OPTIMIZATION AND KINETIC STUDY OF ELECTRO-FENTON PROCESS FOR THE DEGRADATION OF TEXTILE WASTEWATER USING CENTRAL COMPOSITE DESIGN

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Abstract: The study focuses on treatment of textile wastewater using Electro-Fenton process using graphite electrodes. The maximum removal of chemical oxygen demand and colour was evaluated at various operating conditions namely pH, Fe^{2+} dosage, and applied current. The Central composite design was used to optimize the operating conditions for the maximum removal of chemical oxygen demand and colour. The derived model represents good agreement between predicted and experimental results. Maximum reduction of chemical oxygen demand (83.6 %) and color (95.1 %) was achieved at pH 3.5, Fe^{2+} dosage 0.6 mM, and applied current of 0.6 A with electrolysis time of 40 mins. The second order reaction kinetics fit well with experimental data along with values of rate constants 0.0001 and 0.4827 (L/mg min) and R^2 values were 0.9577 and 0.9173 for chemical oxygen demand and color removal, respectively.

Keywords: Electro-Fenton process, Textile wastewater, Response surface methodology, Central composite design, Applied current

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INTRODUCTION

Textile industries require huge amount of fresh water [1] for processing of textile and generates huge quantity of wastewater causing intense water pollution[2,3]. The large quantity of wastewater generated from different processing units of textile industry mainly dying, sizing, scouring and bleaching etc. contribute huge amount of chemical pollutants which results in high colourization, high pH, suspended solids, chemical oxygen demand (COD) and low Biochemical Oxygen Demand (BOD)[4,5]. This wastewater produced in large quantity contain complex organic compounds which cannot be easily treated using conventional treatment methods[6] and can also be hazardous to whole ecosystem, if discharged without treatment[7].The high organic matter present in textile wastewater causes reduction of dissolved oxygen resulting in deleterious effect on aquatic ecosystem[8]. The physico-chemical methods namely coagulation-flocculation, adsorption, and membrane filtration methods etc are not effective in degradation of toxic and water soluble dyes in the wastewater[9]. The biological treatment process are ineffective in degradation of toxic dyes present in the solution[10,11]. Anaerobic process are ineffective in treatment of dye solution resulting in the production of toxic organic compounds[12].

Recently, Electro-fenton (EF) process has been an emerging new technology for the degradation of complex organic compounds due to its faster capacity and effectiveness to degrade toxic wastewater[13]. EF process is one among the advanced oxidation process (AOP's) which involving in-situ generation of highly reactive hydroxyl radicals (•OH) for degradation of industrial wastewater.

In EF process, hydrogen peroxide (H_2O_2) is continuously generated at cathode by two-electron reduction of oxygen molecules in acidic medium (Eq. 1)[14–16]. The catalyst namely Iron (Fe^{2+}) is further added to generate •OH which has electro potential of 2.8V as the classic Fenton's oxidation process (Eq. 2). The Fenton's oxidation process involves formation of Ferric ions which go through a cathodic reduction to produce ferrous ions (Eq. 3) which indeed enhances the efficiency of a degradation system. EF process requires less number of ferrous ions for the degradation of organic compounds as compared to classic Fenton's oxidation process[15].

$2H^{+} + O_2 + 2e \rightarrow H_2O_2$ (1)

$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{-} + HO^{o}$ (2)

$Fe^{3+} + e^{-} \longrightarrow Fe^{2+}$ (3)

The rate of reaction of EF is completely dependent on the production rate of H_2O_2. The factors which effect production of oxidising agent i.e., H_2O_2 are pH, cathode type, oxygen solubility, and Applied Current. The applied current not only regulates the generation of hydrogen peroxide (H_2O_2), but also enhances regeneration of Ferrous ions (Fe^{2+})[17].According to previous literature studies, researchers have reported the generation rate of Hydrogen Peroxide (H_2O_2) as dependent on electrodes used in the electrolytic system. Degradation of textile wastewater has been reported using different electrode material namely carbon, BDD, Pt and metal oxide-coated anodes etc[18]. Among these electrode material, carbon is a majorly used material as the electrode due to its high efficiency in two-electron reduction of oxygen molecules, production of hydroxyl radicals(•OH) and low catalytic activity for H_2O_2 decomposition[19]. Various carbon materials have been used as electrode materials for example carbon sponge, carbon felt, graphite, and activated carbon fiber[20]. Graphite is the widely used electrode material because of its high efficiency and low cost in generation of Hydrogen Peroxide in the electrolytic system[21].

In the present research, the optimization of EF process using graphite electrodes for the degradation of textile wastewater was carried out using response surface methodology (RSM). RSM is an effective statistical and mathematical tool used to analyse the individual and interactive effect among various experimental variables and response or output[22]. Quadratic or polynomial equations can be generated in RSM to evaluate the optimum independent experimental variables[23]..

In the current research, the effect of various operating conditions such as pH, dosage of Fe^{2+} and applied current on response or output (% COD removal and % color removal) has been evaluated. Predicted responses by the model were validated experimentally. At optimum working conditions, the kinetic study of COD and color removal were investigated.

MATERIALS AND METHODS

Textile Wastewater: The textile wastewater was collected from a cotton textile plant located in Northern part of Karnataka. The textile wastewater contains combination of Reactive Red HE7B and Blue HERD dyes majorly used for cotton dyeing[24]. The textile wastewater has a pH = 10.4, total organic content (TOC)= 469 mg/L, COD= 1236 mg/L, total dissolved solids (TDS) = 1820 mg/L and wavelength with maximum absorption of 306 nm.

The Electro-Fenton Experiments: EF experiments were carried out in a batch reactor made from fibreglass sheet of 1.5 L working volume (Figure. 1) with designated electrolysis time of 40 min along with settling time of 30 min at room temperature. Graphite electrodes (anode and cathode) were rectangular in shape with dimensions 5x10x0.3 cm along with spacing of 3cm. A constant digital power was supplied using DC power supply (Aplab, 0-32 V and 0-5A). Continuous supply of air was introduced using commercially available aerator. A set of two experiments was carried out for various pH values (3 to 4), dosage of Ferrous ions, Fe^{2+} (0.5 to 0.7 mM) and applied current, A (0.4 to 0.8 A). After each designed reaction time the samples were withdrawn for the further analysis. The collected samples were filtered using 0.45µ filter paper. Then the final COD, TOC and absorption values were analysed. To eliminate any strong residues on the surfaces after each run, the electrodes were carefully cleaned with water.

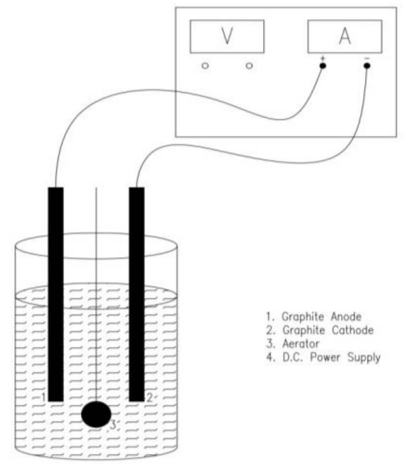


Figure 1. Schematic diagram of Electro-Fenton reactor

Analytical procedure

The pH values were measured using Orion pH meter. The COD (mg/L) was measured using open reflux method. Using UV-Spectrophotometer (Hach D4000) the maximum absorption wavelength was measured at wavelength of 306 nm. TOC values were analysed using TOC-OCTL (Shimadzu).

Central Composite Design (CCD)

In the present study, optimization and design of experiments (DOE) of the operating conditions was performed using a mathematical and statistical tool called CCD a form of RSM[22]. The synergetic effect of various working parameters namely pH, dosage of Fe^{2+} and applied current on reduction of COD and colour was analysed using Design Expert 12 software. The CCD was performed at three-level design and the factors were coded as -1 (lower level), 0 and +1 (higher level) and has axial points which were represented as + α and –α. The value of α depends on number of factors in the factorial design and can be obtained using (Eq.4)[24]

$$\propto = N_p^{1/4} \quad (4)$$

where $N_p = 2^n$, where *n* is number of factors. In the present study pH, Fe^{2+}concentration and applied current were used as operating conditions to investigate individual and synergetic effect on degradation of COD and color. The Eq. 5 represents the generated quadratic equation representing a functional relationship between the set of independent operating variables (Xi) and response (Y)[25] by the model.

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \quad (5)$$

where Y value represents predicted response, X_i value represents the independent operating conditions and β_i values represent the regression coefficient[26].

To acquire the optimum results, Analysis of variance (ANOVA) was used to analyse the functional relationship between independent operating variables and response. The surface plots and regression equation were developed[23].

RESULTS AND DISCUSSION

Experimental design and statistical analysis

In this research, a three-level CCD consisting of 20 experiments and second order polynomial equation for analysis of interaction between dependent and independent parameters was employed. The ranges of the various operating parameters are shown in Table 1. The total number of twenty experimental runs were conducted as shown in Table 2 with different operating parameters namely pH, Fe^{2+} dosage and applied current and experimental output parameters such as removal of COD and color as well as predictions by CCD. The experimental and predicted results show good agreement for COD and Color removal.

Table 1. Five levels of independent operating parameters on Electro-Fenton degradation on textile wastewater

Code	Variables	-α	+1	0	+1	+α
X_1	pH	2.5	3.00	3.50	4.00	4.5
X_2	Fe^{2+}(mM)	0.43	0.5	0.6	0.7	0.76
X_3	Applied Current (A)	0.26	0.4	0.6	0.8	0.94

Equation 6 and 7 represents the Quadratic equation developed using Design Expert for % removal of COD and Color, respectively.

$$COD\ (\%) = +84.39 + 0.5302\, pH + 0.1977\, Fe^{2+} + 0.8714\, A + 0.0125 * pH * Fe^{2+} - 0.1375 * Fe^{2+} * A + 0.1625 * Fe^{2+} * A - 5.39 * pH^2 - 2.55 * Fe^{2+^2} - 5.34 * A^2 \quad (6)$$

$$Color(\%) = +96.49 - 1.30 * pH - 0.9958 * Fe^{2+} + 1.39 * A - 0.1850 * pH * Fe^{2+} - 1.40 * pH * A + 1.32 * Fe^{2+} * A - 6.43 * pH^2 - 0.7130 * Fe^{2+^2} - 4.75 * A^2 \quad (7)$$

ANOVA results for the best fit quadratic model are shown in Table 3. A high *F*-ratio value represents that the model best fit for representation of COD and color removal. ANOVA results represent a significant model with 95 % confidence level with *P*-value less than 0.05. R^2 and R^2_{adj} (Regression co-efficient values) represents the quadratic model is in best fit with experimental results. The R^2 value (0.975 and 0.953) and R^2_{adj} value (0.953 and 0.911) for COD and Color removal represents a good fit model.

Response Surface plots

Response surface plots were produced for the graphical representation of interactive effect of various operating parameters on reduction of COD and Color, respectively. With constant in-situ production of hydrogen peroxide (H_2O_2) in EF process, the solution pH and Fe^{2+} dosage becomes important factor to produce hydroxyl radicals(•OH) and subsequent decrease of COD and color.

From Figures 2 (a) & b a sharp decrease of COD and colour was observed with an increase in pH from 3 to 3.5 and catalyst dosage from 0.5 to 0.65 mM. With further increase in Fe^{2+} dosage, H_2O_2 becomes limiting factor for the further production of •OH radicals. At pH 3.5 and Fe^{2+} 0.6 mM, a maximum reduction of COD (84.65 %) and color (96.87 %) was achieved.

Table 2. CCD for experimental and predicted responses (% COD and % Color reduction)

Run	Independent Variable			Response			
	X_1	X_2	X_3	Experimental		Predicted	
	pH	Fe^{2+} (mM)	Applied Current (A)	COD	Color	COD	Color
1	4.5	0.6	0.6	69.5	75.5	70.03	76.12
2	3.5	0.6	0.94	68.29	81.65	70.75	85.38
3	3.5	0.43	0.6	76.2	93.58	76.86	96.15
4	3	0.5	0.4	69.2	85.69	69.55	85.23
5	3.5	0.6	0.6	84.5	96.5	84.39	96.49
6	3.5	0.6	0.6	84.45	96.87	84.39	96.49
7	3	0.7	0.8	73.1	90.62	71.94	89.19
8	2.5	0.6	0.6	66.8	79.3	68.25	80.48
9	3.5	0.6	0.6	84.65	96.5	84.39	96.49
10	3.5	0.6	0.6	84.5	96.5	84.39	96.49
11	3.5	0.6	0.6	84.1	96.1	84.39	96.49
12	3.5	0.6	0.26	68.29	82.65	67.82	80.71
13	3.5	0.76	0.6	76.2	93.58	77.52	92.80
14	4	0.7	0.8	74.5	84.23	72.75	83.42
15	3	0.7	0.4	70.5	79.63	69.60	80.97
16	4	0.5	0.8	72.5	85.75	72.00	83.14
17	3.5	0.6	0.6	84.5	96.8	84.39	96.49
18	4	0.5	0.4	71.1	85.65	70.86	85.81
19	4	0.7	0.4	70.5	79.63	70.96	80.81
20	3	0.5	0.8	73.1	90.62	71.24	88.17

Table 3. ANOVA for optimization of real textile wastewater by Electro-Fenton process

	Source	Sum of squares	Degree of Freedom	Mean Square	F-Value	P-value
	Model	807.03	9	89.67	44.08	0.001
	Residual	20.34	10	2.03		
COD Removal	Lack of Fit	20.17	5	4.03		
	Pure Error	0.17	5	0.03		
	R^2	0.975	R^2_{adj}	0.953		
	Model	936.94	9	104.10	22.50	0.001
	Residual	45.97	10	4.60		
Color Removal	Lack of Fit	45.60	5	9.12		
	Pure Error	0.37	5	0.07		
	R^2	0.953	R^2_{adj}	0.911		

Figures 3 (a) & (b) represent the interaction effect of applied current (A) and pH on % of COD and color removal. Increase in the applied current increases the generation of oxidising agent (H_2O_2) on the cathode. However, it was observed that acidic solution was favourable for production of H_2O_2 in EF system. According to Eq. 8, in acidic solution the conversion of dissolved oxygen to H_2O_2 consumes the protons present in the solution. However, according to Eq. 9, low pH of the solution also promotes evolution of hydrogen resulting in lesser number of active sites for production of H_2O_2 [27]. Hence it concludes that an optimum pH and applied current is required for maximum degradation of the wastewater in EF process. Maximum reduction of COD (%) and color (%) were observed at optimum conditions with applied current 0.6 A and pH 3.5.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad E^0 = 0.67\,V \qquad (8)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad E^o = 0\,V \qquad (9)$$

Figures 4 (a) & (b) show the combined effect of Fe^{2+} and applied current on % degradation of COD and color. Increase in the applied current and dosage of Fe^{2+} generates more hydroxyl radicals (•OH) which indeed increases the degradation of textile wastewater. With further increase in applied current increases the production of hydroxyl radicals due to increase in production of in-situ H_2O_2 in electrolyte medium. It was observed that the efficiency of EF chain reaction decreases with further increase in Fe^{2+} dosage, H_2O_2 becomes limiting factor for the further generation of •OH radicals. Hence it states that at optimum EF conditions, maximum removal of COD (%) and color (%) was observed (Applied current 0.6 A, Fe^{2+} dosage of 0.6 mM and pH 3.5).

To obtain the optimum operating conditions for the maximum reduction of COD and color removal, an experiment was carried out at optimum operating conditions such as pH 3.5, Fe^{2+} dosage 0.6 mM, and applied current 0.6 A (Electrolysis time of 40 mins). The results show that the model predictions were in good agreement with experimental responses with 83.6 % of COD removal and 95.1 % of color removal [28].

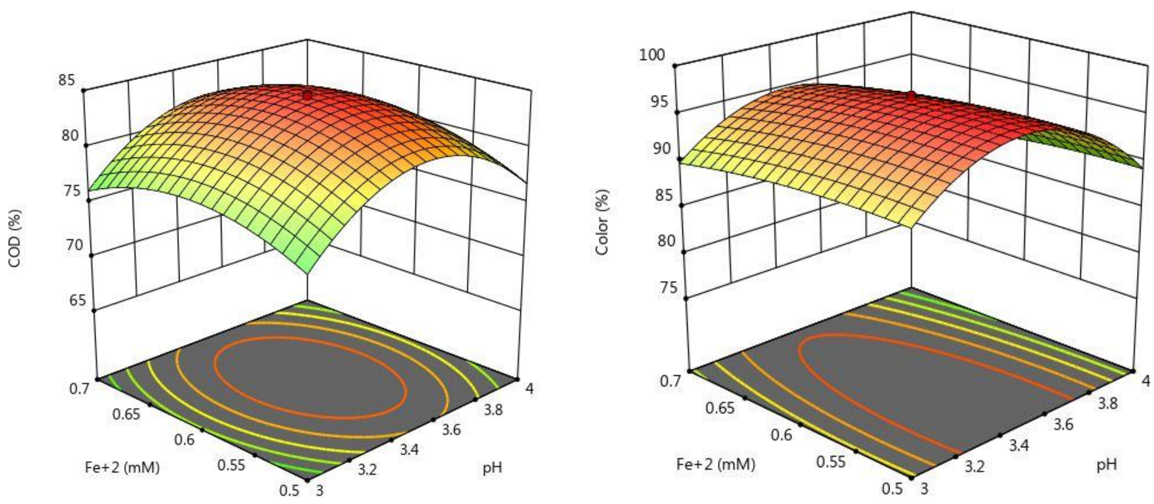
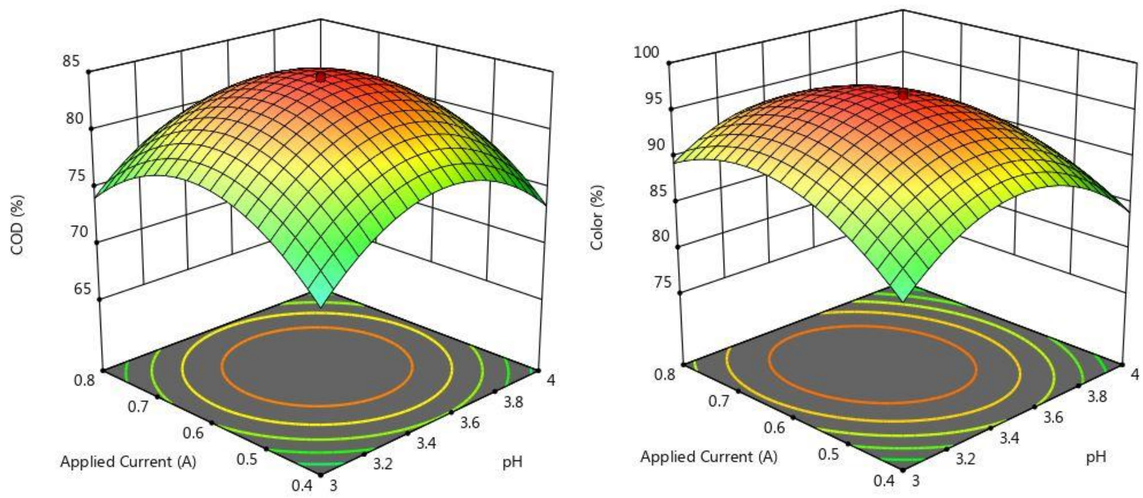
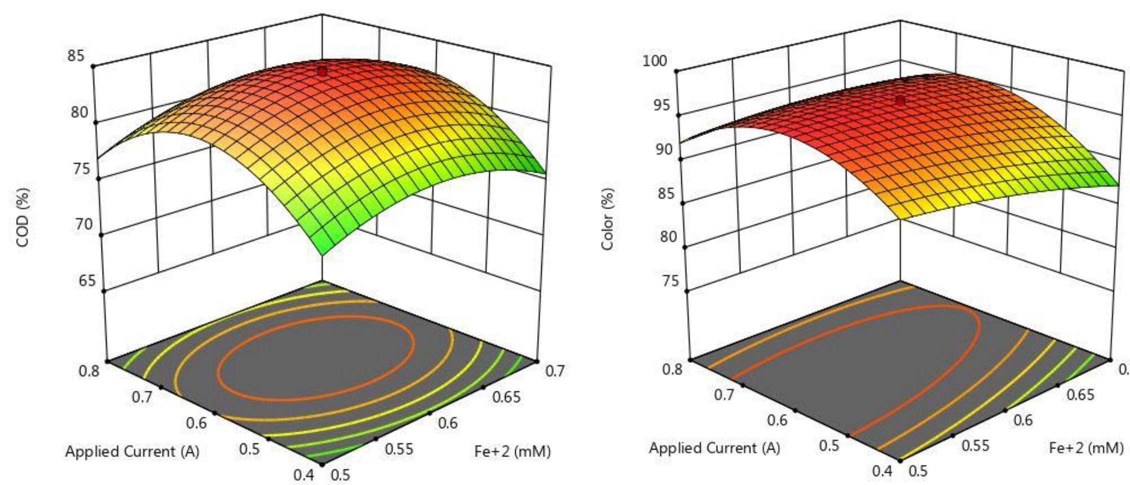


Figure 2. Response surface plots showing COD (%) reduction (a) versus pH and Fe2+ dosage and color (%) reduction (b) from versus pH and Fe2+ dosage (Applied current = 0.6 A and reaction time of 40 mins)



(a) (b)

Figure 3. Response surface plots showing COD (%) reduction (a) versus pH and applied current and color (%) reduction (b) from versus pH and applied current (Fe2+ dosage = 0.6 mM and reaction time of 40 mins)



(a) (b)

Figure. 4 Response surface plots showing COD(%) reduction (a) versus applied current and Fe2+ dosage and color (%) reduction (b) from versus applied current and Fe2+ dosage (Applied current= 0.6 A and reaction time of 40 mins)

Reaction Kinetics

The kinetics of COD and color removal was studied at optimum operating conditions for the degradation of textile wastewater using EF process. Table 4 represents the raw kinetic data used for the kinetic study. The experimental responses at optimum operating conditions namely, pH 3.5, Fe^{2+} dosage 0.6 mM and applied current 0.6 A (Electrolysis time of 40 mins) follows the second order kinetics. The rate equation for COD and color removal can be described as follows:

$$-\frac{dC_t}{dt} = k[C_t]^2 \quad (10)$$

Upon integration and rearranging the terms, the equation can be written as follows:

$$\frac{1}{[C_t]} = \frac{1}{[C_o]} + kt \quad (11)$$

where C_o is the initial COD concentration or color intensity, C_t is the final COD concentration or color intensity, t is time of degradation (min) and k is the second order rate constant (L/mg min). Figure 5 shows the second order fitting of reaction kinetics. The values of rate constants 0.0001 and 0.4827 (L/mg min) and R^2 value are 0.9577 and 0.9173 for COD and color removal, respectively.

Table 4. The raw kinetic data for degradation of textile wastewater using EF process

Time (min)	COD (mg/L)	Color (Abs)*
0	1236	1.108
10	650	0.163
20	325	0.125
30	210	0.085
40	201	0.045

*Absorbance value measured at 306 nm using UV spectrophotometer

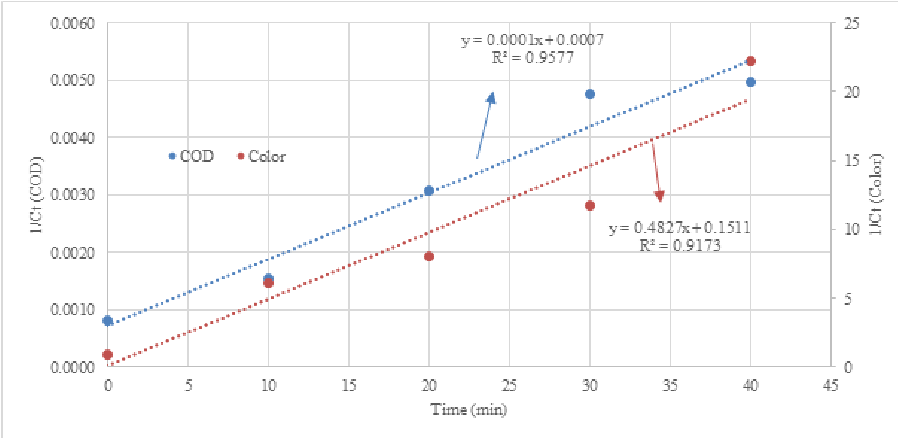


Figure 5. Second order fitting of reaction kinetics

CONCLUSION

In this study, EF process was used for removal of COD and color from textile wastewater. The CCD of RSM was used to investigate the optimum operating conditions for the maximum percentage removal of COD and color. The derived second order polynomial model stands in good agreement between the experimental and predicted values. The degradation of COD and color increases with an increase in catalyst dosage and decreases with an increase in the pH above 3.5. It was observed that the presence of Fe^{2+} concentration plays a vital role in EF process. Maximum reduction of COD (83.6 %) and color (95.1 %) was observed at optimum working conditions at pH 3.5, Fe^{2+} dosage 0.6 mM, and applied current 0.6 A with electrolysis time of 40 mins. The experimental data at optimum operating conditions follows the second order kinetics along with values of rate constants 0.0001 and 0.4827 (L/mg min) and R^2 values are 0.9577 and 0.9173 for COD and color removal, respectively. EF process provides most efficient environmentally friendly process for the degradation of textile wastewater.

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