

R. Saravanathamizhan<sup>1</sup>  
N. Mohan<sup>2</sup>  
N. Balasubramanian<sup>1</sup>  
V. Ramamurthi<sup>1</sup>  
C. Ahmed Basha<sup>3</sup>

<sup>1</sup>Department of Chemical Engineering,  
A.C. College of Technology, Anna  
University, Chennai, India.

<sup>2</sup>Centre for Environment & Explosive  
Safety, Defense Research &  
Development Organization, Delhi, India.

<sup>3</sup>Department of Pollution Control, Central  
Electrochemical Research Institute,  
Karaikudi, India.

## Research Article

# Evaluation of Electro-Oxidation of Textile Effluent Using Response Surface Methods

In the present investigation, treatment of textile effluent using an electrochemical technique was designed and analyzed using the Box-Behnken method. The influence of individual parameters on electro-oxidation of textile effluent has been critically examined using the response surface method (RSM), and a quadratic model for chemical oxygen demand (COD) reduction has been developed. It has been observed from the present analysis that the predicted values are in good agreement with experimental data with a correlation coefficient of 0.945.

**Keywords:** Box-Behnken method; COD reduction; Electrochemical oxidation; Response surface method

*Received:* January 14, 2007; *revised:* April 27, 2007; *accepted:* July 3, 2007

**DOI:** 10.1002/clen.200700005

## 1 Introduction

Textile industries consume large amounts of water and generate considerable amounts of wastewater. The textile industry's effluents are known to be strongly colored, contain large amount of suspended solids (SS), have broadly fluctuating pH values, and have high chemical oxygen demand (COD). The textile effluents are treated conventionally by adsorption, biological oxidation, coagulation, etc. The conventional aerobic biological process, e.g., the activated sludge process, cannot readily treat textile wastewater because most commercial dyes are toxic to the organisms used in the process and result in sludge bulking. Further, the dyestuff, dyeing additives present in textile effluents, are highly complex structures, which are difficult to decompose biologically. Additionally, biological and chemical methods generate a considerable quantity of sludge, which itself requires treatment. The conventional methods for treating these effluents are becoming inadequate. There have been increased economic, social, legal, and environmental pressures to adopt the best technology at lower cost and to aspire to "zero discharge". In recent years, there has been special focus on treatment of industrial wastewater using advanced oxidation technologies such as catalytic wet air oxidation, and electrochemical oxidation process, etc. [1–3]. Among these techniques, electrochemical oxidation appears to be one of the most promising technologies for the treatment of wastewaters containing organic pollutants.

Electrochemical technology continues to make many contributions to environmental treatment, recycling, and monitoring. These include:

- Treatment by electrochemically generated species, such as chlorination of swimming pools and sterilization of medical

**Correspondence:** N. Balasubramanian, Department of Chemical Engineering, A.C. College of Technology, Anna University, Chennai-600 025, India.

**E-mail:** nbsbala@annauniv.edu

**Abbreviations:** ANOVA, analysis of variance; COD, chemical oxygen demand; EC, energy consumption; IEC, initial effluent concentration; RSM, response surface method; SS, suspended solids

instruments using a powerful cocktail of oxidizing reagents in "super oxidized" water.

- Removal of contaminants, such as metal ions and organics from industrial process streams.
- Conversion of chemical to electrochemical energy using fuel cell and photovoltaic devices.

Electrochemical methods have been successfully applied to the purification of several industrial wastewaters [4, 5]. Lin and Ming [6] experimented with electrochemical techniques in conjunction with chemical coagulation and ion exchange to treat effluent from the secondary wastewater treatment plant of a large-scale dyeing/finishing unit and reported that the quality of treated wastewater is comparable with deionized water. The other major contributions to the application of electrochemical techniques for industrial effluent treatment are due to Panizza et al. [7], Montilla et al. [8], and Raghu and Ahmed Basha [9], etc. In our earlier studies [10–12], we have reported that textile effluents can be effectively treated using an electrochemical method for effective color removal and COD reduction. The electrochemically treated textile effluent can be reused for the dyeing process.

The existing literature focuses on the electrochemical treatment of industrial effluent and the influence of individual parameters on process efficiency. In electro-oxidation, the oxidation efficiency depends on several parameters and many times the combined effect plays an important role. It is attempted in the present investigation to study the electro-oxidation of Acid Blue 113 dye using the Box-Behnken method and to critically examine the effect of various parameters on COD reduction.

## 2 Response Surface Method

In conventional experimentation, the experiments are conducted keeping all the variables constant except the parameter whose influence is being studied. This type of experiment reveals the effect of the chosen parameters under set conditions, assuming that variables are independent and that the effect will be the same at other values of the remaining variables. However, it does not show what

would happen if other variables are changed. Experimental design is an effective and efficient optimization strategy to overcome this drawback, which has gained wide application in chemical engineering optimization [13]. The combined effect of variables can be predicted and optimization can be achieved with the help of the experimental design tool, which is practically difficult in conventional experimentation. In the present investigation, it is attempted to evaluate electro-oxidation of textile effluent using the response surface method.

The response surface method (RSM) is a statistical and mathematical technique used for modeling and optimization of processes in which a response of interest is influenced by several variables. The RSM has important application in the design, development and formulation of new products, as well as in the improvement of existing product designs. It defines the effect of the independent variables on the process, either individually or collectively. Further, the experimental methodology generates a mathematical model, which describes the chemical or biochemical processes. The response surface method has been very popular for optimization studies in recent years. The design procedure of the response surface methodology is as follows [14]:

- The determination of the independent parameters and their levels are carried out.
- A mathematical model of the second order response surface with the best fittings is developed.
- The optimal set of experimental parameters that produce a maximum or minimum value of response are found.
- The response surface plot and contour plot of the response as a function of the independent parameters and determination of optimal points are determined.

RSM attempts to analyze the influence of the independent variables on a specific dependent variable (response). The independent variables, denoted by  $x_1, x_2, \dots, x_k$ , are presumed to be continuous and can be controlled with negligible error. The response ( $y$ ) is postulated to be a random variable. The individual variables ( $x_1, x_2, \dots, x_k$ ) and the response ( $y$ ) can be related as follows [15]:

$$y = f(x_1, x_2, \dots, x_k) + \varepsilon \quad (1)$$

where  $y$  is the response of the system,  $f$  is the unknown response function,  $x_1, x_2, \dots, x_k$  are the independent variables,  $k$  is the number of independent variables, and  $\varepsilon$  is the statistical error.

The primary function of RSM is to postulate a suitable approximation for the true functional relationship between the response ( $y$ ) and the set of independent variables. Initially, a low-order (first-order) polynomial in some region of independent variables is employed. A first-order RSM can be expressed as follows:

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \varepsilon \quad (2)$$

For maximization problems, experiments are conducted along the path of steepest ascent until no further increase in the response is observed. The set of values of independent variables where no further increase in response is observed is known as the optimal region. In most cases, a second-order response surface model is used which can be given as [16]:

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^k \beta_{ij} x_i x_j + \varepsilon \quad (3)$$

**Table 1.** The level and range of variables chosen for electrochemical oxidation.

Factor	Variables	Unit	Range of actual and coded variables		
			-1	0	+1
$X_1$	pH	-	4.0	6.5	9.0
$X_2$	Dye concentration	g/L	0.16	0.25	0.333
$X_3$	Supporting electrolyte concentration	ppm	580	1160	1740
$X_4$	Charge	Ahr	0.144	0.22	0.288

Where  $x_i, x_j$  are coded independent variables,  $\beta_0, \beta_i, \beta_{ii}, \beta_{ij}$  ( $i = 1, 2, \dots, k$ ),  $\beta_{ij}$  ( $i = 1, 2, \dots, k; j = 1, 2, \dots, k$ ) are the regression coefficients for the intercept and linear, quadratic and interaction terms, respectively, and  $\varepsilon$  is the statistical error.

In the present study, the RSM has been used to determine the relation between COD removal and operating parameters such as pH, effluent concentration (dye concentration), supporting electrolyte concentration and applied charge.

The uncoded variables are converted to coded variables using the following equation [17]:

$$x = \frac{X - [X_{\max} + X_{\min}]/2}{[X_{\max} - X_{\min}]/2} \quad (4)$$

where,  $X$  = natural variable and  $x$  = coded variable.

The dimensional coded variables  $x_1, x_2, x_3, x_4$  vary between -1 and +1 (see Tab. 1), while the variables are designated as: -1, 0, and +1. The mathematical representation of the response  $Y$  and the variables is given as [18]:

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{44} x_4^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 \quad (5)$$

and

$$\beta_{i,j} = 0, 1, 2, 3, 4, \dots, k \quad (6)$$

Where  $\beta$  and  $k$  are regression coefficients and variables.

In the present work, the Box-Behnken experimental design has been chosen to find the relationship between the response functions and variables. The Box-Behnken design is a rotatable second-order design based on three-level incomplete-factorial designs. The special arrangement of the Box-Behnken design levels allows the number of design points to increase at the same rate as the number of polynomial coefficients. The Box-Behnken method has been preferentially selected for designing experiments, as in this method, relatively fewer combinations of the variables are sufficient to estimate the potentially complex response functions [19]. A class of three-level complete-factorial designs for the estimation of the parameters in a second-order model has been developed by Box-Behnken. Table 2 gives the experimental runs for a three-level four-factor Box-Behnken experimental design with five center points. The design was analyzed using Minitab 14 (PA, USA). The analysis focused on how the COD reduction is influenced by independent variables, i.e., electrolyte pH ( $X_1$ ), initial effluent concentration ( $X_2$ ), supporting electrolyte concentration ( $X_3$ ), and applied charge ( $X_4$ ). The dependent output variable is maximum COD reduction.

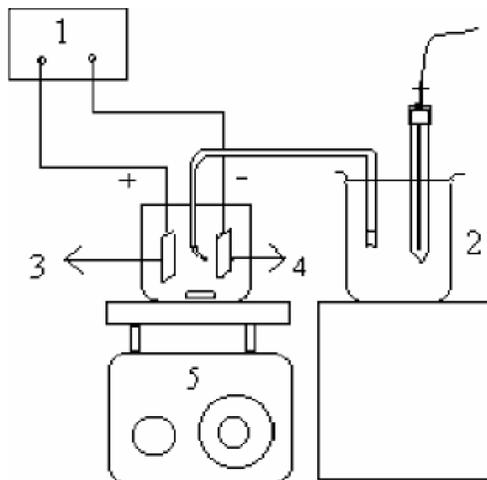
**Table 2.** The actual design of experiments and response for electrochemical oxidation.

Run	Factor 1 X <sub>1</sub>	Factor 2 X <sub>2</sub>	Factor 3 X <sub>3</sub>	Factor 4 X <sub>4</sub>	% COD	Energy Consumption KWh kg of COD
1	4	0.16	1160	0.22	84.38	74.9
2	4	0.25	1160	0.14	64.72	34.15
3	4	0.33	1160	0.22	45.75	91.24
4	4	0.25	1160	0.29	70.82	63.42
5	4	0.25	1740	0.22	73.47	71.69
6	4	0.25	580	0.22	50.50	144.96
7	6.5	0.25	580	0.29	65.00	81.12
8	6.5	0.16	1160	0.14	80.21	61.78
9	6.5	0.25	1740	0.14	60.25	46.84
10	6.5	0.16	1160	0.29	84.38	117.47
11	6.5	0.25	1740	0.29	88.75	66.15
12	6.5	0.33	580	0.22	48.75	117.03
13	6.5	0.16	1740	0.22	81.25	91.48
14	6.5	0.16	580	0.22	81.77	11.84
15	6.5	0.33	1160	0.14	50.65	90.47
16	6.5	0.25	580	0.14	64.15	49.18
17	6.5	0.33	1160	0.29	70.18	103.11
18	6.5	0.33	1740	0.22	72.75	82.89
19	9	0.25	580	0.22	78.78	63.85
20	9	0.25	1160	0.14	62.86	38.95
21	9	0.25	1740	0.22	82.25	53.88
22	9	0.25	1160	0.29	73.47	66.66
23	9	0.16	1160	0.22	84.38	87.43
24	9	0.33	1160	0.22	64.75	101.08
25	6.5	0.25	1160	0.22	55.75	71.72
26	6.5	0.25	1160	0.22	55.75	71.72
27	6.5	0.25	1160	0.22	55.75	71.72
28	6.5	0.25	1160	0.22	55.75	71.72
29	6.5	0.25	1160	0.22	55.75	71.72

### 3 Experimental

Synthetic effluents of Acid Blue 113 were chosen for this investigation. The basis for the selection of Acid Blue 113 dye is the toxicity impact of azo dyes to the environment. It has generally been observed that the dye exhaustion has been 93% with a M:L ratio of 1:30 for a dye shade of 0.5%. The effluents come out of the dye-processing unit containing 0.15 to 0.33 g/L unused dye. Accordingly, in the present investigation, effluents are prepared synthetically having concentrations of 0.333 g/L, which corresponds to the dye bath wash water, and 0.16 g/L, which corresponds to the combined wastewater (dye bath, scouring, bleaching, etc.).

Experiments were conducted in an undivided electrode cell having 100 mL capacity (see Fig. 1). Different oxide coated titanium metals were used as the anode, while stainless steel was used as the cathode in the present investigation. All the experiments were carried out under galvanostatic conditions using a DC-regulated power source (HIL model 3161) of 0 to 2 A and 0 to 30 V. The anode potential was monitored using a reference electrode (saturated calomel electrode) connected to the working electrode, and sufficient agitation was provided inside the electrochemical cell to maintain uniform concentration. The pollutant concentrations are presented in terms of chemical oxygen demand estimated by a standard estimation procedure. Samples were collected at different intervals of time and analyzed for COD and pH.



**Figure 1.** Experimental setup schematic diagram: 1) DC power supply, 2) saturated calomel electrode, 3) anode, 4) cathode, 5) magnetic stirrer.

### 4 Analysis of Variance (ANOVA)

ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variation for the purpose of testing hypotheses on the parameters of the model [20]. The analysis of variance (ANOVA) on the statistical significance of the ratio of mean square variation due to regression and mean square residual error was performed where *m* is the total number of the experiments, and  $\eta_i$  is the S/N ratio at the *i*<sup>th</sup> test. The sum of squares from the tested factors, *SS<sub>p</sub>*, can be calculated as:

$$SS_p = \sum_{j=1}^t \frac{(S_{nj})^2}{t} - \frac{1}{m} \left( \sum_{i=1}^m ni \right)^2 \tag{7}$$

where *p* represents one of the tested factors, *j* the level number of this specific factor *p*, *t* the repetition of each level of the factor *p*, and *S<sub>nj</sub>* the sum of the S/N ratio involving this factor and level *j*.

*Degree of freedom (D).* *D* denotes the number of independent variables. The degree of freedom for each factor (*D<sub>p</sub>*) is the number of its levels minus one. The total degrees of freedom (*D<sub>T</sub>*) are total number of the result data points minus one, i.e., the total number of trials times the number of repetition minus one. The degree of freedom for the error (*D<sub>e</sub>*) is the number of the total degrees of freedom minus the total degree of freedom for each factor.

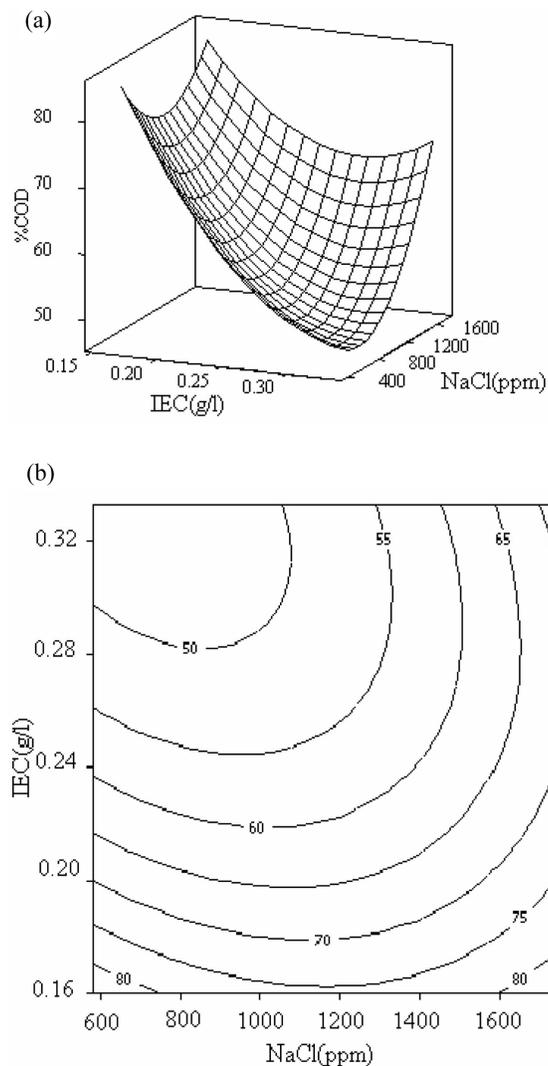
*Variance (V).* Variance is defined as the sum of squares of each trial sum result involving the factor, divided by the degrees of freedom of the factor:

$$V_p (\%) = \frac{SS_p}{D_p} \times 100 \tag{8}$$

*The corrected sum of squares (SS'<sub>p</sub>).* *SS'<sub>p</sub>* is defined as the sum of squares of factors minus the error variance times the degree of freedom of each factor:

$$SS'_p = SS_p - D_p V_e \tag{9}$$

*Percentage of the contribution to the total variation (P<sub>p</sub>).* *P<sub>p</sub>* denotes the percentage of the total variance of each individual factor:

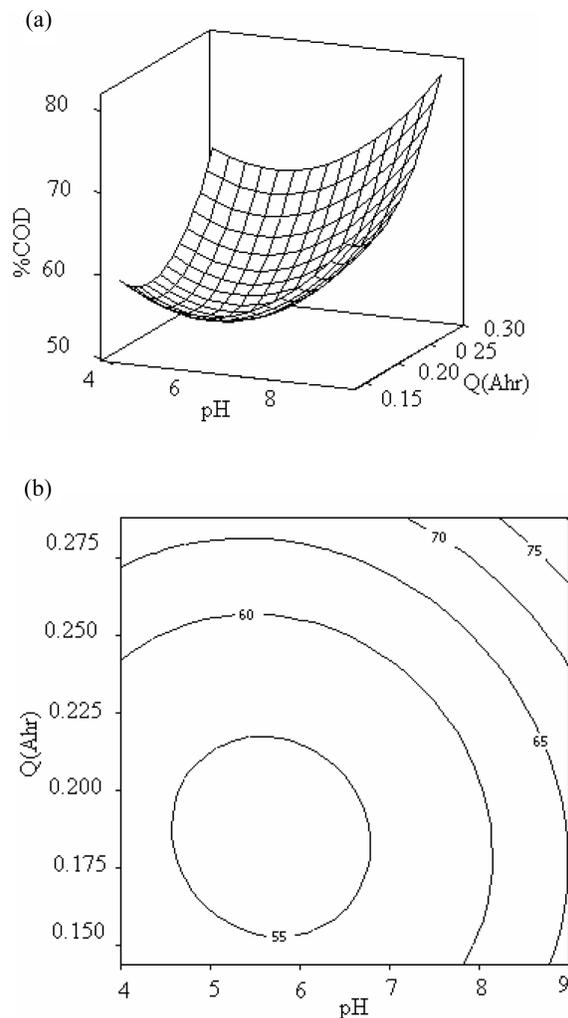


**Figure 2.** The combined effects of initial dye concentration and supporting electrolyte concentration on percentage COD removal, (a) Response surface, (b) Contour plot; pH 6.5; Q: 0.22 Ahr.

$$P_p(\%) = \frac{SS'_p}{SS_T} \times 100 \quad (10)$$

## 5 Result and Discussion

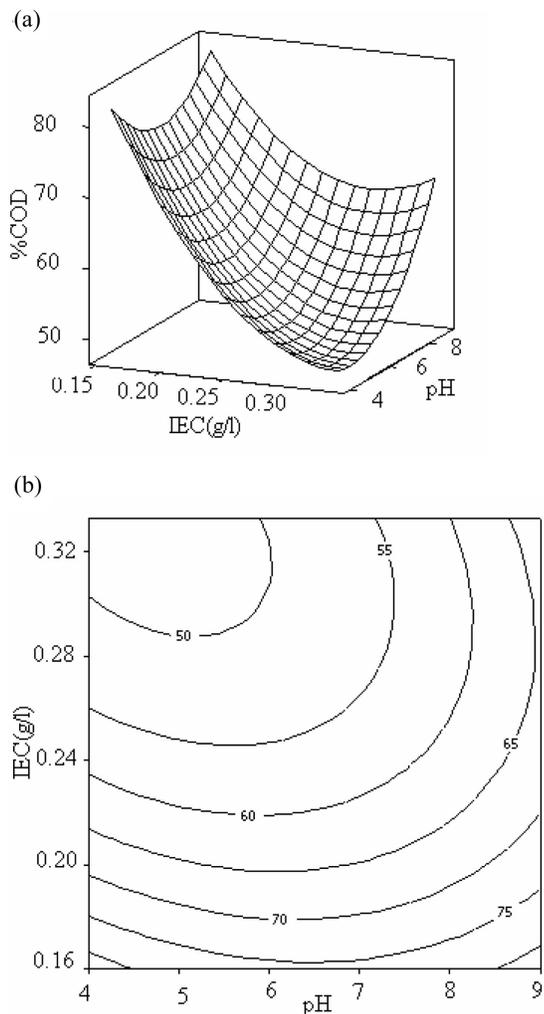
The response surface methodology was applied to the electro-oxidation of Acid Dye 113 effluent, and the results are presented in both surface and contour plots. The analysis was carried out to check the influence of various operating parameters on pollutant degradation and the optimization was determined based on the influence of individual parameters. The effects of variables on the electro-oxidation of Acid Blue 113 [11] are given in Figs. 2 to 4. The interaction between varying concentrations of supporting electrolyte and initial dye concentration is given in the 3-dimensional surface plots (see Fig. 2(a)) and the contour plot (see Fig. 2(b)). It can be ascertained from the surface plot that the COD reduction increases with increas-



**Figure 3.** The combined effects of charge and pH on percentage removal of COD, (a) Response surface, (b) Contour plot; initial dye concentration: 0.25 g/L; supporting electrolyte concentration: 1160 ppm.

ing supporting electrolyte concentration and decreases with increasing initial dye concentration. This is because an increase in supporting electrolyte concentration increases the electrochemically generated active chlorine, and in turn, the rate of COD reduction. On the other hand, the ratio of dye concentration to  $\text{OCl}^-$  radical concentration increased with the initial dye concentration, and in turn, decreases with COD removal.

The combined effects of applied charge and electrolyte pH on COD reduction are shown in Figs. 3(a) and 3(b). It can be noticed from Fig. 3(a) that the rate of COD removal increases with applied charge and electrolyte pH. The increase of COD removal rate with pH can be explained by the observation that the reaction is reduced in an acidic solution due to  $\text{OH}^-$  instability and considerably increased in basic solution due to the ready formation of  $\text{OCl}^-$  ions, with the result that basic or neutral pH conditions are more favorable for COD reduction. On the other hand, the rate of generation of hypochlorite ions increased with current density, which eventually increases the COD reduction.

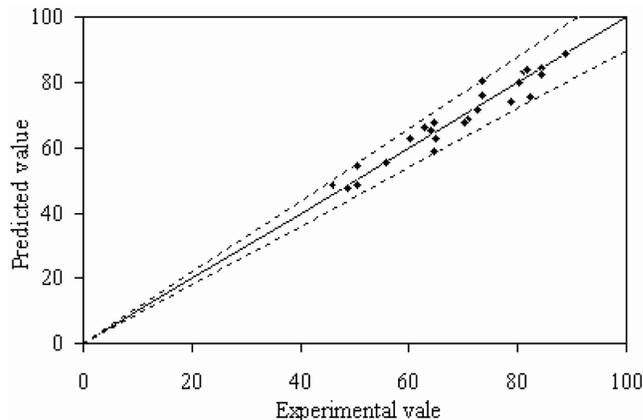


**Figure 4.** The combined effects of initial dye concentration and pH on percentage COD removal, (a) Response surface, (b) Contour plot; supporting electrolyte concentration: 1160 ppm; Q: 0.22 Ahr.

The analysis on the combined effect of electrolyte pH and initial dye concentration on COD removal is given in the 3-dimensional surface plots in Fig. 4(a) and the contour plot in Fig. 4(b). It can be ascertained from Fig. 4(a) that the COD reduction increases with increasing electrolyte pH while it decreases with increasing initial dye concentration. As stated earlier, the reaction is favorable in basic conditions due to increased formation of  $\text{OCl}^-$  ions. On the other hand, the degradation load (effluent concentration to  $\text{OCl}^-$  radicals) increases with increasing initial dye concentration, which eventually decreases the COD removal rate.

The mathematical relationship between percentage COD removal and variables such as the electrolyte pH ( $X_1$ ), initial effluent concentration, IEC ( $X_2$ ), supporting electrolyte concentration ( $X_3$ ), and the applied charge  $Q$  ( $X_4$ ) was determined as:

$$\begin{aligned} \%COD = & 55.750 + 4.738X_1 - 11.962X_2 + 5.814X_3 + 5.813X_4 + 6.465X_1^2 \\ & + 8.099X_2^2 + 7.908X_3^2 + 6.379X_4^2 + 4.750X_1X_2 - 4.875X_1X_3 \\ & + 1.128X_1X_4 + 6.130X_2X_3 + 3.840X_2X_4 + 6.913X_3X_4 \end{aligned} \quad (11)$$



**Figure 5.** Comparison of predicted value using Eq. (11) with experimental value for percentage COD.

The prediction of COD removal using the above equation has been compared with the experimental values given in Tab. 2 and shown in Fig. 5. It can be ascertained from the figure that the model equation predictions satisfactorily match the experimental values within (10% error). Similarly, the energy consumption [EC] is related to the variables of pH ( $X_1$ ), initial effluent concentration ( $X_2$ ), supporting electrolyte concentration ( $X_3$ ), and applied charge ( $X_4$ ) in coded factors as given below:

$$\begin{aligned} EC = & 71.723 - 5.708X_1 + 11.744X_2 - 4.586X_3 + 14.711X_4 + 0.185X_1^2 \\ & + 17.497X_2^2 - 1.228X_3^2 - 8.931X_4^2 - 0.673X_1X_2 + 15.824X_1X_3 \\ & - 0.391X_1X_4 - 28.448X_2X_3 - 10.762X_2X_4 - 3.156X_3X_4 \end{aligned} \quad (12)$$

The predicted energy consumption using Eq. (12) is compared with the experimental values given in Tab. 2 and shown in Fig. 6. It can be noticed from the figure that the equation predictions satisfactorily match the experimental values within (20% error). The parameters in Eqs. (11) and (12) are optimized for maximum conversion and minimum energy consumption, and the optimized values are given in Tab. 3. It can be noticed from Tab. 3 that the optimum values of parameters correspond to a maximum COD removal of 95%.

The significance of the regression coefficients were analyzed using the  $p$  test and the  $t$  test [21]. The  $p$ -values are used to check the consequences of interactions among the variables and, in turn, indicates the patterns of the interactions among the variables. In general, the larger the magnitude of the  $t$ -value and smaller the  $p$ -value, the greater is the significance of the corresponding coefficient term. It can be noticed from Tab. 4 that the coefficients for the linear effect of initial effluent concentration, supporting electrolyte concentration, and applied charge ( $p = 0.000$ ) are significant compared to the other linear effect, i.e., pH ( $p = 0.002$ ). While the coefficients in the quadratic term for effluent and supporting electrolyte concentration ( $p = 0.0000$ ) are significant compared to coefficients in the quadratic term for pH and charge ( $p = 0.002$ ). Finally, the coefficients in the interaction terms for supporting electrolyte charge are found to be more significant ( $p = 0.005$ ) than the other interactive terms (i.e., pH-IEC, pH-supporting electrolyte concentration, pH-applied charge, IEC supporting electrolyte concentration, and IEC applied charge). Similar analyses was performed for the energy consumption and the results are presented in Tab. 5.

**Table 3.** Optimized parameters of percentage removal of COD and energy consumption.

Factor	$X_1$	$X_2$	$X_3$	$X_4$	% COD removal	Energy Consumption kWh kg of COD
Parameter	pH	Initial effluent concentration (g/L)	Supporting electrolyte concentration (ppm)	Charge (Ahr)	95	71.26
Optimized value	9	0.28	1740	0.28		

**Table 4.** Estimated regression coefficient and corresponding  $t$  and  $p$  values for percentage removal of COD.

	Coefficient	Standard error	$t$	$p$
Model	55.750	1.877	29.707	0.000
$X_1$	4.738	1.211	3.911	0.002
$X_2$	-11.962	1.211	-9.875	0.000
$X_3$	5.814	1.211	4.800	0.000
$X_4$	5.813	1.211	4.799	0.000
$X_1X_1$	6.465	1.648	3.924	0.002
$X_2X_2$	8.099	1.648	4.916	0.000
$X_3X_3$	7.908	1.648	4.800	0.000
$X_4X_4$	6.379	1.648	3.872	0.002
$X_1X_2$	4.750	2.098	2.264	0.040
$X_1X_3$	-4.875	2.098	-2.323	0.036
$X_1X_4$	1.128	2.098	0.537	0.599
$X_2X_3$	6.130	2.098	2.922	0.011
$X_2X_4$	3.840	2.098	1.830	0.089
$X_3X_4$	6.913	2.098	3.295	0.005

**Table 5.** Estimated regression coefficient and corresponding  $t$  and  $p$  values for energy consumption.

	Coefficient	Standard error	$t$	$p$
Model	71.7232	10.547	6.800	0.000
$X_1$	-5.7084	6.808	-0.838	0.416
$X_2$	11.7435	6.808	1.725	0.107
$X_3$	-4.5856	6.808	-0.674	0.512
$X_4$	14.7112	6.808	2.161	0.049
$X_1X_1$	0.1849	9.260	0.020	0.984
$X_2X_2$	17.4972	9.260	1.890	0.080
$X_3X_3$	-1.2284	9.260	-0.133	0.896
$X_4X_4$	-8.9310	9.260	-0.964	0.351
$X_1X_2$	-0.6726	11.792	0.057	0.955
$X_1X_3$	15.8242	11.792	1.342	0.201
$X_1X_4$	-0.3912	11.792	-0.033	0.974
$X_2X_3$	-28.4482	11.792	-2.413	0.030
$X_2X_4$	-10.7616	11.792	-0.913	0.377
$X_3X_4$	-3.1563	11.792	-0.268	0.793

An analysis of variance to determine the significant effects of process variables was conducted and the results are presented in Tabs. 6 and 7. It can be noticed from Tabs. 6 and 7 for the COD and energy consumption output responses, that the  $F$ -statistics values for the regressions are higher. The large  $F$ -values indicates that most of the variation in the response can be explained by the regression model equation. The associated  $p$ -value is used to estimate whether the  $F$ -statistics are large enough to indicate statistical significance. The lower  $p$ -value ( $<0.01$ ) indicates that the model is considered to

**Table 6.** ANOVA results for the percentage  $\delta$  COD removal.

Source	Degrees of freedom	Sum of squares	Mean square	$F_{\text{statistics}}$	$P$
Regression	14	4269.62	304.973	17.32	0.000
Linear	4	2797.50	699.374	39.72	0.000
Square	4	881.30	220.325	12.51	0.000
Interaction	6	590.82	98.470	5.59	0.004
Residual error	14	246.52	17.609		
Lack-of-fit	10	246.52	24.652		
Pure error	4	0.00	0.000		
Total	28	4516.14			

$$R^2 = 0.945; R^2_{\text{adj}} = 0.891$$

**Table 7.** ANOVA results for the energy consumption.

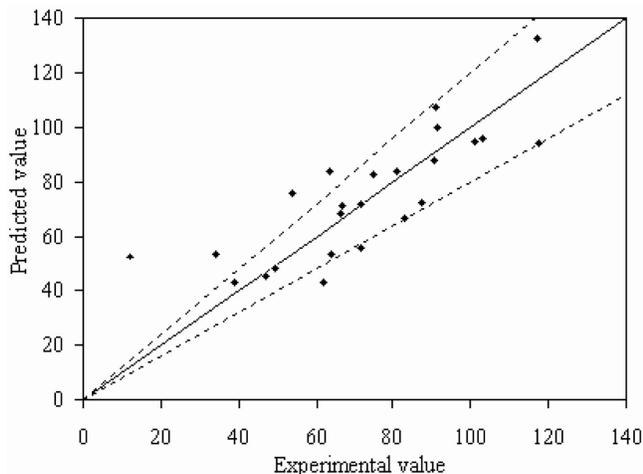
Source	Degrees of freedom	Sum of squares	Mean square	$F_{\text{statistics}}$	$P$
Regression	14	12684.67	906.05	1.63	0.186
Linear	4	4895.33	1223.83	2.20	0.122
Square	4	3045.02	761.25	1.37	0.294
Interaction	6	4744.33	790.72	1.42	0.274
Residual error	14	7786.71	556.19		
Lack-of-fit	10	7786.71	778.67		
Pure error	4	0.00	0.00		
Total	28	20471.4			

$$R^2 = 0.620; R^2_{\text{adj}} = 0.239$$

be statistically significant. The model adequacies were checked by  $R^2$  and adj.- $R^2$ . A higher value of  $R^2$  ( $>0.94$ ) shows that the model can explain the response successfully. The model adequacy has also been verified with the adj.- $R^2$  value. The ANOVA indicates that the second-order polynomial model (see Eqs. (11) and (12)) is significant and adequate to represent the actual relationship between the response (removal efficiency) and the variables, with a small  $p$ -value (0.0000) and a high value of  $R^2$  (0.945) for percentage COD removal and energy consumption with an  $R^2$  value of 0.62.

## 6 Conclusions

Experiments were carried out on dye house effluent using an electrochemical technique covering a wide range of operating conditions. The influence of effluent initial concentration, pH, supporting electrolyte concentration and applied charge on the rate of degradation was critically examined. It was observed from this investigation that the percentage COD reduction is significantly influ-



**Figure 6.** Comparison of predicted value using Eq. (12) with experimental value for energy consumption.

enced by the initial effluent concentration, pH, supporting electrolyte concentration, and applied charge.

The experimental data were analyzed using response surface methodology and the individual and combined parameter effects on COD reduction were analyzed. Three-level four-factor Box-Behnken experimental design was applied. Regression equations were developed for COD removal and energy consumption using sets of experimental data and solved using the statistical software tool Minitab 14. It was observed that model predictions of COD removal and energy consumption are in good agreement with experimental observations. Further, the parameters were optimized for effective electro-oxidation of dye house effluents using the response surface method. The optimized values for 95% of COD removal through electro-oxidation are: pH 9; applied charge of 0.28 Ahr, supporting electrolyte concentration of 1740 ppm, and energy consumption of 71.26 kWh kg of COD for the given initial effluent concentration of 0.28 g/L.

## Symbols

$\varepsilon$	error
$\beta_0$	intercept
$\beta_i$	linear effect
$\beta_{ii}$	squared effect
$\beta_{ij}$	interaction effect
Q	charge (Ahr)
$X_1$	pH
$X_2$	dye concentration (g/L)
$X_3$	supporting electrolyte concentration (ppm)
$X_4$	charge (Ahr)

## References

- [1] I. Arslan-Alaton, I. A. Balcioglu, D. W. Bahnemann, Advanced Oxidation of a Reactive Dye bath Effluent: Comparison of  $O_3$ ,  $H_2O_2/UV-C$  and  $TiO_2/UV-A$  Processes, *Water Res.* **2002**, 36, 1143.
- [2] L. C. Chiang, J. E. Chang, S. C. Tseng, Electrochemical Oxidation Pretreatment of Refractory Organic Pollutants, *Water Sci. Technol.* **1997**, 36, 123.
- [3] M. Hepel, J. Luo, Photoelectrochemical Mineralization of Textile Diazo Dye Pollutants Using Nanocrystalline  $WO_3$  Electrodes, *Electrochim. Acta* **2001**, 47, 729.
- [4] S. H. Lin, C. F. Peng, Treatment of Textile Wastewater by Electrochemical Method, *Water Res.* **1994**, 28 (2), 277.
- [5] F. Vigo, C., Uliana, M. Novi, Electro-Oxidation of Sodium Lauryl Sulfate Aqueous Solutions, *J. Appl. Electrochem.* **1988**, 18, 904.
- [6] S. H. Lin, M. L. Chen, Treatment of Textile Wastewater by Chemical Methods for Reuse, *Water Res.* **1997**, 31 (4), 868.
- [7] M. Panizza, P. A. Michaud, G. Cerisola, C. Comninellis, Anodic Oxidation of 2-Naphthol at Boron-Doped Diamond Electrodes, *J. Electroanal. Chem.* **2001**, 507, 206.
- [8] F. Montilla, P. A. Michaud, E. Morallón, J. L. Vázquez, C. Comninellis, Electrochemical Oxidation of Benzoic Acid at Boron-Doped Diamond Electrodes, *Electrochim. Acta* **2002**, 47, 3509.
- [9] S. Raghu, C. Ahmed Basha, Electrochemical Treatment of Procion Black 5B Using Cylindrical Flow Reactor – a Pilot Plant Study, *J. Hazard. Mater.* **2007**, 139 (2), 381.
- [10] N. Mohan, Studies on Electrochemical Oxidation of Acid Dye Effluent, *Ph.D. Thesis*, Anna University, Madras **2000**.
- [11] N. Mohan, N. Balasubramanian, V. Subramanian, Electrochemical Treatment of Simulated Textile Effluent, *Chem. Eng. Technol.* **2001**, 24, 749.
- [12] N. Mohan, N. Balasubramanian, In Situ Electrocatalytic Oxidation of Acid Violet 12 Dye Effluent, *J. Hazard. Mater.* **2006**, 136, 239.
- [13] C. M. Pey, A. Maestro, I. Solé, C. González, C. Solans, J. M. Gutiérrez, Optimization of Nano-Emulsions Prepared by Low-Energy Emulsification Methods at Constant Temperature Using a Factorial Design Study, *Colloids Surf., A* **2006**, 288, 144.
- [14] N. Aslan, Y. Cebeci, Application of Box-Behnken Design and Response Surface Methodology for Modeling of Some Turkish Coals, *Fuel* **2007**, 86, 90.
- [15] D. Bas, I. H. Boyaci, Modeling and Optimization I: Usability of Response Surface Methodology, *J. Food Eng.* **2007**, 78, 836.
- [16] J. M. Rodríguez-Nogales, N. Ortega, M. Perez-Mateos, M. D. Busto, Experimental Design and Response Surface Modeling Applied for the Optimisation of Pectin Hydrolysis by Enzymes from A. Niger CECT 2088, *Food Chem.* **2007**, 101, 634.
- [17] R. M. Banik, A. Santhiagu, S. N. Upadhyay, Optimization of Nutrients for Gellan Gum Production by *Sphingomonas Paucimobilis* ATCC-31461 in Molasses Based Medium using Response Surface Methodology, *Bioresour. Technol.* **2007**, 98, 792.
- [18] K. Murugesan, A. Dhamija, I. H. Nam, Y. M. Kim, Y. S. Chang, Decolorization of Reactive Black 5 by Laccase: Optimization by Response Surface Methodology, *Dyes Pigm.* **2006**, 75, 176.
- [19] K. Ravikumar, K. Pakshirajan, T. Swaminathan, K. Balu, Optimization of Batch Process Parameters Using Response Surface Methodology for Dye Removal by a Novel Adsorbent, *Chem. Eng. J.* **2005**, 105, 131.
- [20] K. Ravikumar, B. Deebika, K. Balu, Decolourization of Aqueous Dye Solutions by a Novel Adsorbent: Application of Statistical Designs and Surface Plots for the Optimization and Regression Analysis, *J. Hazard. Mater.* **2005**, 122, 75.
- [21] J. Segurola, N. S. Allen, M. Edge, A. M. Mohan, Design of Eutectic Photo Initiator Blends for UV/Curable Curable Acrylated Printing Inks and Coatings, *Prog. Org. Coat.* **1999**, 37, 23.