and also to optimize the process efficiency. As the Chemical Oxygen Demand (COD), Total Suspension Solid (TSS) and Turbidity are the most undesirable pollutants in textile wastewater (Can et al., 2006; Daneshvar et al., 2006; Chithra et al., 2008); the response of the pollutant removal percent was chosen to be a function indicator for the effectiveness of electrocoagulation on textile wastewater treatment.

Selection of the experiment factor levels was carried out based on results obtained according to the previous study (Ajjam and Ghanim, 2012). The selected operation time levels of 20, 40 and 60 min., interferes sequentially with the effective current density levels of 10, 15 and 20 mA/cm², were conducted the experimental set. In this sense, 14 runs of each pollutant were established for the prediction of responses using central composite design (CCD).

2.5 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 (Montgomery, 2005; Bradley, 2007; Khuri and Mukhopadhyay, 2010). When process factors satisfy an important assumption that they are measurable, continuous, and controllable by experiments, with negligible errors (İLHAN et al., 2009; Trinh and Kang, 2010), the present RSM procedure was carried out as follows:

- 1) A series of 14 experiments were designed of reliable measurement for each of COD, TSS and Turbidity removal responses.
- 2) Mathematical models of the second-order response surface were developed.
- 3) The optimal set of experimental factor variables producing the maximum response values was determined.

A central composite design (CCD), which is a very efficient design tool for fitting second-order models (Dean and Voss, 1999; Montgomery, 2005), was selected for use in this study. The number of tests required for a CCD include: the standard 2^k factorial (cube) points, $2k$ axial points fixed axially at a distance, say α , from the center to generate quadratic terms, and replicate tests at the center of experimental region; where k is the number of factors. Thus, the total number of design points in a CCD is $n = 2^k + 2k + n_c$. The values of α (the axial distance) and n_c , the number of center-point replications, are chosen so that the CCD can acquire certain desirable properties causes the CCD to be rotatable. A CCD for 2 factors (operation time and current density), with 1 replicates at the center and 2 blocks resulting cube points $2^k = 4$, axial points $2k = 4$ and center points in cube = 3, center points in axial = 3, so $n_c = 6$ and the total $4+4+6 = 14$ runs, with α designated to be 1.

In order to obtain the optimum operation time and current density, three dependent parameters were analyzed as responses; COD, TSS and Turbidity removals. 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 (Montgomery, 2005; Khuri and Mukhopadhyay, 2010) according to Eq. (2):

$$Y = f(x) = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \sum_{j=1}^k \beta_{ij} x_i x_j + \sum_{i=1}^k \beta_{ii} x_i^2 \quad (2)$$

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. Analysis of variance (ANOVA) was used for graphical analysis of data to obtain the interaction between factors and responses. 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 (Montgomery, 2005). 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 15), also used to find the residuals, 3-D surface and 2-D contour plots of the response models.

3. Results and discussion

3.1 Statistical Analysis

The relationship between the two factor variables and the three responses for EC process was analyzed using response surface methodology (RSM). The CCD shown in Table (1) allowed the development of mathematical equations where predicted responses Y was assessed as a function of operation time and current density. Once the desired value ranges of the factors had been defined by CCD, they were coded to lie at ± 1 for the factorial points, 0 for the center points (Dean and Voss, 1999; Montgomery, 2005). This study involves 24 runs of experiment for each response. The CCD reduces the number of experimental trials, however 14 runs were performed with five being repeatability tests for each response. All experimental results were treated and interpreted by statistical analysis, modeling and optimal design.

Table (1) Data Matrix and CCD Results

Turbidity Removal Percent		TSS Removal Percent		COD Removal Percent		Current Density (mA/cm ²)	Time (min.)	Block	Run No.
Exp.	Pred.	Exp.	Pred.	Exp.	Pred.				
90.1	91.68	83.3	82.33	85.2	85.64	20[1]	60[1]	1	1
62.0	60.41	43.5	44.80	58.1	57.95	10[-1]	60[1]	1	2
80.5	77.74	65.2	65.50	72.1	72.48	20[1]	20[-1]	1	3
59.4	58.21	41.3	42.45	57.1	57.72	10[-1]	40[0]	2	4
43.5	46.47	30.2	27.76	49.5	50.14	10[-1]	20[-1]	1	5
79.1	79.20	63.2	63.10	70.5	70.48	15[0]	40[0]	1	6
88.3	89.47	79.8	80.27	83.8	83.25	20[1]	40[0]	2	7
67.7	67.47	46.3	48.23	63.7	61.83	15[0]	20[-1]	2	8
79.3	79.50	63.5	63.20	70.2	70.48	15[0]	40[0]	1	9
62.2	60.69	43.2	44.40	58.6	57.95	10[-1]	60[1]	1	10
43.4	46.48	30.3	27.92	49.3	50.14	10[-1]	20[-1]	1	11
90.1	91.68	83.1	82.10	85.4	85.64	20[1]	60[1]	1	12
80.3	77.70	65.5	65.95	72.5	71.80	20[1]	20[-1]	1	13
81.2	81.41	65.6	66.20	72.3	73.52	15[0]	60[1]	2	14

3.2 Model Fitting

Observed responses were utilized to conduct models using response surface methodology (RSM) (Montgomery, 2005; Lenth, 2009). The three responses (COD, TSS and Turbidity removals) were 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 experimental observations of the responses: COD removal percent (Y_1), TSS removal percent (Y_2), and Turbidity removal percent (Y_3) and quadratic regression models were obtained, as shown in Eq.'s (3), (4) and (5) for Y_1 , Y_2 , and Y_3 , respectively:

$$Y_1 = 13.9875 + 0.8220 X_1 + 2.1233 X_2 - 0.0092 X_1^2 + 0.0107 X_1 X_2$$

(3)

$$R^2 = 0.9946, R^2_{(pred)} = 0.9633, R^2_{(adj)} = 0.9922$$

$$Y_2 = -51.4333 + 1.6908 X_1 + 5.8333 X_2 - 0.01587 X_1^2 - 0.06800 X_2^2$$

$$(4) \quad R^2 = 0.9941, R^2_{(pred)} = 0.9752, R^2_{(adj)} = 0.9915$$

$$Y_3 = -48.9333 + 1.3007 X_1 + 9.5608 X_2 - 0.0119 X_1^2 - 0.2145 X_2^2$$

$$(5) \quad R^2 = 0.9876, R^2_{(pred)} = 0.9431, R^2_{(adj)} = 0.9821$$

Where: X_1 is Time factor, X_2 is current density factor and X_1X_2 is interaction factor.

The results obtained were then analyzed by ANOVA to assess the "goodness of fit". The first 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 major effect on COD removal were the linear effect of operation time and current density factors, having p-values of 0.000, followed by operation time quadratic factor, operation time×current density interaction factor and current density quadratic factor, with p-values of 0.000, 0.022 and 0.118, respectively. Whilst, the factors with major effect on TSS removal were the linear effect of operation time and current density factors, having p-values of 0.000, followed by operation time quadratic factor, current density quadratic factor and operation time×current density interaction factor, with p-values of 0.000, 0.021, and 0.057, respectively. In addition, the factors with major effect on turbidity removal were the linear effect of operation time and current density factors, having p-values of 0.000, followed by operation time quadratic factor, current density quadratic factor and the interaction factor, with p-values of 0.000, 0.000, and 0.052, respectively.

Accordingly, equations from the first ANOVA analysis were modified by eliminating the terms found statistically insignificant (high p-value). Table (2) illustrates the modified quadratic models in terms of statistical parameters; standard error, T-test and probability value. Data given in this table demonstrates that all the models were significant at the 95% confidence level since p-values were less than 0.05. However, in the second ANOVA the quadratic factor time×current density predicts p-value (0.031) on COD removal and quadratic current density factor predicts p-value of (0.0063) on TSS, (0.000) on turbidity removal, while other quadratic factors with high p-values were excluded.

The difference between first and second ANOVA implies that the models were 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 (coded unit)

Turbidity Removal Percent			TSS Removal Percent			COD Removal Percent			Term
P	T	SE	P	T	SE	P	T	SE	
0.64	123.61	0.000	0.51	121.5	0.000	0.29	236.6	0.000	Constant
0.68	10.21	0.000	0.55	15.25	0.000	0.34	14.49	0.000	Time
0.68	22.91	0.000	0.55	34.36	0.000	0.34	37.12	0.000	Current Density
0.99	-4.79	0.001	0.80	-7.902	0.000	0.45	-8.06	0.000	Time*Time
0.99	-5.40	0.000	0.80	-2.11	0.006				C.Dens.*C.Dens.
						0.42	2.55	0.031	Time*C.Density

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

3.3 Validation of Model

The response surface models were developed in this study with values of R^2 higher than 98%, say 99.46, 99.41% and 98.76 for COD, TSS and turbidity removals, respectively. Furthermore, an R^2_{adj} close to the R^2 values insures a satisfactory adjustment of the quadratic models 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) (Dean and Voss, 1999; Montgomery, 2005). In this study high regression coefficient (R^2) values were predicted and give a reasonable conformity with adjusted R^2 , and ensure a satisfactory agreement of the quadratic model to the experimental data.

Graphical method usually used to validate models, and also characterizes the nature of residuals of the models. A residual is defined as the difference between an observed value Y and its fitted $\hat{Y}$ (Montgomery, 2005). In the normal probability plot, this was used to check the normality distribution of the residuals as shown in Figs. 1, 2, and 3. The error distribution may be slightly skewed, with the right tail being equal or longer than the left. Usually, the normal probability plot has a tendency to bend up or down slightly on the left or right sides implies that the error distribution is somewhat thinner than would be anticipated in a normal distribution (Montgomery, 2005); that is, the negative residuals are not quite as large (in absolute value) as expected.

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. A simple check is to plot the residuals versus the fitted values $\hat{Y}$ (Montgomery, 2005; Bradley, 2007; Trinh et al., 2010); these plots should not reveal any obvious pattern. The plots of residuals versus the fitted COD, TSS and Turbidity removal responses were shown in Figs. 4, 5 and 6 indicates more or less than or equal to its value, along a fitted distribution line (the horizontal straight line) and no unusual structure is apparent.

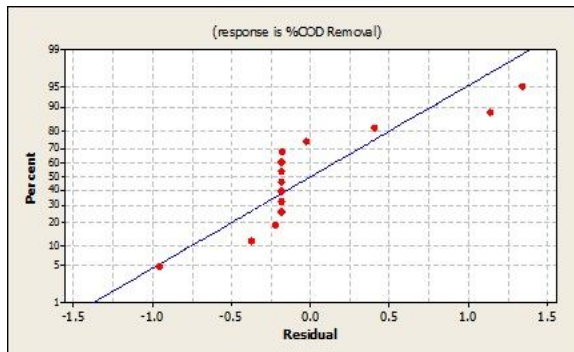


Fig.1 Normal Probability of %COD Removal Response Removal Response

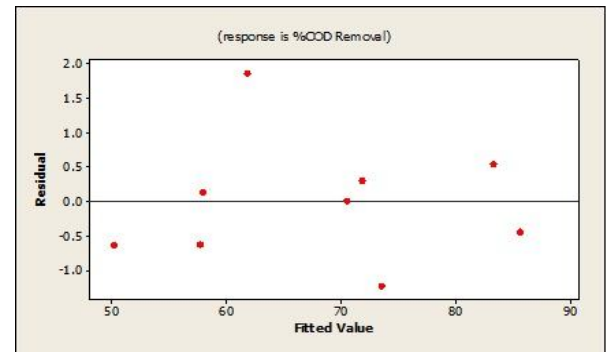


Fig.4 Residuals vs. Fits of %COD

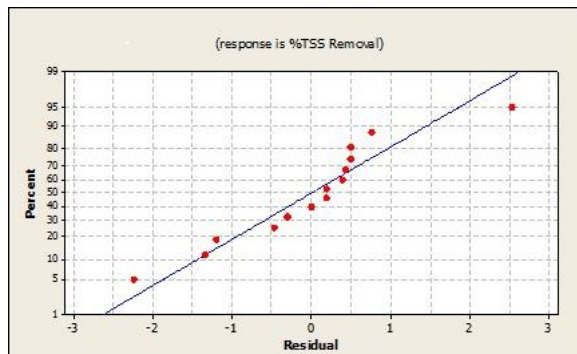


Fig.2 Normal Probability of %TSS Removal Response Removal Response

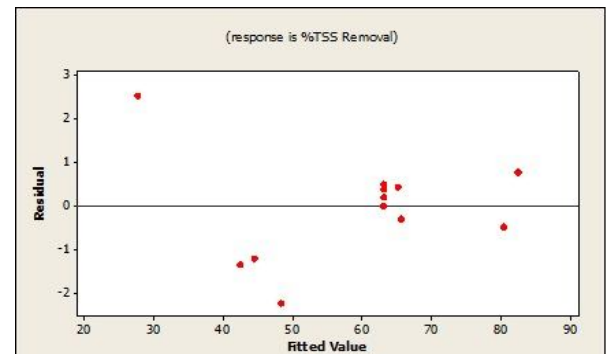


Fig.5 Residuals vs. Fits of %TSS

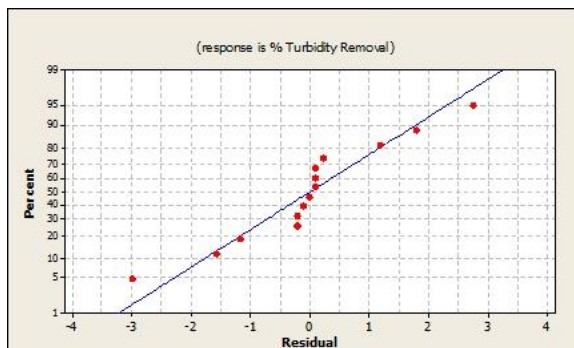


Fig.3 Norm. Prob. of %Turbidity Removal Response Removal Response

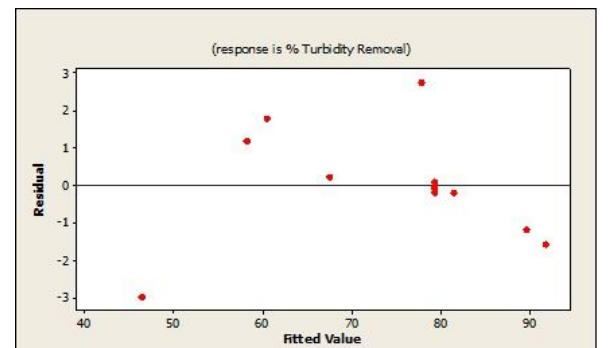


Fig.6 Residuals vs. Fits of %Turb.

3.4 Analysis of Variance (ANOVA)

Analysis of variance results of quadratic models presented in Table (3) indicated the reduced quadratic models statistical parameters of regression, residual error, lack of fit and pure error.

The p-values of ANOVA Table (2), indicates that the relationship between responses and factors is statistically significant at a level of $\alpha = 0.05$ (maximum acceptable level of risk for rejecting a true null hypothesis, Montgomery, 2005).

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-values for lack of fit (> 0.05) equals 0.105, 0.090 and 0.0503 for COD, TSS and turbidity removals, respectively, shows that the F-statistic was insignificant, implying significant model correlation between the factor variables and process responses.

Moreover, the ANOVA on these models, as shown in Table 3, demonstrates that the models were highly significant, as evident from the very low probability of p-values in the regressions equal 0.001, 0.001 and 0.002 for COD, TSS and turbidity removals, respectively. Equations (3), (4) and (5) presents high lack of fit F-values of 109.55, 101.54 and 391.32, implies the significance for the removals of COD, TSS and Turbidity, respectively.

Table (3) Analysis of variance (ANOVA)

P-value	F-value	Mean SS	SS	DF	Response
0.001	414.94	1177.75	1177.75	4	COD Removal %
		6.39	6.39	9	Regression
0.105	109.55	6.39	6.39	4	Residual Error
		0.00	0.00	5	Lack-of-Fit
					Pure Error
0.001	377.92	2762.45	2762.45	4	TSS Removal %
		16.45	16.45	9	Regression
0.090	101.54	16.25	16.25	4	Residual Error
		0.2	0.2	5	Lack-of-Fit
					Pure Error
0.002	179.72	2006.87	2006.87	4	Turbidity Removal %
		25.12	25.12	9	Regression
0.0503	391.32	25.04	25.04	4	Residual Error
		0.08	0.08	5	Lack-of-Fit
					Pure Error

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

3.5 Optimization Analysis

The result indicates that all linear and quadratic factors were significant in determining the response value of pollutant removal and also significant in the statistical analyses except quadratic current density factor on COD removal model and quadratic time×current density interaction factor on TSS and Turbidity removal models. Moreover, this difference implies that the models were strong influenced by the two factors (operation time and current density) in a linear manner, but their influences decreases relatively in a quadratic manner.

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. These plots can be observed in Figs. 7, 8, 9 show 3D response surface plots of COD, TSS and Turbidity removal models for all curves showing very noticeable changes. 3D surface plots of the response COD removal, TSS removal and turbidity removals on z-axis display the three dimensional relationship with factor variables operation time and current density on y and x axis's, respectively. Resulted data of textile wastewater treatment by electrocoagulation was represented by irregular surface with highest plate zone at right end of plate. This trend was clearly viewed for all three responses. An explicit observation for turbidity removal percent is shown in Fig.9, implying that the optimum conditions for maximum pollutant removal are within the proposed design.

Figs. 10, 11 and 12 shows the 2D contour plots of COD, TSS and turbidity removal models, respectively. In a contour plot, the values for two factor variables are represented on the y-time and x-current density axes, and the values for a response variable COD, TSS and Turbidity removals are represented by homogeneous shaded zones, called contours. These plots present the overall distribution of

electrocoagulation process. As shown, increased pollutant removal was observed with increasing operation time and current density values. However, an increase in both factors result an optimum zone for effective pollutants removal within a dark shade. At current density higher than 18 mA/cm^2 and operation time over 30 min. the COD removal began to establish the optimum zone. Whilst a current density higher than 19 mA/cm^2 and operation time more than 40 min. was marked for TSS removal to establish the optimum zone. Likewise, the optimum region for Turbidity removal was established within a 19 mA/cm^2 current density but higher operation time was required. As a result the study ranges were chosen as operation time 30-60 min. and current density $18\text{-}20 \text{ mA/cm}^2$ to establish the optimum zone for pollutants removal.

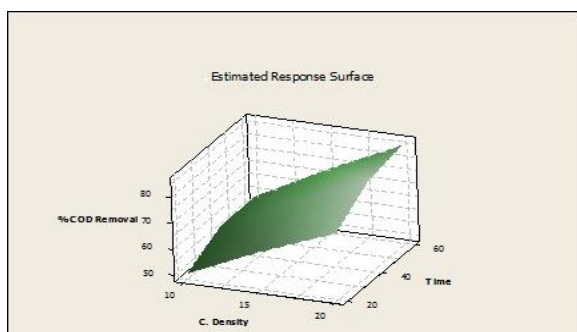


Fig. 7 Estimated %COD Removal with Model (eq.3) with Model

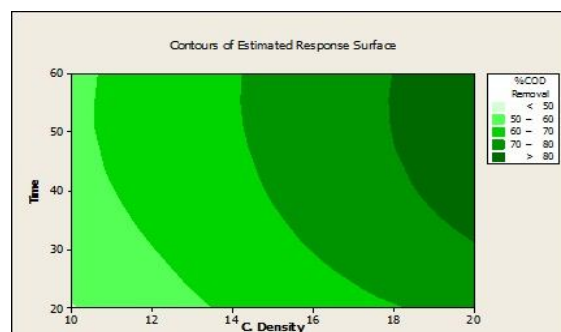


Fig. 10 Estimated %COD Removal

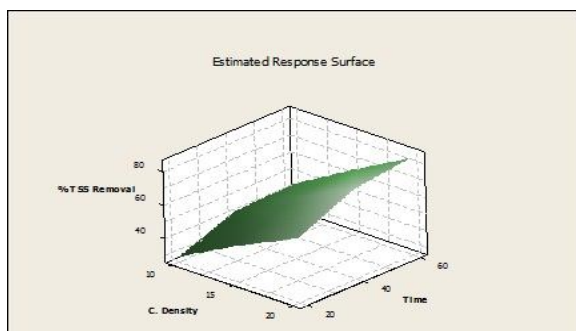


Fig. 8 Estimated %TSS Removal with model (eq.4) Model

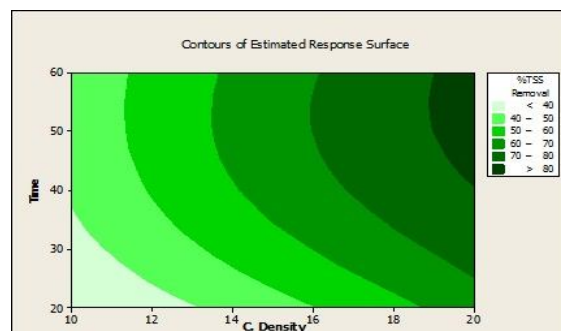


Fig. 11 Estimated %TSS Removal with

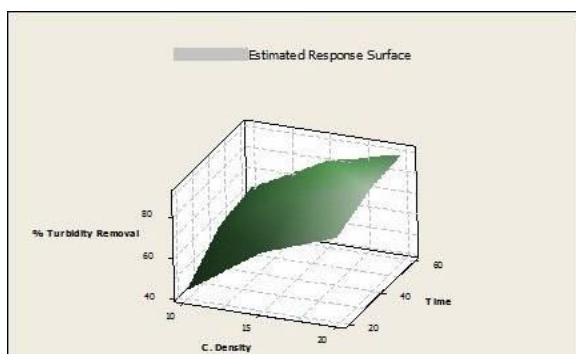


Fig. 9 Estimated %Turbidity Removal with Model (eq.5) with Model

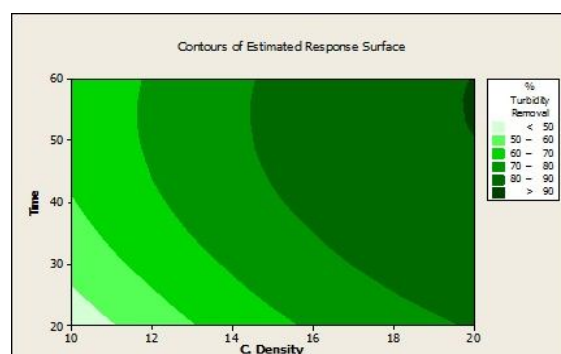


Fig. 12 Estimated %Turbidity Removal

The optimum conditions for predicting maximum responses have been obtained by using Minitab response optimizer as global solution. The optimization plot shows the effect of each factor (columns) on the responses or composite desirability (rows).

The vertical lines on the graph represent the current factor settings. The numbers displayed at the top of a column show the present factor level settings. The horizontal dotted lines and numbers represent the responses for the factor level. Minitab calculates that response efficiency is maximized when the two factors are at their highest settings.

Fig. 13 shows the maximum COD removal percent with the following predicted factors:

Operation time; 56.5403 min., current density; 20 mA/cm². The predicted COD removal percent response was equal 85.7538% at composite desirability (0.630153).

Fig. 14 shows the maximum TSS removal percent with the following predicted factors:

Operation time; 53.1313 min., current density; 20 mA/cm².

The predicted TSS removal percent response was equal 83.0554% at composite desirability (0.884257).

Fig. 15 shows the maximum Turbidity removal percent with the following predicted factors:

Operation time; 54.7475 min., current density; 20 mA/cm².

The predicted Turbidity removal percent response was equal 92.0225% at composite desirability (0.945863).

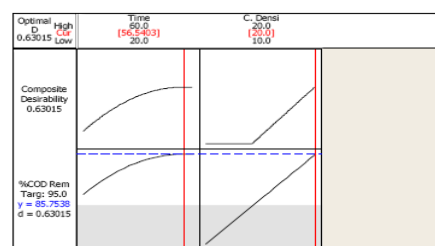


Fig.13 Response Optimization Plot of maximum %COD Removal

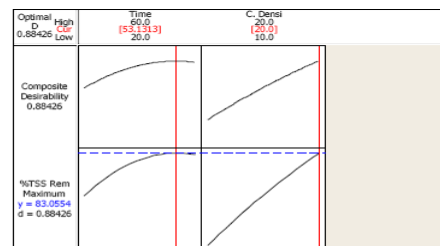


Fig.14 Response Optimization Plot of maximum %TSS Removal

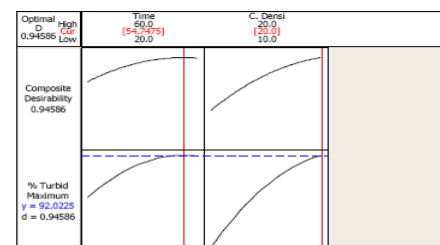


Fig.15 Response Optimization Plot of maximum %Turbidity Removal

4. Conclusion

A response surface methodology (RSM) has been applied to optimize a previously experimental data of textile wastewater treatment of local plant by electrocoagulation process. A central composite design (CCD) was performed for adequate and reliable measurements, and mathematical quadratic polynomial models of response surface were developed for each of COD, TSS and Turbidity removals. From statistical analyses, it was found that the operation time and current density at ambient temperature of 25°C and initial pH of 4.52 have significant effects on pollutants removal by electrocoagulation process. The response surface models were developed in this study with values of correlation coefficient R^2 equals 0.9946, 0.9941 and 0.9876, for COD, TSS and Turbidity removals, respectively. Moreover, the ANOVA on these models demonstrates that the models were highly significant, as evident from the very low probability values of regressions. Furthermore, the models were presented as 3-D response surface and 2-D contour graphs to investigate the optimum zones of pollutants removal, therefore, the regression models explained the removal efficiency were optimized to find maximum levels. Accordingly, maximum responses of 85.7538, 83.0554 and 92.0225 were predicted for COD, TSS and Turbidity removal percent's, respectively, with operation time and current density of (56.54 min. and 20 mA/cm²), (53.13 min. and 20 mA/cm²) and (54.74 min. and 20 mA/cm²), respectively.

References

- APHA (American Public Health Association) (2000) Standard Methods for the Examination of Water and Wastewater 20th ed. Washing, DC., USA.
- Ajjam S. and Ghanim A. (2012) "Electrocoagulation of Textile Wastewater with Fe Sacrificial Anode", the Iraqi journal for mechanical and material engineering, Vol.12, No.2.
- Aleboye, A.; Daneshvar, N.; Kasiri, M.B. (2008) "Optimization of C.I. Acid Red 14 azo dye removal by electrocoagulation batch process with RSM", Chem. Eng. Process, 47, 827-832.
- Arslan-Alaton, I.; Kobya, M.; Akyol, A.; Bayramolu, M. (2009) "Electrocoagulation of azo dye production wastewater with iron electrodes: Process evaluation by multi-response CCD", Color. Tech. 25, 234 - 241.
- Bhatti, M.S.; Reddy, A.S.; Thukral, A.K. (2009) " Electrocoagulation removal of Cr (VI) from simulated wastewater using response surface methodology", J. Hazard. Material, 172, 839-846.
- Bradley N., (2007), "The Response Surface Methodology, MSc Thesis, Indiana University South Bend".
- Can, O.T., Kobya, M., Demirbas, E. and Bayramoglu, M. (2006) "Treatment of the textile wastewater by combined electrocoagulation", Chemosphere, 62: 181-187.
- Carneiro, P.A., Fugivara, C.S., Nogueira, F.P., Boralle, N. and Zanoni, V.B. (2003), "A Comparative on Chemical and Electrochemical Degradation of Reactive Blue 4 Dye", Port. Electro. Acta, (21):49-67.
- Chavalparit O., Ongwandee M., (2009),"Optimizing electrocoagulation process for the treatment of biodiesel wastewater using response surface methodology", J. Environ. Science, 21, 1491-1496.
- Chen X., Shen Z., Zhu X., Fan Y., Wang W., (2005) "Advanced treatment of textile wastewater for reuse using electrochemical oxidation and membrane filtration", Water SA, January Vol. 31 No. 1.
- Chithra, K., Thilakavathi, R., Arul Murugan, A., Marimuthu, C., Balasubramanian, N. (2008) "Treatment of Textile Effluent Using Sacrificial Electrode", Modern applied science, Vol. 4 No 4 July.
- Daneshvar, N., Oladegaragoze, A. and Djafarzadeh, N. (2006) "Decolorization of basic dye solutions by electrocoagulation: an investigation of the effect of operational parameters" J. of Hazardous Materials, B129: 116 – 122.
- Dean A. and Voss D. (1999) "Design and Analysis of Experiments", Springer-Verlag, New York Inc.
- Environmental Protection Agency (EPA) (1996) "Best Management Practices for Pollution Prevention in the Textile Industry", U.S. Environmental Protection Agency, Document No. EPA/625/R-96/004, USA.
- Ghafari S., Abdul Aziz H., Isa M. H., Zinatizadeh A. (2009) "Application of RSM to optimize coagulation- flocculation treatment of leachate using PAC and alum, J. of Hazardous Materials, 163 650-656.
- İLHAN F., GÖNÜLLÜ T., ARSLANKAYA E., KURT U. and APAYDIN U. (2009) "Optimization of Organic Pollutants Removal with Iron Electrodes by Electrocoagulation, 1st Inter. Workshop on Application of Redox Technologies in the Environment", Arte September 14-15, İstanbul, Türkiye.
- Khuri, A.I., Cornell, J.A., 1996 "Response Surfaces", 2nd ed. Marcel Dekker, New York.
- Khuri A. and Mukhopadhyay S. (2010) "Response surface methodology" ,WIREs Computational Statistics Volume 2, March/April.
- Lenth R.V., (2009) "Response-Surface Methods in R, Using RSM", J. of Statistical Software Oct., V 32,7.
- Mollah M. Y. A., Schennach, R., Parga, J. R., and Cocke, D. L. (2001) "Electrocoagulation (EC) Science and Applications". Journal of Hazardous Materials, B84: 29-41.

- Moh Faiqun Ni'am , Fadil Othman , Johan Sohaili, Zulfa Fauzia (2007) "Removal of COD and Turbidity to Improve Wastewater Quality Using Electrocoagulation Technique" The Malaysian Journal of Analytical Sciences, Vol. 11, No 1 :198-205.
- Montgomery D. C., (2005) "Design and Analysis of Experiments" 6th ed. New York: John Wiley & Sons, Inc.
- Neşe Tüfekci, Nüket Sivri1, İsmail Toroz (2007) "Pollutants of Textile Industry Wastewater and Assessment of its Discharge Limits by Water Quality Standards", Turk. J. of Fisheries and Aquatic Sciences 7:97-103.
- Ölmez, T. (2009) "The optimization of Cr(VI) reduction and removal by electrocoagulation using response surface methodology" J. Hazardous Material 162, 1371-1378.
- Philippe C., Vandevivere, Bianchi R. and Verstraete W. (1998) "Treatment and Reuse of Wastewater from the Textile Wet-Processing Industry: Review of Emerging" Tech. J. Chem. Tech. Biotech. 72, 289E302.
- Suárez A., Agudelo Affil. N. (2011) "Optimizing the removal of Heavy Metals of an artificial wastewater by electrocoagulation using response surface methodology" CTSI Organization, Clean Tech. P: 248–250.
- Trinh T.K., Kang L.S (2010) "Application of Response Surface Method as an Experimental Design to Optimize Coagulation Tests", Environ. Eng. Res. June, 15(2): 063-070.
- Vepsäläinen M., Ghiasvand M., Selin J, Pienimaa J, Eveliina Repo E. (2009) "Investigations of the effects of temperature and initial sample pH on natural organic matter (NOM) removal with electrocoagulation using response surface method (RSM)", Separation and Purification Tech. Vol. 69 Issue 3:255–26