Applying Response Surface Methodology to Optimize the Fenton Oxidation Process in the Removal of Reactive Red 2

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Abstract

This study evaluated the influence of experimental factors on reactive red 2 oxidation by the Fenton process using response surface methodology (RSM). Experiments were conducted based on a central composite design (CCD) using operating variables such as H_2O_2, Fe^{+2}, and reaction time. The responses were evaluated using a second-order polynomial multiple regression model. The analysis of variance (ANOVA) showed a high coefficient of determination (R^2) value of more than 0.98. It confirms a satisfactory adjustment of the second-order regression model with the achieved data. H_2O_2 had a significant effect on the removal of RR2 and COD. When the initial concentration of H_2O_2 was 90 mg/l, the efficiency of RR2 removal was 94%. The experimental findings were in close agreement with the model prediction.

Keywords: reactive red 2, sewage, Fenton's process, hydroxyl radicals, central composite design

Introduction

Textile industries are known as one of the most important sources of synthetic dyes, which are classified into different groups: acid, reactive, direct, basic, vat, disperse, metal complex, mordant, and sulphur dyes [1-2]. Azo dyes are regarded as the greatest groups of synthetic dyes, which have one or more azo bounds (-N=N-), and due to their high solubility, low cost, stability, and color variety are widely used in many applications [1, 3]. Reactive red 2 (RR2) is a reactive azo dye because its strong covalent bond is hard to disintegrate in nature [4].

The discharge of textile effluent into the environment, especially receiving waters because of especial characteristics of colored effluents such as complex composition, toxicity, poor degradability, and high solubility, can cause deterioration of environmental quality such as reducing the receiving waters' self-purification capacity and decreasing the rate of photosynthesis. Therefore, in the last few years removing azo dyes has attracted great interest [5-7]. In this regard, numerous physicochemical methods – including precipitation, coagulation, flocculation, adsorption [2], reduction, electrochemical treatment [8], and photo degradation [9, 10] – have been used to remove dyes from aqueous solutions [7, 11].

Among different methods that have been applied for removing dyes, AOPs are known as the proper

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techniques to remove toxic aqueous pollutants. They are based on producing highly potent oxidants such as hydroxyl radical (OH˙), which has a strong potential to remove pollutants [6]. In recent years, the Fenton process because of high oxidation power, easy operation and maintenance, rapid oxidation kinetics, and relatively low cost and effectiveness has been successfully used as a reagent for removing pollutants from different media [12-13]. Fenton's reagent (FR) has been applied to treat inorganic and organic components such as phenol, LAS, atrazine, trihalomethanes, and textile sewage [1, 13-17]. According to the different studies that have applied the Fenton process, this reagent is affected by concentrations of oxidant (H_2O_2), catalyst (Fe^{+2}), and contaminant. Furthermore, other parameters such as contact time, pH, and temperature are important factors that affect the efficiency of process [12, 14]. Therefore, optimizing them has a significant effect on the selecting process by operators of sewage treatment sectors.

The present work was undertaken to develop experimental tests employing the Fenton oxidation process in treating RR2 from synthetic solution. In this regard, it developed a model that provides optimum concentration of catalyst ($FeSO_4$), oxidant (H_2O_2), and oxidation time by using central composite design (CCD) and response surface methodology (RSM) as mathematical and statistical techniques that are useful for analyzing the effects of several independent variables in the response [18-19].

Materials and Method

Chemical and Feeding

Lab-grade RR2 with formula ($C_{19}H_{10}C_{12}N_6O_7S_{2.2}$ Na; 98%; Fig. 1), Ferrous Soulphat ($FeSO_4 \cdot 7H_2O$; 99.5%), and hydrogen peroxide (H_2O_2, 35% W/W) were supplied by E. Merck, Germany. A 50% H_2SO_4 solution was used to prepare its one molar solution, which is used to adjust pH at 3. A 50% NaOH stock solution was used to prepare its one molar solution, which is used to stop the Fenton reaction at the wanted reaction times.
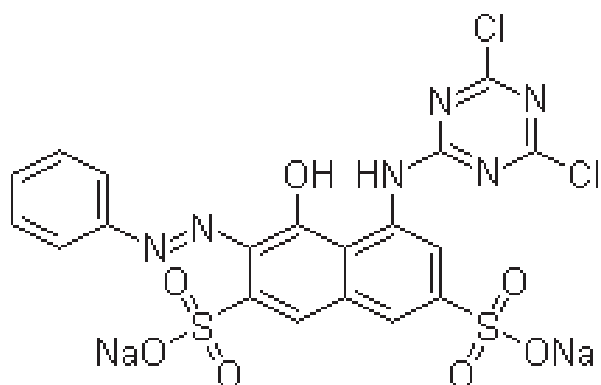

Fig. 1. Chemical structure of reactive red 2.

Experimental Method

Batch reactors were employed in this work using six series of Pyrex glass with working volume 1 L, each flax was applied for specific concentration of Fenton reagent at different reaction times throughout a cycle with sequencing stages of react, settle, and decant. Settle, decant, and fill stages were always accomplished within 1 hour. The flaxes were filled to capacity of 1 L by stock RR2 solution with initial concentration of 10 mg/L. Then pH was adjusted at 3 with a lab pH meter (model E537). Furthermore, hydrogen peroxide was used as a variable at the arranged concentrations of 10, 50, and 90 mg/L. The concentrations of Fe^{+2} as catalysts 10, 50, and 90 mg/L were tested in this study.

Sample Preparation and Analytical Methods

In the case of designed experiments, sampling was carried out after the aforementioned reaction time. Using 0.45 μm filter papers, the collected supernatants were filtered and analyzed every day for RR2 by a Jenway 6305spectrophotometer at λmax 645 nm. Chemical oxygen demand (COD) was determined according to standard methods [20], and pH was adjusted with a Meter Lab E537 pH meter. All the tests were carried out in triplicate to fulfill reproducibility.

Experimental Design and Data Analysis

Design-Expert software (version 8.0.0) was applied for the statistical design of the experiments and data analysis through the CCD technique and response surface methodology. RSM is a statistical technique that can be used to optimize and model of achieved experimental data through three steps: statistical design of experiments, assessing the coefficients in a mathematical model and predicting the responses, and examining the adequacy of the model [21]. A standard RSM design called central composite design is a suitable method to fit a quadratic surface. The application of this method allows us to estimate the synergetic or antagonist effect of factors with a minimum number of experiments, as well as to analyze the interaction between them [22]. The aforementioned ability of RSM using the CCD was quite enough to use this method to design the experimental works, to optimize the obtained data, and to study the interactive effects of main factors. The number of runs calculated is based on CCD according to the relation $2n + 2n + nc$ (where n is the number of factors and nc is the number of center points). The center points are developed to evaluate the experimental error and the reproducibility of the data [23]. The experimental data was analyzed and modeled through an empirical second-degree polynomial as Equation 1 [24].

$$Y = \beta_{\circ} + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i<j}^{k} \sum \beta_{ij} x_i x_j + e$$

(1)

…where i represents the linear coefficient, j stands for the quadratic coefficients, β is the regression coefficient, x represents independent variables, k is the number of studied and optimized factors in the experiment, and e is the random error.

The modeling process was fulfilled by analysis of variance (ANOVA) for concentrations of H_2O_2 and Fe^{+2} and reaction time as independent factors with two main responses: dye removal and COD removal. According to Table 1, the CCD includes eight factorial points, six axial points, and center point with six additional experimental trials as the replicates of this point. The term of coded value was used to present independent variables at three levels: -1 (minimum), 0 (central), and +1 (maximum). The accuracy of the polynomial model was explicated by the coefficient of determination R^2. In addition, model terms were selected or rejected based on the P value with 95% confidence levels. Surface plot (three-dimensional) and respective contour plots (two-dimensional) were provided for removing RR2 and COD based on the effects of H_2O_2 and Fe^{+2} doses in the actual values (AV) at different reaction times.

Results and Discussion

Development of Mathematical Model

The results of modeling using RSM and CCD based on achieved data are summarized in Table 2. RR2 and COD are dye removal and COD removal in terms of coded factors (CF), and actual factors (AF) for H_2O_2, Fe^{+2}, and reaction time. The amount of the coefficients for A, B, and C in models confirms the more effective role of H_2O_2 concentration and the inferior effect of Fe^{+2} dosage in removing the dye and COD. According to the results of statistical analysis that have been denoted in Table 2, "model F-value" for percentage removal of dye and COD were 923 and 64, respectively. The value of "Prob- F" was 0.0001 for achieved data. The Prob – F > 0.05 indicates that model terms are significant [21, 24]; therefore, the model is significant and there is only a 0.01% chance that a "model F-value" this large could occur due to noise. In this case A, C, A^2, and B^2 are significant model terms. Values greater than 0.1 indicate that the model terms are not significant. Adequate precision measures the ratio of signal to noise, and a ratio greater than 4 is desirable [24-25]. According to Table 2, a ratio of 24.65 indicates an adequate signal. This model can be used to navigate the design space. The "Pred. R-Squared" of 0.98 is in reasonable agreement with the "Adj. R-Squared" of 0.99.

Table 1. Results of experiments according to CCD for three-level factorial of variables.

Run	Factor A: H_2O_2 (mg/L)	Factor B: Fe^{+2} (mg/L)	Factor C: time (h)	Response 1: (% dye removal)	Response 1: (% COD removal)
1	50	90	10	85	90
2	10	10	5	30.13	34
3	50	50	10	93	93.7
4	50	50	10	93	93.7
5	50	50	10	93	93.7
6	50	50	10	93	93.7
7	10	10	15	37	46
8	10	50	10	46	60
9	10	90	5	28.1	25
10	90	90	5	84.7	83.3
11	50	50	5	84.6	83.3
12	90	50	10	98	96
13	50	10	10	82	84
14	50	50	15	96	95.83
15	10	90	15	40	58
16	50	50	10	93	93.7
17	50	50	10	93	93.7
18	90	10	5	93.69	81.25
19	90	10	15	88	96
20	90	90	15	89	93.8

Table 2. Developed quadratic models and ANOVA results using Design Expert 8.0.0 for studied responses.

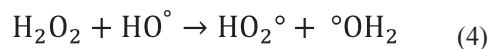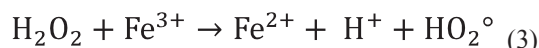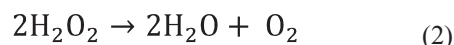| Response	Final model with significant terms coded factors (CF) and actual factors(AF)	Prob > F"	R^2	Adj. R^2	PredictedR-Squared	Adequate Precision	CV	PRESS	Sequential p-value
Dye removal (%)	CF: Dye =+92.96+26.22 * A+0.60 * B+3.88 * C +0.13 * A * B-1.27 * A * C+0.63 * B * C-20.90 * A^2-9.40 * B^2-2.60 * C^2 AF: Dye =-7.45426+2.02103 * A+0.56696 * B +3.01550 * C+8.12500E-005 * A * B-6.35000E-003 * A * C+3.13750E-003 * B * C-0.013062 * A^2-5.87443E-003 * B^2-0.10396 * C^2	< 0.0001	0.99	0.99	0.98	84.3	1.5	155	< 0.0001
COD removal (%)	CF: COD = +94.06+22.73 * A +0.88 * B+8.28 * C-0.39 * A * B-2.47 * A * C+2.09 * B * C-16.61 * A^2-7.61 * B^2-5.04 * C^2 AF: COD =-11.57820+1.74210 * A+0.40523 * B+5.78353 * C-2.46094E-004 * A * B-0.012344 * A * C+0.010469 * B * C-0.010380 * A^2-4.75483E-003 * B^2-0.20171 * C^2	< 0.0001	0.98	0.96	0.73	24.6	5	2475	< 0.0001

A: H_2O_2, B: Fe^{+2}, R^2: determination coefficient, Adj. R^2: adjusted R^2, SD: standard deviation, CV: coefficient of variation, PRESS: predicted residual error sum of squares.

Effect of H_2O_2 Concentration

In order to investigate the effect of H_2O_2 concentration on RR2 degradation, experiments were conducted at different H_2O_2 concentrations from 10 to 90mg/L in lab conditions while keeping the dye concentration at 10 mg/L and pH at 3. In the Fenton process, H_2O_2 concentration plays a critical role in contaminant removal efficiency. The results of color removal for 10 mg/L of RR2 for determining optimum H_2O_2 concentration are illustrated in Table 1. As shown in Table 1, by increasing H_2O_2 concentration from 10 mg/L to 90 mg/L, the removal efficiency of RR2 increased from 46% to 98%, when the catalyst and reaction time were 50 mg/L and 10 min, respectively. According to the results, COD removal was 95.8% at 80 mg/L of H_2O_2 as shown in Fig. 1. This result indicates the minimum yielding 34% COD removals at 10 mg/L of H_2O_2 according to aforementioned results in Table 1. By increasing the concentration of H_2O_2 up to 90 mg/L we did not show significant improvement in COD removal, and by increasing it to 100 mg/L the efficiency decreased to 90%, which can be due to self-decomposition of H_2O_2 according to Equation (2).

Several researchers have studied the effect of initial concentration of H_2O_2 on the degradation of organic compounds using the Fenton process. They confirmed that choosing the suitable concentration of H_2O_2 is important for two reasons:

1) The excess H_2O_2 reacts with ferric ion (Fe^{3+}) to form a weaker hydroperoxyl radical ($HO_2°$) as presented in Equations (3) and (4), which is not as active as °OH radicals as confirmed by many researchers [7, 26-29].
2) Due to the high cost of H_2O_2, consuming its excessive value is not cost-effective [7, 10].

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{2}$$

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + H^+ + HO_2° \tag{3}$$

$$H_2O_2 + HO° \rightarrow HO_2° + °OH_2 \tag{4}$$

Figs 2 and 3 shows the percentage of removing dye and COD as a function of the initial concentration of H_2O_2 and Fe^{2+}. The response contour (2a and 3a) and response surface plot (2b and 3b) in Figs 2 and 3 for different dosages of H_2O_2 and Fe^{2+} are shown at constant concentration of dye (10 mg/L) and reaction time 10 min. From Figs 2 and 3 it is clear that the percentage removal of dye and COD removal increased with increasing H_2O_2 until 80 mg/L. The effect of the Fenton process on the removal of two direct dyes, blue 2B (B54) and red 12B (R31), in aqueous solution has been studied by Malik and Saha (2003). The results denoted that the degradation rate depends on the initial concentrations of H_2O_2 [28]. Lin et al. (1997) confirmed that when H_2O_2 starts to be unused in solution,

Fig. 2. The response contour plots and response surface plots of dye (a and b) as response affected by variables H_2O_2, Fe^{+2}, and "reaction time = 10 min" in the Fenton process.
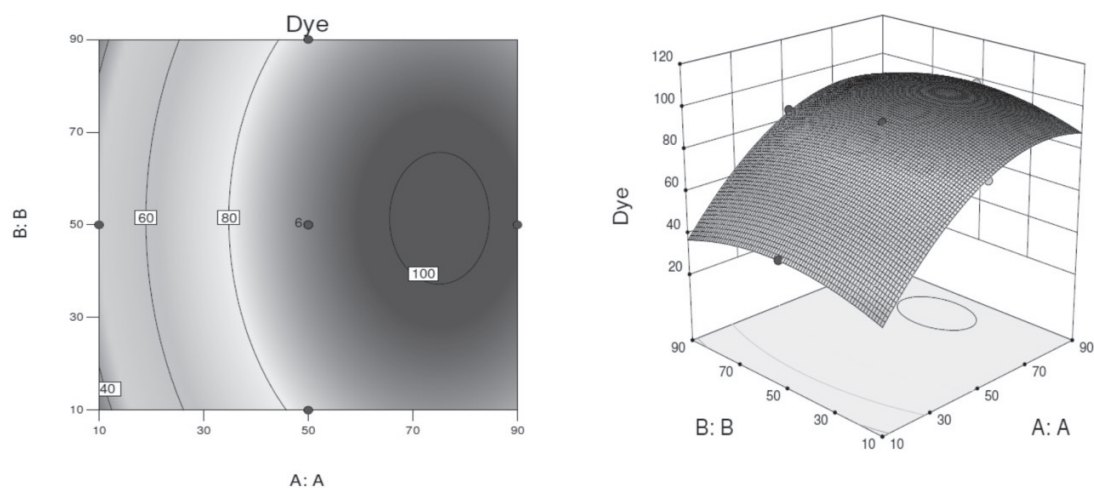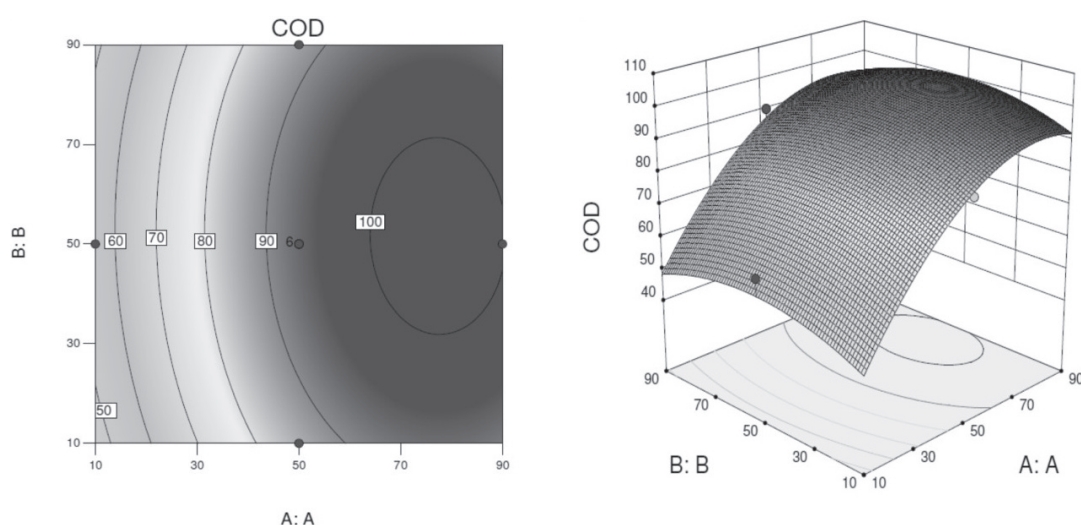

Fig. 3. The response contour plots and response surface plots of COD (a and b) as response affected by variables H_2O_2, Fe^{+2}, and reaction time = 10 min in the Fenton process.

the time can be considered as the end of the reaction time [27]. Jafari et al. (2014) mentioned the significant effect of hydrogen peroxide on the removal of azo dyes (RB-19 and RR-198) from aqueous solution. The result showed when the H_2O_2/Fe^{2+} ratio increased, the process led to greater oxidation of dye and optimum H_2O_2 dosage was 11 mM. They mentioned that the decrease in removal efficiency at a high dosage of H_2O_2 was due to the hydroxyl radical scavenging effect of H_2O_2 and the recombination of the hydroxyl radical [30]. Based on achieved results from previous research, applying stepwise for the H_2O_2 addition could be more effective than using a large initial dosage [30-31].

The Effect of Fe²⁺ Concentration

The effect of Fe^{2+} concentration on dye and COD removal efficiency for 10 mg/L of RR2 is given in Figs 2 and 3. According to Fig. 2, maximum RR2 removal

(% 98) for 10 mg/L of RR2 was obtained by using 50 mg/L of Fe^{2+}, and H_2O_2 and reaction time were kept at 80 mg/L and 10min, respectively. Although the 90 mg/L concentration (density) of Fe^{2+} COD removal was not high as well as using 50 mg/L of Fe^{2+}, which may be explained by redox reactions, since OH radicals might be scavenged by the reaction with the hydrogen peroxide present or with another Fe^{2+} molecule according to Equations 5 and 6 [23, 29, 32].

$$Fe^{2+} + HO^\circ \rightarrow Fe^{3+} + OH^\circ \qquad (5)$$

$$H_2O_2 + HO^\circ \rightarrow HO_2{^\circ} + {^+}OH_2 \qquad (6)$$
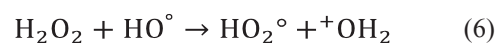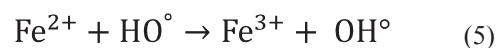
Kavitha and Palanivelu (2005) elucidate the role of Fe^{2+} ion on the degradation of cresols at different concentrations of Fe^{2+} ion from 0 to 1 mM, when H_2O_2 and pH were 31.64 mM and 3 mM, respectively. Results

showed that the process efficiency increased progressively by increasing Fe^{2+} ion concentration due to a higher amount of °OH radical generation. Maximum degradation efficiency about 82% was achieved at 0.90 mM of Fe^{2+} for o- and p-cresol, while it is 0.72mM for m-cresol. A further increase in Fe^{2+} ion concentration did not correspondingly increase its reactivity, probably due to direct reaction of °OH radical with metal ions as mentioned in Equations 5 and 6 [33]. The results show that the H_2O_2 /Fe^{2+} ratio is an important parameter in Fenton's reactions because it directly influences the quantum yield of °OH generation [34]. Its importance was confirmed by previous studies, including Azami et al. (2013) during optimization of the azo dye removal, methyl red, from the wastewater-applied Fenton process. The results confirmed that when increasing Fe^{2+}, an increasing pattern is detected in the dye removal ratio, but increasing the Fe^{2+} more than a specific limit can lead to a fix or decrease the percentage of dye elimination and the optimum ranges of Fe^{2+} was 0.1-0.4 mM [35]. The results of studies by Jafari et al. (2014) and Tuty Emilia A. et al. (2014) showed that increasing the Fe^{2+} ion above optimal dosage cannot be the cause of an increase in the removal efficiency because of the tendency of the $HO^{\wedge \circ}$ to react with Fe^{2+} and H_2O_2 in the oxidation-reduction reaction [4, 30].

The Effect of Reaction Time

The results show that at low doses of FR, degrading dye and COD was low, but by increasing the reaction time from 5 to 15 minutes the dye removal improved at all levels of H_2O_2 and Fe^{2+} dosages (Fig. 4). According to the models that have been developed in this study, the coded factors (CFs) for the effluent concentration of dye as first response represents a coefficient for reaction time of 3.88, which is 6.75 times less than the coefficient for initial concentration of H_2O_2 (26.22). This finding proves that reaction time contributed an effective function in time on the effluent concentration of dye less than H_2O_2. The result of this study is in agreement with previous investigations on the effect of reaction time. Mousavi et

al. (2011) confirmed that in low doses of FR, degrading LAS was very low but by increasing the reaction time from 20 to 80 minutes LAS removal improved to 80%. A further increase of reaction time did not show more effects on process efficiency [22]. Lin and Lo (1997) investigated the effect of reaction time on treatment of desizing sewage by the Fenton process. The result shows that after 120 minutes as the reaction time, degradation did not improve and after this reaction time H_2O_2 remained in solution [27]. However, Mousavi et al. (2016) confirmed that the reaction time had a significant effect on the process. While the reaction time increased from 20 min to 80 min, the percentage removal of Rhodamine B increased from 35% to 55%, when other parameters were constant [10], but increasing reaction time more than a specific limit cannot lead to improved dye elimination [7, 22, 30].

Optimization Process

The experimental results were optimized by Design-Expert software using the generated overlay plot by superimposing the contours of various response surfaces.
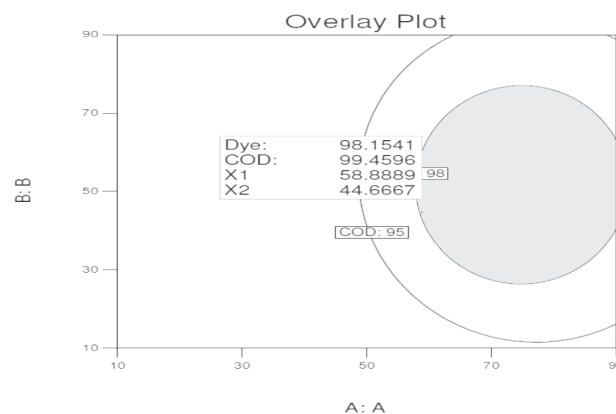

Fig. 5. Overlay plot for optimal region: dye removal >98%, COD removal >99% at different concentrations of oxidant: H_2O_2 (58.8 mg /L), catalyst: Fe^{+2} (44.6 mg/L), and reaction time (11.11 min)
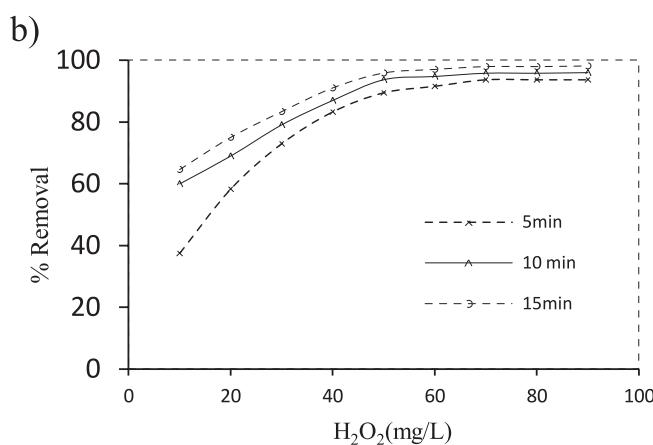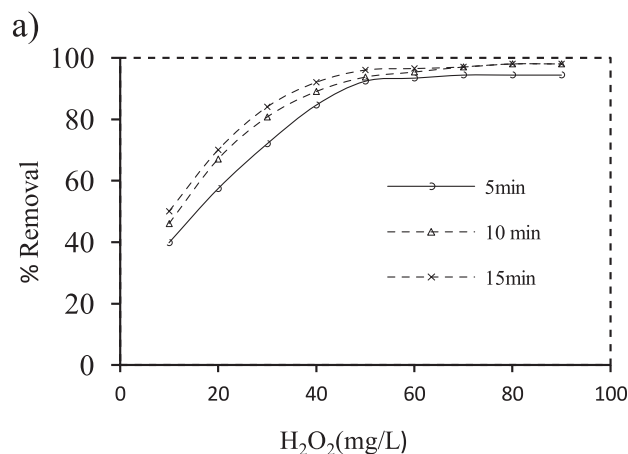

Fig. 4. Effect of reaction time on dye a) and COD b) removal.

The optimum domain was identified by defining the desired limits of dye and COD removal and the shaded region of the overlay plot, which was considered as a promising value of the dependent variables as shown in Fig. 5. The optimum point of process operating for removing dye and COD was obtained at the H_2O_2 of 58 mg/L and Fe^{+2} of 44 mg/L. The process was operated in an optimized condition by accomplishing the experiments with optimum variables to confirm a reasonable prediction in the model. The average removing percentage of dye and COD from a repeated (thrice) test was >98%. The achieved results were in close agreement with the prediction of the model.

Conclusions

H_2O_2 concentration, Fe^{2+} concentrations, and reaction time play an important role on the Fenton oxidation of selected reactive dye RR2. The results indicate that the most favorable H_2O_2 was 80 mg/L for both dye and COD removal as responses. The results also show that there are no significant differences between different reaction times, when other factors were kept. Sufficient models based on the experimental results of CCD and RSM were employed to better understand the direct effect of such factors as H_2O_2 concentration, Fe^{2+} concentrations, and the reaction time on the process' function and development. The optimum operational conditions were determined as H_2O_2 of 58 mg/L and Fe^{2+} of 44 mg/L, with > % 98 dye removal.

Acknowledgements

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