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Decolourization of Safranine Dye by Iron(II)/$HClO_4$/CAB System from Wastewater Assisted by Response Surface Modeling

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The response surface methodology (RSM) is applied for predictive estimation and optimization of decolourization of safranine, a phenazine dye by a chemical oxidation process using iron(II) as homogeneous catalyst and chloramine B (CAB) as an oxidant in acid medium. All experiments were based on the statistical designs in order to develop the predictive regression models and for optimization. Four independent variables (temperature, catalyst, CAB and acid concentration) were chosen to optimize the decolourization of safranine. When variance was analyzed (ANOVA), values of R^2 and adjusted R^2 were 0.9618 and 0.9262, respectively. The data derived from the experiments were in alignment with a second order regression model. In order to achieve a maximum decolourization, the optimal settings were found to be 0.0178 M $HClO_4$, 0.004 M CAB, 0.0016 M iron(II) and 43.1 ºC, respectively. Under optimal reaction conditions, effect of temperature (15, 25, 35, 45 ºC) on decolourization rate was studied. Data received were in congruence with the second order kinetics. Thermodynamic parameters were also computed for the decolourization process. Maximum percentage of decolourization of safranine was predicted and experimentally validated.

Keywords: Decolourization, Safranine, Response surface methodology, Optimization, Kinetic modeling, Wastewater treatment.

INTRODUCTION

Due to rapid industrialization, water pollution has become a major threat to the entire globe. The release of water especially organic dyes from numerous industries is a big problem of the modern era due to its carcinogenic and other health hazard effects. The residue formed after the industrial dyeing process are displeasing. It also interferes with the propagation of light essential for autotrophic photosynthesis. The interference disrupts the ecology of the water bodies. These dyes are toxic in nature [1,2] and contains high percentage of organic compounds. The COD and TOC levels are quite high in these effluents. It has become an enormous task to optimize the procedures for the decolourization of dyes to meet the new discharge values given by the regulatories [3-5]. It has become important to remove or decrease the toxicity of the dye from the effluent before it is discharged. Therefore, research on decolourization and decomposition of dyes from industrial effluents are receiving increased attention.

Safranine is a cationic phenazine dye. It is a 3,7-diamino-2,8-dimethyl-5-phenylphenazin-5-ium chloride. It is widely utilized as a dye in histology [6,7]. The common application of the dye is to stain Gram-negative bacteria red. This draws a contrast with the Gram-positive organisms that are blue. Cartilage, mast cell granules and mucin are detected with the help of the compound. It also finds further use in dyeing tannin, wool, paper, cotton, silk, bast fibres and leather. The dye is proved to be carcinogenic. This threatens the marine life even if present in small amounts [8-10].

A wide variety of methods such as chemical, biological and physical (sorption, membrane separation, coagulation, flocculation, *etc*.), photocatalytic processs, *etc*. though available, some or the other shortcomings are associated with each method [11]. Physical and biological methods results in sludge

formation. Coagulation and flocculation requires physico-chemical monitoring and sorption and membrane processes requires high cost and maintenance. Therefore, a convenient method for the removal of safranine dye is important. One of the most favourable processes and cost effective method to remove dye from wastewater sewage is by chemical oxidation. It is a powerful process because it can decompose even the doubles bonds and the complex aromatic rings of dyes [12]. In this work, a simple redox system using chloramine B (CAB) as an oxidant, iron(II) as homogeneous catalyst and perchloric acid to maintain acidic pH are chosen to decolourize safranine dye in wastewater effectively.

Chloramine B is a well-known, mild and environmentally friendly oxidant containing *N*-halogen, which is highly polarized. The oxidation state of chlorine in chloramine B is +1. Based on the reaction conditions, it acts as electrophiles as well as nucleophiles [12-16]. It also has an advantage of being a disinfectant when compared to other agents such as ozone, ultraviolet light and ultrafiltration which has temporary actions.

Appropriate experimental designs are essential to assess the effect of treatments on quality characteristics. If one needs to study how two or more variables interact, response surface methodology (RSM) is proved to be effective. Since it is not feasible to completely explore the experimental space, especially when there are interactions among the variables, a statistical approach was applied [17]. In literature, RSM, built on the central composite design (CCD) has many environmental applications which includes heavy metal ion removal, adsorption of dye, production of biofuel, *etc*. [18-21]. The foremost benefit of RSM is the reduction in the frequency of performing experimental trials. These trials are needed to evaluate multiple parameters and interactivity. However, this is the first study on the optimization of safranine decolourization using chemical oxidation process. In present study, the application of central composite design is applied for detecting the most optimal environment, conducive for the process of decolourization and investigating the effect of four independent parameters *viz*. concentration of $HClO_4$, CAB and Fe(II) and temperature, simultaneously on the percentage of decolourization of safranine as response. Although, the present redox system is used to decolourize many dyes by various researchers, statistical analysis of decolourization of safranine dye using iron(II)/$HClO_4$/CAB redox system have never been reported.

EXPERIMENTAL

Chloramine-B (CAB) was purchased from Aldrich. The purification was performed using the method suggested by Morris *et al.* [15]. Fresh solution of CAB in water was made. Using iodometric methods, the aqueous solution was standardized. To prevent the solution to deteriorate photochemically, it was stored in brown bottles. Safranine, ferrous sulphate and perchloric acid was bought from Nice Chemicals Pvt. Ltd., India. The chemicals were used the way they were received. During the entire experiment, water prepared through double distillation was used.

Decolourization studies: The measurement of safranine decolourization was performed by observing the amount of dye absorbed in the aqueous medium. The absorption wavelength was kept at the respective maximum value of 520 nm. The concentration of safranine dye is maintained at 0.0002 M for all the experimental runs. The progress of the decolourization reactions were followed using UV-Vis spectrophotometer (Systronics PC Based Double Beam Spectrophotometer 2202). The decolourization was calculated using eqn. 1:

$$\text{Decolourization (\%)} = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

where C_o denotes concentration of dye at time instant t = 0, C_t denotes concentration of dye at time instant t.

Experimental design: Full factorial search was incorporated in response surface methodology (RSM) using central composite design (CCD). This was achieved by the examination of systematic, simultaneous and efficient variance of notable parameters. All of these were incorporated to model the process of decolourization, identification of possible interactions and effects of higher order and the determination of operational environment that is optimum [22]. Optimum conditions for the decolourization of safranine by iron(II)/$HClO_4$/CAB was fixed using CCD under RSM.

Four important parameters, concentrations of $HClO_4$ (A), CAB (B), iron(II) (C) and temperature (D) were the independent entities. Percentage decolourization depends on the above chosen parameters. Thirty experiments were performed totally. Each independent variable was studied at five different levels under CCD in four variables.

Factors as exhibited in the experiment involving 4 quantities (A, B, C and D) each at 5 steps, were written as $-\alpha$, -1, 0, +1 and $+\alpha$, respectively. The range of α values with respect to rotatable design depends on the number of points based on the equation $\alpha = (F)^{1/4}$, where, F is the number of points in the cube section of the design and is given by 2^k, where k is the number of independent variables. Here, we have four independent variables and hence $F = (2^4)^{1/4} = 2$. In this study, CCRD was used to predict the optimum values of process parameters and their interactions. The variation of the output was constant when the design is turned about its centre and the α value was fixed at 2 (rotatable) as per the above formula, where α is the distance of the axial points from the center and makes the design rotatable. Percentage decolourization of dye was considered as dependant factors.

Table-1 shows the range values and levels of the chosen independent variables. The CCD was utilized, taking into consideration the highest and the lowest levels of acid (0.002-0.02 mol/dm^3), CAB (0.0005-0.006 mol/dm^3), iron(II) (0.0001-0.0016 mol/dm^3) and temperature (25-45 ºC) for the decolourization of safranine. The dye concentration (0.0002 mol/dm^3) was kept constant throughout 30 experiments.

A polynomial model function (second order) was used with the objective of correlating the response to the operational floating parameters. The quadratic model is shown in full eqn. 2 as:

$$Y = a_o + \Sigma_{i=1}^{n} a_i X_i + \Sigma_{i=1}^{n} a_{ii} X_{i^2} + \Sigma_{i=1}^{n-1} \Sigma_{j=2}^{n} a_{ij} X_i X_j + e \quad (2)$$

TABLE-1
CODED LEVELS OF THE INDEPENDENT PARAMETERS

Independent parameters	Factor coded	Level				
		-2(-α)	-1	0	1	+2(+α)
$HClO_4$ (M)	A	0.007	0.002	0.011	0.02	0.029
CAB (M)	B	0.00225	0.0005	0.00325	0.006	0.00875
Fe^{2+} (M)	C	0.00065	0.0001	0.00085	0.0016	0.00235
Temperature (°C)	D	15	25	35	45	55

[Safranine] = 0.0002 M (for all experimental runs)

where Y represents the response of the predicted decolourization of safranine, i and j denote the coefficients of linear quadratic equation, the constant coefficient is a_o, the linear coefficient is a_i, the interactive coefficient is a_{ii}, the quadratic coefficient is a_{ij} and the model error is e. Statistical calculations were made to produce 3D curves making use of the regression models by using the regression coefficients. To analyze the obtained data graphically and to perform regression, design expert software, namely StatEase, USA was used. A 2^4 model of CCD was established. It is imperative to have replicates of the examination process at the center. The replicates provide an independent idea of the error related to the experiments. If the number of variables is 4, suggested number of examinations to be performed at the center is 6 [23]. Therefore, the total number of experimental tests run for the 4 independent parameters was 30.

$$N = 2^n + 2n + n_c = 2^4 + (2 \times 4) + 6 = 30$$

where 'N' is the total number of experiments required and 'n' is the number of factors taken into consideration in the model. All the 30 trials, in alignment with the experimental design, were applied to evaluate the experimental error. The results are given in Table-2. Modeling and optimization of the results and the respective parameters was performed by analyzing variance (ANOVA). It helps in identification of significant variables and their corresponding individual and interactive results on the process of removal of dye. To perform statistically designed experiments, the three considerable steps *viz.* estimation of the coefficients in the mathematical design, the prediction of the responses and the examination of adequacy of the model, are involved in the optimization process. The coefficient of determination (R^2) was used to express the quality of fit of the polynomical model. The *p* value and *F* value gives the significance of process variables.

TABLE-2
EXPERIMENTAL DESIGN (AS PER CODED FACTORS) AND THE CCD RESULTS

Run number	Codified values				Experimental values				Actual (%)	Predicted (%)
	A	B	C	D	$HClO_4$ (M)	CAB (M)	Fe^{2+} (M)	Temp. (°C)		
1	1	-1	1	-1	0.02	0.0005	0.0016	25	21.31	30.31
2	0	0	0	2	0.011	0.00325	0.00085	55	90.65	91.58
3	-1	-1	-1	-1	0.002	0.0005	0.0001	25	0	0.8508
4	1	-1	1	1	0.02	0.0005	0.0016	45	56.21	59.20
5	0	0	0	-2	0.011	0.00325	0.00085	15	66	55.98
6	-1	1	1	-1	0.002	0.006	0.0016	25	56.21	72.63
7	-1	1	-1	-1	0.002	0.006	0.0001	25	77.05	75.91
8	1	1	1	-1	0.02	0.006	0.0016	25	74.62	71.23
9	1	1	-1	1	0.02	0.006	0.0001	45	88.7	95.78
10	0	0	0	0	0.011	0.00325	0.00085	35	78.11	78.98
11	-1	-1	-1	1	0.002	0.0005	0.0001	45	0	5.24
12	-1	1	1	1	0.002	0.006	0.0016	45	84.62	80.64
13	0	0	0	0	0.011	0.00325	0.00085	35	78.85	78.98
14	-1	-1	1	1	0.002	0.0005	0.0016	45	1	0.4457
15	1	-1	-1	1	0.02	0.0005	0.0001	45	64.5	55.33
16	0	0	2	0	0.011	0.00325	0.00235	35	79.29	71.87
17	0	-2	0	0	0.011	-0.00225	0.00085	35	23.08	22.18
18	0	0	0	0	0.011	0.00325	0.00085	35	79.03	78.98
19	-1	1	-1	1	0.002	0.006	0.0001	45	84.38	82.63
20	0	0	-2	0	0.011	0.00325	-0.00065	35	81.66	76.44
21	1	1	1	1	0.02	0.006	0.0016	45	96.05	102.45
22	0	0	0	0	0.011	0.00325	0.00085	35	78.05	78.98
23	0	2	0	0	0.011	0.00875	0.00085	35	84.35	75.57
24	-2	0	0	0	-0.007	0.00325	0.00085	35	52.63	50.85
25	0	0	0	0	0.011	0.00325	0.00085	35	77.50	78.98
26	2	0	0	0	0.029	0.00325	0.00085	35	76.26	67.83
27	0	0	0	0	0.011	0.00325	0.00085	35	78.15	78.98
28	-1	-1	1	-1	0.002	0.0005	0.0016	25	0	-5.23
29	1	-1	-1	-1	0.02	0.0005	0.0001	25	21.91	27.74
30	1	1	-1	-1	0.02	0.006	0.0001	25	59.05	65.85

RESULTS AND DISCUSSION

Statistical analysis and modeling: Response surface methodology is a great tool as it saves, time, space, reagents, than single parameter optimization [24]. In current CCD, a total of 30 runs were carried out with four independent variables, *viz.* concentration of $HClO_4$, CAB, iron(II) and temperature (Table-2) for optimization of decolourization of safranine dye.

The quadratic model resulted in lowest standard deviations, PRESS (prediction error of sum of squares), the probability values < 0.05 and high values of R^2 (Table-3). Therefore, second order polynomial model, recommended by Design-Expert, was implemented to analyze the data. When all the experimental data was utilized, the final quadratic model thus generated as per coded factors for decolourization of safranine dye could be represented by the second order polynomial equation:

$$\% \text{ Decolourization} = + 79.13 + 12.18\,A + 29.58\,B + 0.1532\,C + 8.90\,D - 9.24\,AB + 2.16\,AC + 5.80\,AD + 0.7006\,BC + 0.5831\,BD + 0.3231\,CD - 8.92\,A^2 - 15.68\,B^2 - 1.89\,C^2 - 1.33\,D^2 \quad (R^2 = 0.9618)$$

where A: concentration of $HClO_4$, B: concentration of CAB, C: concentration of iron(II) and D: temperature.

TABLE-3
DIFFERENT MODEL - FIT SUMMARY

Source	Linear	2FI	Quadratic	Cubic
Sum of squares	9028.27	7035.02	1041.01	29.19
Mean squares	451.41	502.5	104.1	291.9
F value	1415.55	1575.75	326.44	91.52
Lack of Fit p-value	<0.0001	<0.0001	<0.0001	0.0002
P value	<0.0001	0.517	<0.0001	0.0006
Std. deviation	19.01	19.24	8.34	2.27
R^2	0.6695	0.7425	0.9618	-
Adj. R^2	0.6166	0.6069	0.9262	0.9946
Predicted R^2	0.5158	0.2491	0.681	
PRESS	13227.94	20516.97	8716.54	
Remarks			Suggested	Aliased

Analysis of variance (ANOVA): The virtue of the models for the decolourization study of safranine was confirmed by ANOVA. Table-4 represents the importance of each term. The same is governed by considering the respective *p* value, F value and sum of squares. Each coefficient's importance was governed by *p* values and F values. Significance of particular variable was checked by considering SS and they are found to be dependent on each other. In the present case A, B, D, AB, AD, A^2, B^2 are significant model terms. Content of Table-4 demonstrates statistical significance of regression response R at F values of 27.01 analogous to the *p* values of 0.0001. The significance of the corresponding coefficient term depends on the *p* value (small) and the F value (large) [25]. Hence, $HClO_4$, CAB and temperature, with largest F values and *p* values (< 0.0001), presented the most significant control on the response (Table-4). High regression at 95% confidence level is specified by remarkable terms of the model with *p* values less than 0.0500.

The merit of R^2 for decolourization was 0.9618 and Adj. R^2 was 0.9262. The accepted correlation coefficients might have been decided by 4 different variables (over a wide range) with the less number of experiments, the insignificant values of Table-4 and the non-linear effect of the investigated variables on process response. The model fits a given set of data (Table-4) is suggested by the high values of R^2 (0.9618), which implies that regressions model furnishes a supporting relationship between the independent variables (concentration of $HClO_4$, CAB, iron(II) and temperature) and decolourization efficiency. The values of the variables determined by numerical optimization supports the authenticity of the model and was confirmed by carrying out the experimental studies. The almost linear data points plotted in proximity to the predicted straight line response of the model *versus* actual response plot confirms that the model is reliable (Fig. 1).

Analysis of models by 3D response surface plots

Effect of variables associated with the process: The response surface plots shows the function of two factors, keeping other factors fixed at a firm level [26,27]. The impact of 4 different parameters involved in the process including concentration of $HClO_4$, metal ion concentration, concentration of CAB and temperature on % decolourization are shown in the 3D plots (Figs. 2a-f). Based on ANOVA results obtained [$HClO_4$], [CAB], temperature were found to have remarkable effects on the decolourization of dye. With CAB dose, imposing greatest

TABLE-4
REGRESSION ANALYSIS RESULTS (ANOVA) FOR THE DECOLOURIZATION OF DYE

Source	Sum of squares (SS)	Df	Mean Square	F-value	p-value	
Model	26279.36	14	1877.1	27.01	< 0.0001	Significant
A-$HClO_4$	2925.31	1	2925.31	42.09	< 0.0001	
B-CAB	17073.81	1	17073.81	245.64	< 0.0001	
C-Iron(II)	0.4524	1	0.4524	0.0065	0.9368	
D-Temperature	1901.22	1	1901.22	27.35	0.0001	
AB	1364.75	1	1364.75	19.63	0.0005	
AC	74.95	1	74.95	1.08	0.3155	
AD	538.59	1	538.59	7.75	0.0139	
BC	7.85	1	7.85	0.113	0.7414	
BD	5.44	1	5.44	0.0783	0.7835	
CD	1.67	1	1.67	0.024	0.8789	
A^2	1365.85	1	1365.85	19.65	0.0005	
B^2	4170.21	1	4170.21	60	< 0.0001	
C^2	59.8	1	59.8	0.8604	0.3683	
D^2	50.93	1	50.93	0.7327	0.4055	

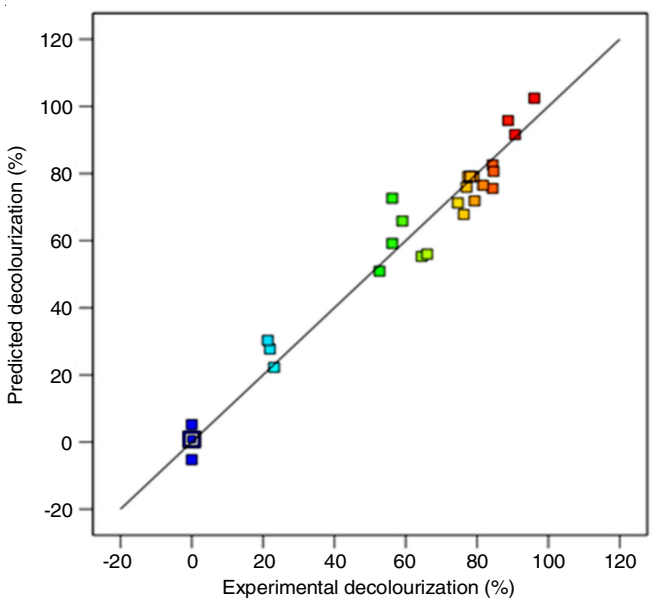

Fig. 1. Predicted and experimental data relationship graph

effects on the decolourization of the dye. On a different note, Fe^{2+} had least effect on the response. The quadratic effects of concentration of initial feed of iron(II) and the effect of interactions among AC, BC, BD, CD were considered moderate.

Fig. 2a illustrates 3D response surfaces, the combined effect of initial concentration of $HClO_4$ and CAB on dye decolourization at temperature (35 ºC) and fixed initial feed concentration of iron(II) (0.001 M). At low concentration of CAB, concentration of $HClO_4$ increases from 0% to 40%, however, with increase in concentration of CAB, a maximum decolourization of 90% is attained, which indicates the involvement of protonation species of oxidant CAB interaction with the dye in acid medium.

The interactive effect of concentration of iron(II) and $HClO_4$ of the solution on percentage decolourization of dye is shown in Fig. 2b. It shows that there is slight increase in decolourization with increase in concentration of $HClO_4$ and later exhibited a slight decrease. The maximum value of decolourization of dye > 80% was recorded at initial feed concentration of CAB of 0.005615 M and temperature (35 ºC). Iron(II) has very little influence on decolourization of dye.

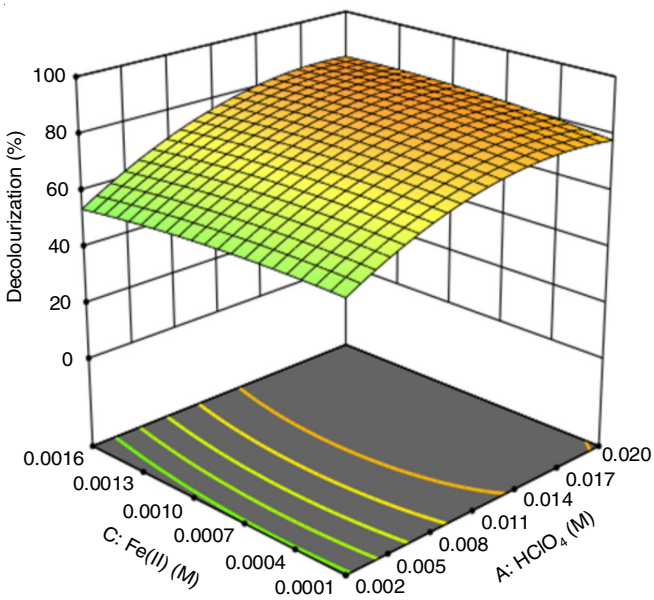

Fig. 2b. Mutual effect of initial concentration of iron(II) and $HClO_4$on decolourization of dye at fixed initial [CAB] 0.005615 M at 35 ºC

The combination of effects of initial feed concentration of $HClO_4$ and temperature on decolourization of dye at fixed initial concentration of CAB of 0.005615 M and concentration of iron(II) of 0.001 M is shown in Fig. 2c. The highest decolourization of dye > 95% was recorded when there was an increment in the temperature from 25 to 45 ºC and with increase in concentration of $HClO_4$.

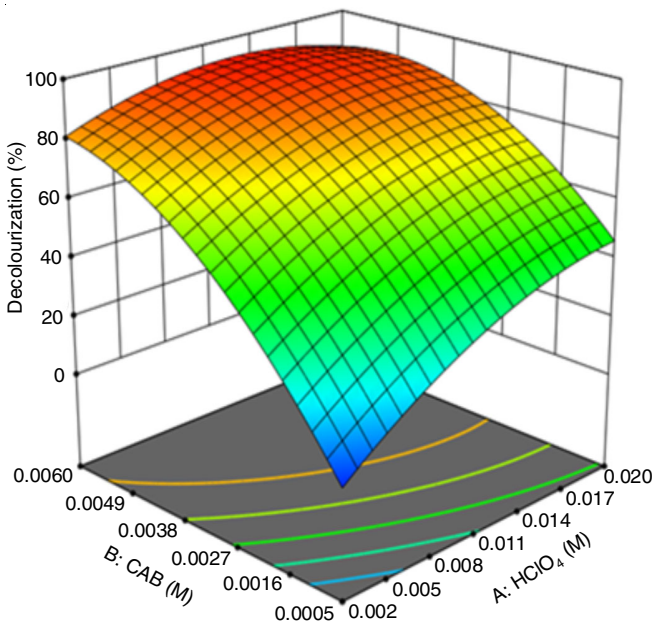

Fig. 2a. Mutual effect of initial concentration of $HClO_4$ and CAB (a), on decolourization of dye at fixed initial [iron(II)] 0.001 M at 35 ºC

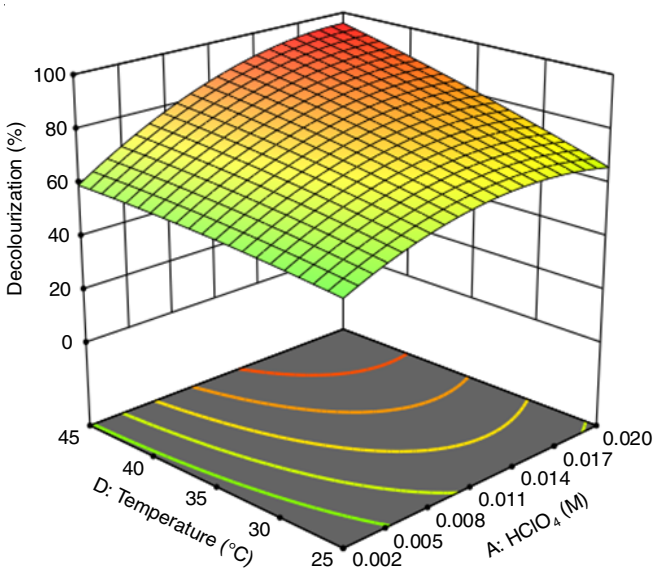

Fig. 2c. Simultaneous effect of initial concentration of $HClO_4$ and temperature on decolourization of dye at fixed initial [CAB] 0.005615 M and [Iron(II)] 0.001 M

The 3D response surface of the combination of effects of initial concentration of CAB and iron(II) on decolourization of dye at fixed initial feed concentration of $HClO_4$ of 0.011 M at 35 ºC is shown in Fig. 2d, which depicts a maximum decolourization of dye >85% with increase in concentration of CAB. Effect of iron(II) on decolourization of dye is found to have a feeble effect which is reflected in the statistical fit where the predicted and adjusted R^2 difference was found to be greater than 0.2, which indicates a block effect.

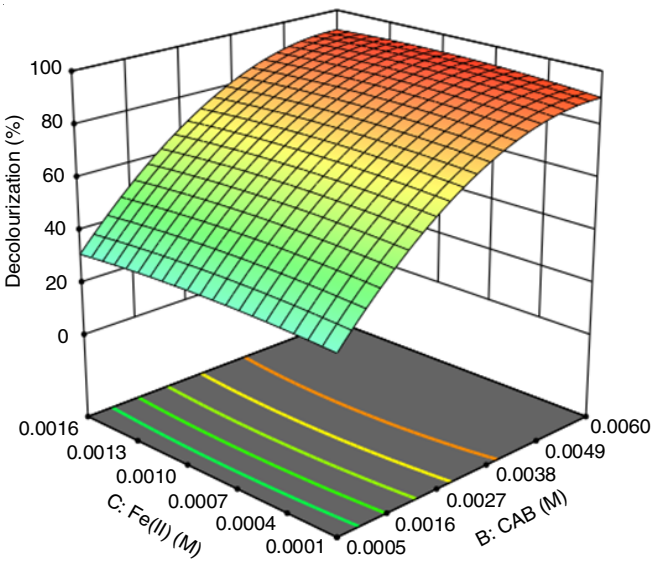

Fig. 2d. Effects of combined initial feed concentration of CAB and iron(II) on decolourization of dye at fixed initial [$HClO_4$] 0.011 M at 35 ºC

Fig. 2e shows the percentage decolourization increases sharply with increase in concentration of CAB and reaches almost a constant value at constant initial concentration of $HClO_4$ of 0.011 M and concentration of iron(II) of 0.001 M. When there was an increment in the temperature from 25 to 45 ºC, only a slight increase in decolourization is been observed.

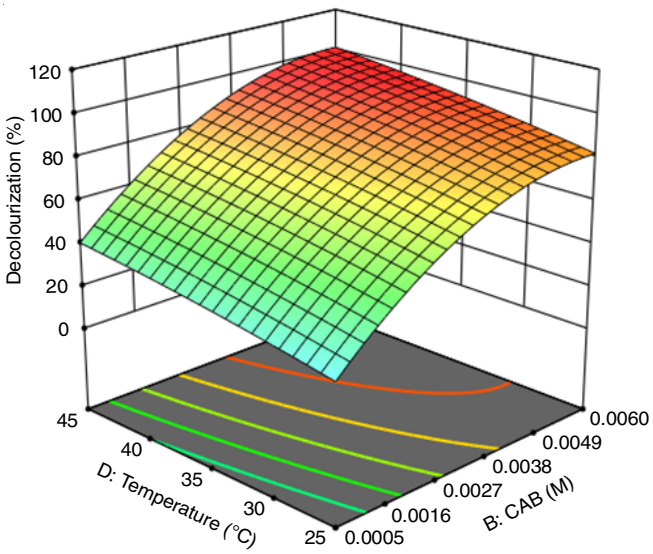

Fig. 2e. Effects of combined initial feed concentration of CAB and Temperature on decolourization of dye at fixed initial [$HClO_4$] 0.011 M and [Iron(II)] 0.001 M

It can be clear from Fig. 2f that the combination of effects of initial concentration of iron(II) and temperature on decolourization of dye at fixed concentration of $HClO_4$ of 0.011 M and concentration of CAB of 0.005615 M shows a maximum decolourization of > 95% with increase in temperature however not much significant decolourization is observed with increment in concentration of iron(II).

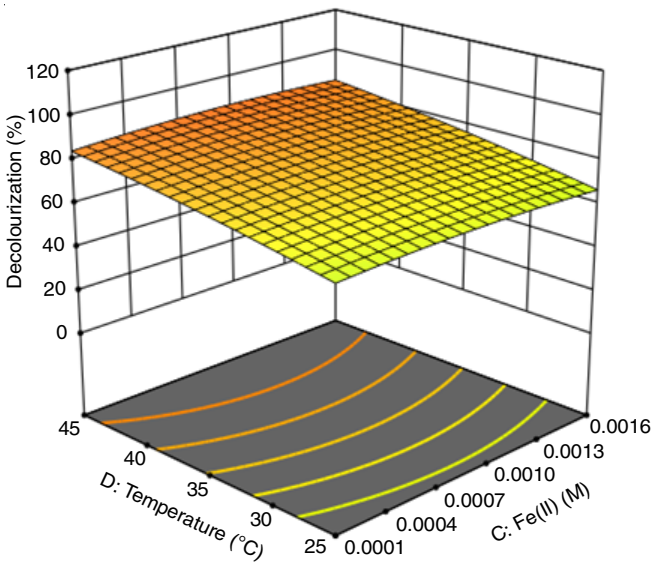

Fig. 2f. Combined effects of initial feed concentration of iron(II) and temperature on decolourization of dye at fixed [$HClO_4$] 0.011 M and [CAB] 0.005615 M

Optimization of experimental model: The quadratic equation which was developed by response surface methodology was utilized to obtain the optimum environment for maximum decolourization of the dye. Simultaneous influence of two or more independent variables on responses is the common difficulty happens during the optimization process which were easily executed using Design-Expert software [28]. The values of variables corresponding to 0.0178 M $HClO_4$, 0.004 M CAB, 0.0016 M Fe(II) and 43.1 ºC were determined for the maximum decolourization (98.8%) of optimal process condition by numerical optimization with a desirability value of 1 (Table-5). The decolourization of safranine dye under the optimal conditions is shown in Fig. 3.

Kinetics and thermodynamics studies: The kinetic models used to study the kinetics of the decolourization of dye are the pseudo-first order and the pseudo-second order [29]. The above mentioned models are shown as:

$$C_t = C_o e^{-k_1 t} \quad (2)$$

$$\frac{C_t}{C_o} = 1 - \frac{kC_o t}{kC_o t + 1} = \frac{1}{kC_o t + 1} \quad (3)$$

Rearranging eqn. (3):

$$\frac{1}{C_t} - \frac{1}{C_o} = Kt \quad (4)$$

where C_t denotes the dye concentration after time t, k_1 denotes the pseudo-first order rate constant (min^{-1}) and k_2 (L mol^{-1} s^{-1}) denotes the pseudo-second-order rate constant. It can be seen

TABLE-5
VALIDATION OF THE EXPERIMENTAL DESIGN

Experimental values				Decolourization		Error (%)
$HClO_4$ (M)	CAB (M)	Fe(II)	T (°C)	Predicted (%)	Experimental (%)	
0.015	0.004	0.00065	25	75.19	74.17 ± 0.98	1.36
0.020	0.006	0.00065	35	86.12	83.22 ± 0.68	3.37
0.020	0.006	0.00010	45	95.78	89.59 ± 0.21	6.46

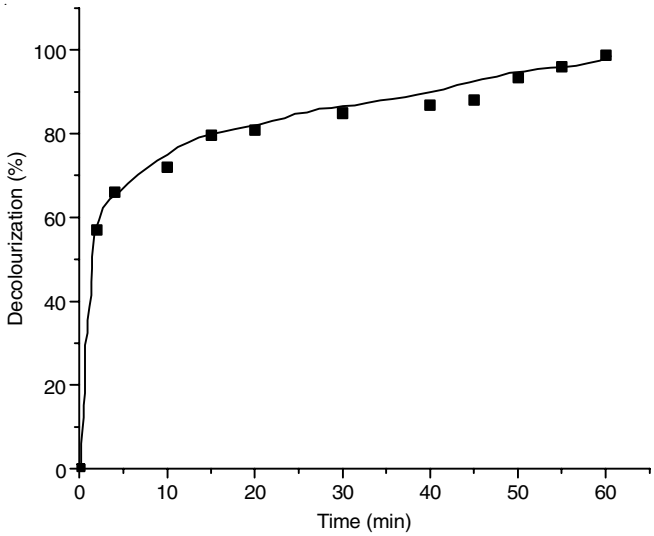

Fig. 3. Decolourization of safranine dye at optimum reaction conditions

from the Table-3. that the pseudo-first order kinetic model fits poorly with low R^2 value (0.6695) to the experimental data for decolourization as compared with that of pseudo-second-order kinetic model. The R^2 value for the pseudo-second-order kinetic equation was 0.9618. Therefore, it adjusted well with the model. Fig. 4 shows the dependence of UV-visible absorption spectra of aqueous dye solution on the reaction time. Decolourization was monitored with respect to the reaction time at 4 different temperature ranges (15, 25, 35, 45 °C). The outcomes are illustrated in Fig. 5a-d. The coefficient of determination (R^2) and the kinetic parameters of the second-

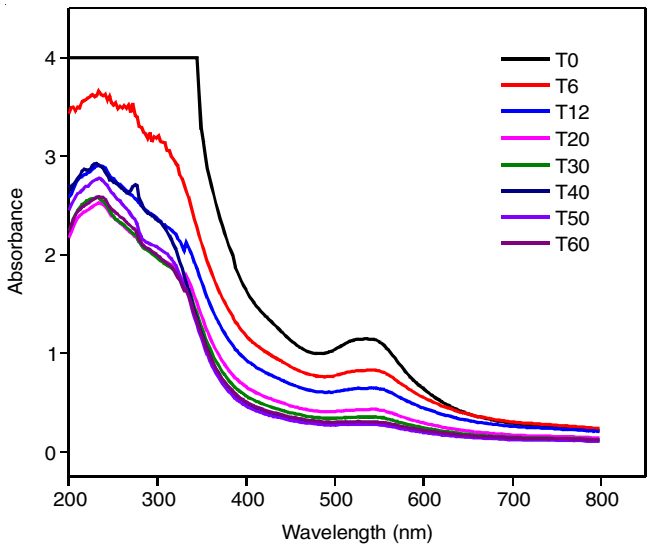

Fig. 4. Dependence of UV-visible absorption spectra of aqueous safranine dye solution on the reaction time

order model fit for the safranine decolourization using Iron(II)/$HClO_4$/CAB system at different temperatures are tabulated in Table-6. The linear relationship based on Arrhenius plot of log k′ *versus* 1/T is shown in Fig. 6. The measured apparent activation energy (E_a) derived from Arrhenius plot regression (Fig. 6) was 54.95 kJ/mol. The data are in conformity with the other studies *viz.*, the degradation of reactive orange 16 (E_a = 54.8 kJ/mol) and acid orange 7 (E_a = 55.3 kJ/mol) by catalytic oxidation in acid medium [12,15].

TABLE-6
KINETIC PARAMETERS AS A RESULT OF SECOND ORDER MODEL FITTING

Temp. (°C)	10^4 k (L mol^{-1} s^{-1})	R^2
15	5.77	0.9795
25	5.36	0.8791
35	9.15	0.9264
45	21.22	0.9829
55	12.4	0.9756

By fixing the other investigational conditions same, the reactions rates were quantified at 306, 311, 316.1 and 321 K temperatures, with the aim to assess the activation parameters. Calculations of activation parameters for net reaction were drew on the basis of the Arrhenius plots of log k′ *versus* 1/T (R^2 = 0.9956), values of activation parameters for overall reaction were calculated and presented in Table-7. Activation parameters were calculated by conventional thermodynamic equations.

TABLE-7
TEMPERATURE DEPENDENCE AND ACTIVATION PARAMETERS FOR THE OXIDATIVE DECOLOURIZATION OF SAFRANINE BY CAB IN ACID MEDIUM IN PRESENCE OF Fe(II) CATALYST

Temperature (K)	k′ × 10^4 (s^{-1})
306	8.51
311	11.75
316.1	17.78
321	22.91
E_a (kJ mol^{-1})	54.95
$\Delta H^{\#}$ (kJ mol^{-1})	52.34 (± 0.03)
$\Delta G^{\#}$ (kJ mol^{-1})	94.00 (± 0.42)
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	-132.88 (± 0.03)

Comparison of results with literature: Table-8 shows the decolourization of safranine dye effluent using various techniques. The reported methods have some disadvantages like high set up cost, less decolourization efficiency, operational costs maintenance cost and high investment. Though analogy of the present study with other different techniques applied for decolourization of safranine may incongruous, it can be

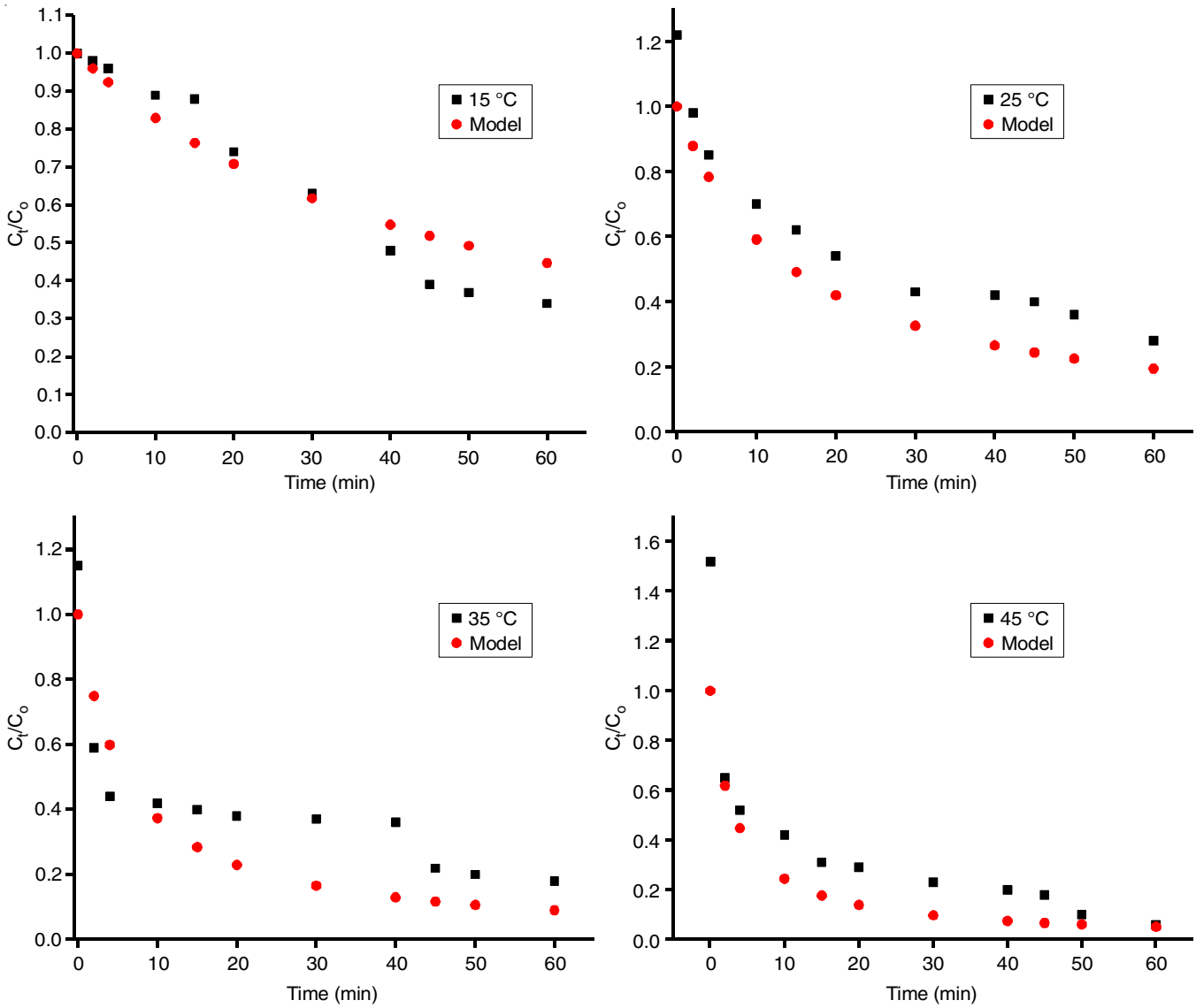

Fig. 5. Plots of concentration of safranine dye (c_t/c_o) as related to time at different temperature ranges

TABLE-8
COMPARISON OF DECOLOURIZATION OF SAFRANINE DYE EFFLUENT INCORPORATING DIFFERENT METHODS

S. No.	Removal technique	R (%)	Disadvantages	Ref.
1	Biodegradation by			
	a) Microbial crude laccase	a) 40.8%	Economical concerns	[30]
	b) *Penicillium expansum*	b) 41.1%	Necessary to create an optimally favourable environment	[33]
	c) *Aspergillus niger*	c) 38.9%		[33]
	d) *Pseudomonas putida*	d) 30%		[34]
2	Photocatalytic process (TiO_2 assisted)	88-98%	Fast charge rejoining and back reaction Incapacity to utilize visible light effectively	[31]
3	Non-conventional process	–	Non economical for bulk production Requires highly skilled labours High set up cost	[36]
4	Laser induced photocatalytic degradation using self synthesized nanocrystalline WO_3	94%	Size, cost and maintenance of instruments used	[37]
5	Hetergeneous Fenton process (UV Assisted)	74.76%	Size, cost and maintenance of instruments used Ineffective at high pH	[40]
6	Photodegradation using biotechnologically obtained ZnS-TiO_2 nanocomposites	100%	High running costs	[41]
7	Adsorption			
	a) Activated carbon from tamarind seeds	88.3%	Very expensive	[7]
	b) Pineapple peels	43.3%	Regeneration essential	[42]

8	Adsorption using natural zeolite	88-96%	High cost	[32]
9	Photocatalytic removal using synthetic		High cost and regeneration issues	
	a) Bentonite/PANI@Ni_2O_3	65.8%		[38]
	b) Hu/PANI@Ni_2O_3	80-100%		[39]
10	Oxidation using Fenton's reagent	–	High maintenance and operational costs	[44]
11	Adsorption using			
	a) Demineralized lignin	–	Relatively high investment	[43]
	b) Red mud waste	–		[9]
12	A novel homodimer laccase from Cerrena unicolor BBP6	97.1%	–	[35]
13	Photocatalytic degradation			
	a) Using modified and unmodified Au/ZnO	95%	High cost and regeneration issues	[45]
	b) FGS/ZnO NCs	94.5%		[46]
14	Decolourization using CAB/$HClO_4$/Fe(II)	98.8%		Present work

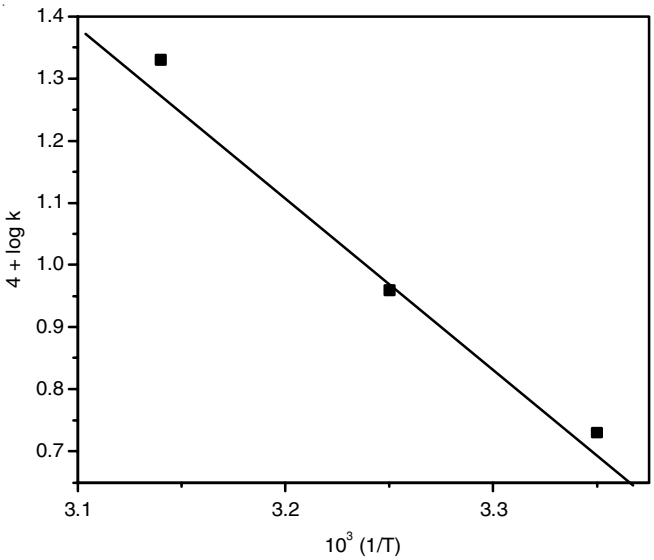

Fig. 6. Apparent second order rate constant (Arrhenius plot)

referred from Table-8 that decolourization of safranine dye from colour-bearing wastewater is fairly good and near with other techniques.

Conclusion

The optimization of decolourization of safranine dye from wastewater effluents by iron(II)/$HClO_4$/CAB redox system showed that initial chloramine-B (CAB) concentration, initial $HClO_4$ concentration and temperature had a remarkable effect on % decolourization. At the optimum operation conditions: 0.0178 M $HClO_4$, 0.004 M CAB, 0.0016 M Fe(II) and 43.1 ºC, the maximum decolourization of safranine dye (98.8%) was achieved. Also, study of central composite design (CCD) and response surface methodology (RSM) on the decolourization of safranine dye facilitated the determination of optimal operating conditions in this mutually dependent multivariate system.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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