Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.24943

172 (2019) 106–114
December

Removal of Reactive Black 5 dye using Fenton oxidation from aqueous solutions and optimization of response surface methodology

Y. Süzen*, C. Ozmetin

Engineering Faculty, Department of Environmental Engineering, Balikesir University, 10145, Balıkesir, Turkey, Tel. +902666121194; emails: yelizsuzen@balikesir.edu.tr (Y. Süzen), cozmetin@balikesir.edu.tr (C. Ozmetin)

Received 20 May 2019; Accepted 22 September 2019

ABSTRACT

In this study, optimum conditions of color removal from aqueous solution of anionic Reactive Black 5 (RB5) dye through the Fenton oxidation process were investigated. Central composite design (CCD) of response surface methodology (RSM) was used to optimize the Fenton process. The pH, dye concentration, Fe^{2+} dosage and H_2O_2 dosage were selected as independent variables of method, and design experiments were carried out. Intervals of independent variables were initial pH of solution pH (2.5–5.5), dye concentration (50–350 mg/L), Fe^{2+} dosage (25–55 mg/L) and H_2O_2 dosage (175–425 mg/L) at a constant temperature of 30°C. The color removal performance of Fenton reactive increased with decreasing pH value and dye concentration and increasing reactive amount. The experimental studies showed that the RB5 removal efficiency of Fenton oxidation was over 99%. The conditions of maximum removal were obtained as initial solution pH 2.5, dye concentration 120 mg/L, Fe^{2+} dosage 25 mg/L and H_2O_2 dosage 240 mg/L. A full quadratic model equation which interacts response variables with independent variables was developed. The model data agreed with experimental data very well. R^2 value confirming the reliability of the model equation was 96.19%.

Keywords: Color removal; Fenton process; Optimization; Reactive Black 5; Dye

1. Introduction

In the world, 700,000 metric tons of synthetic dyes with more than 100,000 kinds used in different industries (such as textiles, paper, leather, cosmetics, plastic, etc) are produced every year. Textile products are used in various fields in our daily life. Because of the differences in production processes, dyed wastewaters are produced in large quantities and contain different pollutants [1].

The dyeing materials are used for textile dyeing for more than 4,000 years [2]. The volume of dyestuffs discharged to receiving media is very high and poses a threat to the environment. It affects aesthetically the environment, obstructs the light and oxygen input to the aquatic atmosphere and causes negative results on the ecosystem [3]. Dyestuffs have a synthetic origin and contain complex aromatic structures. Due to toxicity content, the living things in the receiving environment are adversely affected [4]. Color removal from wastewaters is difficult because of the low biodegradability of dye materials [5].

Dyes, especially acidic and reactive dyes, cannot be treated with conventional methods due to its resistive structures to degradation like microbial, chemical and photolytic [6]. In the cotton and synthetic textile sectors, 50%–75% of total dye consumption comes from reactive dyes which are biologically difficult to degrade [7]. For this reason, color removal in wastewater requires the use of mechanical, chemical and advanced treatment techniques instead of conventional treatment methods such as biological treatment, adsorption and coagulation [8]. Most of traditional studies

* Corresponding author.

Presented at the 4th International Conference on Recycling and Reuse 2018 (R&R2018), 24–26 October 2018, Istanbul, Turkey

such as chemical precipitation [9], adsorption using cheaper natural clays like montmorillonite [10], illite [11], clinoptilolite [12] and various bio sorbents (fly ash, corn stalk, walnut shells, rice husks, and cotton wastes) [13] are focused on the color removal.

The advanced oxidation processes (AOPs) comprise the generation of hydroxyl radical ($OH^{\bullet}$) which is a reactive intermediate and has high oxidation potential. The purpose of oxidation is to convert the chromophoric groups into colorless and reduced intermediates to forms suitable for biological oxidation. Components such as chlorine, chlorine dioxide, hydrogen peroxide and ozone can be used as oxidative reactivity [14].

AOPs are extensively applied to oxidize several classes of pollutants, including different dyes and characters [15–19]. Also AOPs like; electrocoagulation [20], photocatalytic oxidation [21], ozonation [22,23], and Fenton's oxidation [7,24–26], UV/H_2O_2 [27], TiO_2/UV [28] and ultrasound [29] have been attempted to decolorize and detoxify of textile wastewaters and different dyes. AOPs might be a good alternative for traditional treatment methods. Fenton oxidation, one of the oldest AOPs, is a mixture of iron salt and hydrogen peroxide-based on the formation of hydroxyl radicals at acidic pH and this process is defined as an iron-catalyzed H_2O_2 decomposition reaction [7]. Fenton peroxidation mechanism of an organic compound is formed by a few steps such as the formation of the $OH^{\bullet}$ radical and its oxidative reaction with organic compounds [30].

Recently, traditional methods are replaced by statistical experiment design methods because of the decrease in many experiments and time and cost-saving [31]. Response surface methodology (RSM) is a statistical technique that can be used to the model of various systems, to evaluate simultaneous and separately effects of different factors. It provides a model equation that gives the most appropriate conditions for the desired conditions. This mathematical model can be used to predict the response of a process for any new and different conditions [32]. In industrial applications, the process conditions that provide the discharge color values of wastewater can be determined by RSM. Under these conditions, it is possible to reduce the operating cost because of the pH setting and the less chemical consumption for reagent dosing.

In this study, the treatability of Reactive Black 5 (RB5) dye synthetic solutions by Fenton advanced oxidation process was investigated. The optimization of experimental conditions for removal of RB5 dye was carried out using the central composite design (CCD) technique under RSM with Minitab 16.0 program. The experiments of Fenton oxidation were designed by CCD to match a model to the least-squares method [33].

2. Materials and methods

2.1. Materials

RB5 dye purchased from Sigma-Aldrich. The chemical properties of dye are given in Table 1 and the chemical structure of dye is given in Fig. 1. H_2O_2 35% (w/w) and $FeSO_4{\cdot}7H_2O$ supplied from Merck were used to prepare stock reactant solutions. The other chemical reagents supplied from Merck were of analytical grade and distilled water was used to prepare solutions.

Table 1
Chemical properties of RB5 dye [7]

Chemical class	Anionic dye
C.I. name	Remazol Black B
C.I. No	17095-24-8
Molecular weight, g/mol	991.82
Dye percentage, %	>50
Chemical formula	$C_{26}H_{21}N_5Na_4O_{19}S_6$
λ_{max}	597

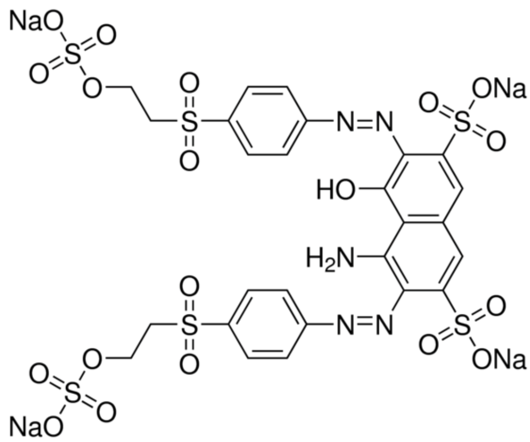

Fig. 1. Chemical structure of RB5 dye [7].

2.2. Experimental method

Experimental studies have been carried out on synthetic dye solutions. RB5 dye was selected because of the common use in the textile industry. Fenton oxidation experiments were performed in a 1 L volume jacketed reactor. Temperature was controlled with a thermometer and set to 30°C. 100 g/L stock H_2O_2 and 20 g/L stock $FeSO_4{\cdot}7H_2O$ solutions were used at specified dosages. Fenton oxidation was performed in four stages: pH adjustment to acidic values, oxidation reaction, neutralization and coagulation [6]. The experimental procedure was applied as follows; pH adjustments in appropriate range for the Fenton process ($2 < pH < 5$) were carried out by using 1 M H_2SO_4 aqueous solution, and then Fenton oxidation reactant solutions were added in dye solutions and rapid and slow mixing were immediately carried out at 120 rpm for 2 min and 30 rpm for 20 min, respectively. The samples were settled for 30 min afterward. The pH of the supernatant sample was adjusted to 7.5 using 1 M NaOH to remove Fe^{2+} salts and left to settle for 90 min. [9]. The sample from the upper phase was centrifuged at 5,000 rpm for 5 min and the color and chemical oxygen demand (COD) values remaining were measured by the spectrophotometer. The absorbance of the samples was analyzed with an SQ Pharo 300 spectrophotometer at a wavelength of 597 nm, which is the maximum absorption wavelength of RB5. COD was determined according to the standard closed reflux and colorimetric method [34]. RSM analysis was used to evaluate the data and develop a regression model effectively. Also, Microtox [35] toxicity tests were applied to RB5 treated solutions at the optimum conditions.

Color and COD removal efficiencies were calculated by the following equations:

$$\text{Color Removal Efficiency, \%} = \left[\frac{C_0 - C_s}{C_0}\right] \times 100 \quad (1)$$

$$\text{COD Removal Efficiency, \%} = \left[\frac{C_0 - C_s}{C_0}\right] \times 100 \quad (2)$$

2.3. Design method

As a design method, RSM identifies the relationship between the controllable input parameters and the response variable [32]. Using RSM analyses the experimental results by the procedure to fit the following second-order polynomial model as shown in Eq. (3).

$$y = \beta 0 + \beta 1x_1 + \beta 2x_2 + \beta 3x_3 + \beta 4x_4 + \beta 11x_1^2 + \beta 22x_2^2 + \beta 33x_3^2 + \beta 44x_4^2 + \beta 12x_1x_2 + \beta 13x_1x_3 + \beta 14x_1x_4 + \beta 23x_2x_3 + \beta 24x_2x_4 \quad (3)$$

where the estimated dependent variable (y), the regression coefficients (β) resulting from the correlation of the affecting factors: the constant of the regression equation (β0), linear coefficients (β1, β2, β3, β4), interaction coefficients (β12, β13, β23, β24, β14), quadratic coefficients (β11, β22, β33, β44) and x_1, x_2, x_3, x_4 are the independent variables that studied [33].

CCD consists of factorial or fractional factorial design with center points, augmented with a group of axial points that allow estimation of curvature. CCD can be used for efficiently estimation of first and second-order terms and can develop a model response with curvature by adding center and axial points to a previously run factorial design [36]. Repeated analysis for center points in the analysis is used to check for deviation of fitness. The (±α) is the axial points that are out of the surface of the cube graph, (0) points represent cube center and (±1) points represent the surface of the cube plots.

CCD, the most widely used approach of RSM, was employed to optimize the four independent variables which are initial pH, dye concentration, Fe^{2+} dosage and H_2O_2 dosage in our study. The four factors with five different levels were determined as independent variables in the design and its two levels were out of experimental factor space. The color removal in percent was taken as a response variable. The levels and ranges of independent variables are shown in Table 2.

3. Results

The experiments were performed at the conditions determined by RSM, experimental and model results are shown in Table 3. Following the experimental design presented in Table 3, an empirical full quadratic model equation, in terms of the four independent variables, as shown in Eq. (4) was developed for color removal (%). The model was confirmed by the high R^2 and fitted well to the experimental data.

Table 2
Levels and ranges of variables in design

Independent variables	Symbol	Response surface and levels				
		−α	−1	0	1	+α
Dye concentration (mg/L)	X_1	50	100	200	300	350
pH	X_2	2.5	3	4	5	5.5
Fe^{2+} dosage (mg/L)	X_3	25	30	40	50	55
H_2O_2 dosage (mg/L)	X_4	175	200	300	400	425

The correlation coefficients of the model equation were defined as R-Sq. = 0.9619 and R-Sq. (adj) = 0.9263.

The experimental data for color removal were analyzed statistically by analysis of variance and the results are submitted in Table 4. According to Table 4, the quadratic and interaction regression models have a very low probability value in Fisher's F-test (Prob > F = 0.0001). Therefore, it is clear that the models are quite significant [30].

Belong to Eqs. (4) the significance of each coefficient was determined by applying the t-test. Also, p-values of each term determined according to the t-test are listed in Table 5. The p values of coefficient $p < 0.05$, it means that these are significant. The model Y_1 terms X_1^2, X_4^2, X_1X_3, and X_1X_4 had significant effects on the percentage of color removal since each p-value was less than 0.05 as seen Table 5.

The model constants given in Table 5 are used to develop the general regression model. The model can help us to find removal efficiency without testing for any conditions in the design range.

$$\text{Color Removal RB5 } (Y_1) = 98.1871 - 0.0487X_1 - 5.2870X_2 - 0.2428X_3 + 0.1570X_4 - 0.0002X_1^2 + 0.2313X_2^2 + 0.0008X_3^2 - 0.0005X_4^2 + 0.0049X_1X_2 - 0.0007X_1X_3 + 0.0005X_1X_4 + 0.0019X_2X_3 + 0.0076X_2X_4 + 0.0011X_3X_4 \quad (4)$$

Fig. 2 shows that there is a linear relationship between the experimental data and predicted values. After developed the model equation, eight new experiments that involve the same factors were planned to check the validity and applicability of the obtained model equation. As seen in Fig. 3, the experimental data and predicted data for these new experiments were compatible with each others.

It has been noted that these factors should be chosen differently at the determined level limits to represent the system well. The generated experiments are given in Table 6.

Model validation control experiments have shown that required results can be achieved without experimentation under the desired conditions using this model. High removal efficiencies were obtained with Fenton oxidation. In addition to decolorization, changes in COD were investigated for eight experiments. Also, the Fenton process was found to be effective in the removal of COD.

Maximum COD removal efficiency was obtained for lower dye concentration. As the used dosage ratios are increased, the efficiency of COD removal increases. COD removal by oxidation with Fenton process is not as effective as color removal. Therefore COD removal efficiencies range from 33% to 97% as seen in Fig. 4.

Table 3
RSM experiments along with actual and predicted values of responses

Run	Dye concentration, mg/L (X_1)	pH (X_2)	Fe^{2+} dosage, mg/L (X_3)	H_2O_2 dosage, mg/L (X_4)	Y, color removal (%)	
					Experimental	Model
1	100	3	30	200	99.7	100
2	300	3	30	200	91.6	90.1
3	100	5	30	200	96.3	97.5
4	300	5	30	200	90.3	89.3
5	100	3	50	200	99.3	99.5
6	300	3	50	200	86.0	86.4
7	100	5	50	200	97.9	96.8
8	300	5	50	200	84.4	85.7
9	100	3	30	300	99.8	98.9
10	300	3	30	300	98.0	98.5
11	100	5	30	300	98.7	97.7
12	300	5	30	300	99.0	99.2
13	100	3	50	300	99.8	100
14	300	3	50	300	97.7	96.9
15	100	5	50	300	97.2	99.1
16	300	5	50	300	98.9	97.8
17	50	4	40	250	99.4	98.4
18	350	4	40	250	88.8	89.8
19	200	2.5	40	250	99.9	100
20	200	5.5	40	250	99.7	99.1
21	200	4	25	250	99.2	100
22	200	4	55	250	99.7	98.6
23	200	4	40	175	92.5	92.1
24	200	4	40	325	99.9	100
25	200	4	40	250	99.4	99.2
26	200	4	40	250	99.3	99.2
27	200	4	40	250	99.2	99.2
28	200	4	40	250	99.2	99.2
29	200	4	40	250	99.4	99.2
30	200	4	40	250	99.2	99.2

Table 4
Analysis of variance results of the response surface quadratic model for color removal

Source	DF	Seq. SS	Adj. SS	Adj. MS	F	P
Model	14	535.568	535.568	38.2548	27.05	0.000
Linear	4	325.925	14.663	3.6656	2.59	0.079
Quadratic	4	95.764	95.764	23.9410	16.93	0.000
Interaction	6	113.879	113.879	18.9798	13.42	0.000
Residual	15	21.214	21.214	1.4143		
Lack of fit	10	21.166	21.166	2.1166	218.96	0.000
Pure error	5	0.048	0.048	0.0097		
Total	29	556.782				

Microtox [35] toxicity test was applied to the sample treated under optimum conditions. Test results are given in Table 7. According to the results, the Fenton process is effective in reducing the toxicity of RB5.

The 2-dimensional contour and 3-dimensional surface plots in Figs. 5–8 which are simulations from Eqs. (4) describe the effect of the selected design variables on color removal performances.

Table 5
Predictions of the model regression for RB5 removal by Fenton oxidation

Relationship	Factor	Coefficient	SE Coefficient	*T*-value	Prob > *F*	Remark
	Model	98.1871	14.6701	6.693	0.000	Significant
Linear	X_1	–0.0487	0.0266	–1.827	0.088	–
	X_2	–5.2870	3.4644	–1.526	0.148	–
	X_3	–0.2428	0.3464	–0.701	0.494	–
	X_4	0.1570	0.0792	1.982	0.066	–
Quadratic	X_1^2	–0.0002	0.0000	–6.529	0.000	Significant
	X_2^2	0.2313	0.3526	0.656	0.522	–
	X_3^2	0.0008	0.0035	0.215	0.833	–
	X_4^2	–0.0005	0.0001	–3.882	0.001	Significant
Interaction	X_1X_2	0.0049	0.0030	1.661	0.118	
	X_1X_3	–0.0007	0.0003	–2.460	0.027	Significant
	X_1X_4	0.0005	0.0001	8.178	0.000	Significant
	X_2X_3	0.0019	0.0297	0.063	0.951	–
	X_2X_4	0.0076	0.0059	1.282	0.219	–
	X_3X_4	0.0011	0.0059	1.282	0.219	–

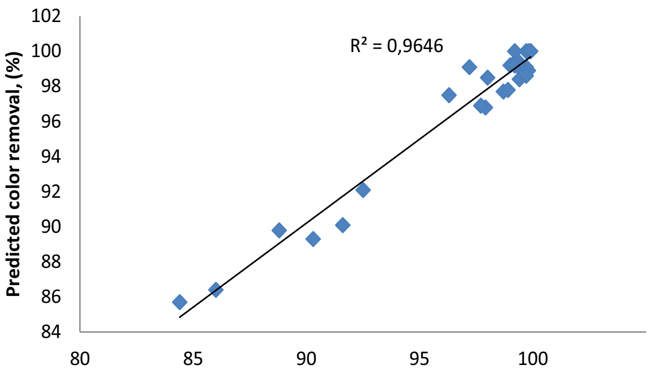

Fig. 2. Observed vs. predicted plot of color removal.

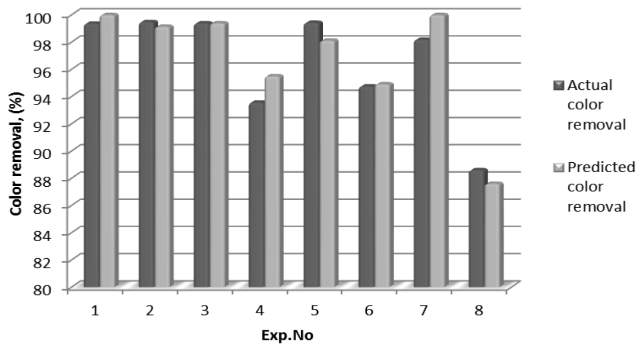

Fig. 3. Observed vs. predicted plot of color removal for eight new control experiments.

Table 6
Model validity control experiments matrix and its results

Run	Dye concentration, mg/L (X_1)	pH (X_2)	Fe^{2+} dosage, mg/L (X_3)	H_2O_2 dosage, mg/L (X_4)	*Y*, color removal (%)	
					Actual	Predicted
1	75	2.8	35	220	99.37	100
2	250	2.8	45	280	99.48	99.14
3	75	3.5	45	280	99.39	99.39
4	325	3.5	35	280	93.57	95.5
5	150	4.5	45	220	99.43	98.12
6	250	4.5	35	220	94.76	94.91
7	150	5.3	35	280	98.18	100
8	325	5.3	45	220	88.6	87.6

3.1. Effect of Fe^{2+} concentration

As seen in Fig. 5, the color removal performance increases with increasing Fe^{2+} ion concentration in sufficient H_2O_2 concentration. The removal performance decreases even in the presence of high dosages of iron if the sufficient H_2O_2 is not available in the solution.

In case of the sufficient iron ion concentration, radicals are formed from hydrogen peroxide with high oxidation potential [3].

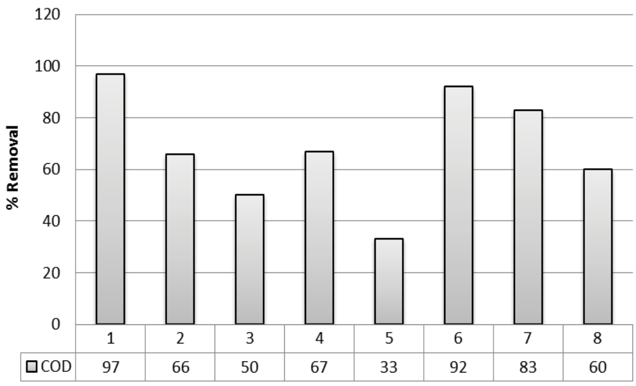

Fig. 4. COD removal efficiency for determined eight experiments.

Table 7
Microtox toxicity test results of RB5

Before Fenton oxidation process	After Fenton oxidation process
Toxic	Low toxic

3.2. Effect of H_2O_2 concentration

As seen in Fig. 6, the percentage of decomposition of pollutants generally increases with increasing hydrogen peroxide concentration which alone does not lead to the generation of hydroxyl radicals. Increased removal efficiency can be explained by an increase in the hydroxide radicals with high oxidation potential. The adjustment of the oxidant dosage is also important in terms of operating costs [1].

3.3. Effect of pH

It is seen from Fig. 7 that decreasing initial pH values affect the removal performance positive. This is because, at pH values lower than 3.5, ferrous ions are more stable for resulting in a better redox system and effective decolorization ratio. The formation of ferric ions, which tend to produce ferric hydroxo complexes, increases with rising pH. Also, H_2O_2 is unstable and easily decomposes itself in alkali solutions [6]. The reaction rate slows down due to the reduction of soluble iron ion types at the high alkaline pH values. If the pH is too alkaline; hydrogen peroxide is catalytically degraded and the activity in the solution decreases [17].

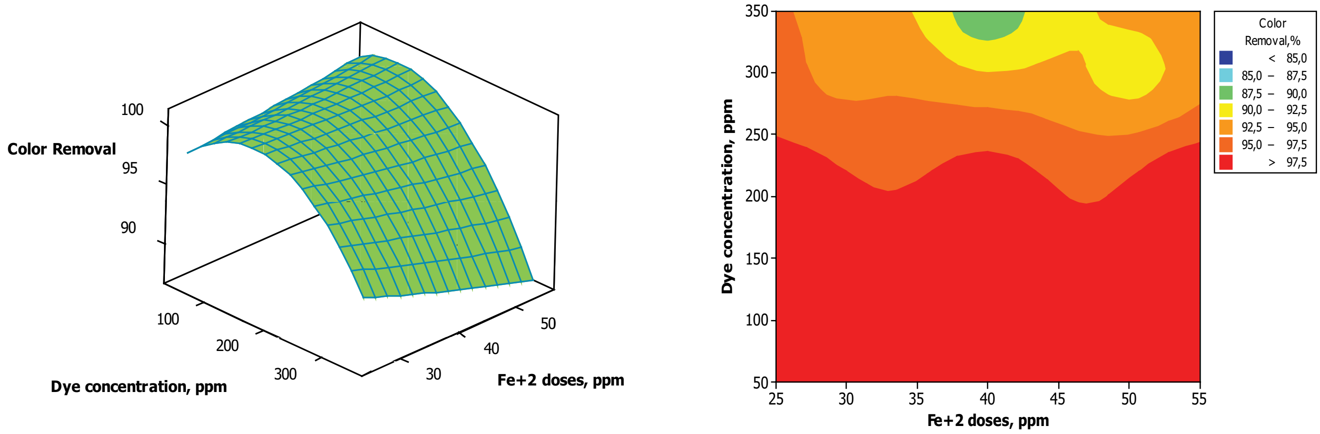

Fig. 5. Effect of iron ion concentration on removal efficiency (constant pH 4, H_2O_2 250 ppm).

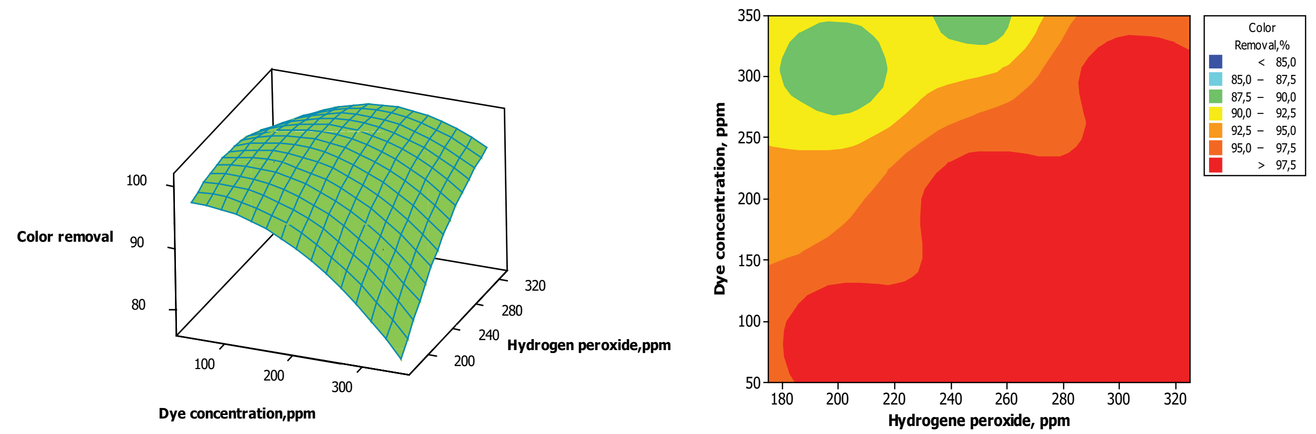

Fig. 6. Effect of hydrogen peroxide concentration on removal efficiency (constant pH 4, Fe^{2+} 40 ppm).

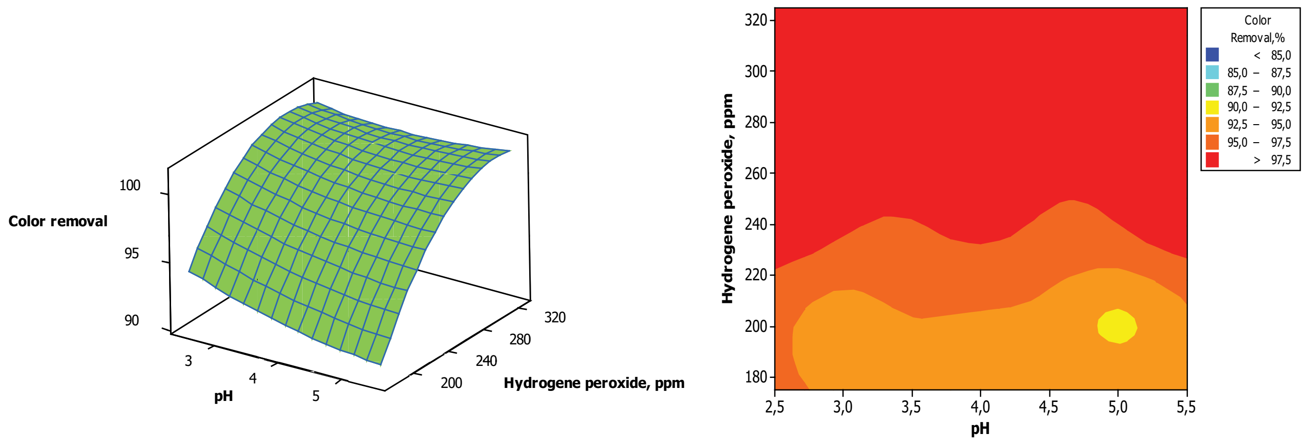

Fig. 7. Effect of initial solution pH to removal efficiency (constant dye concentration 200 ppm, Fe^{2+} 40 ppm).

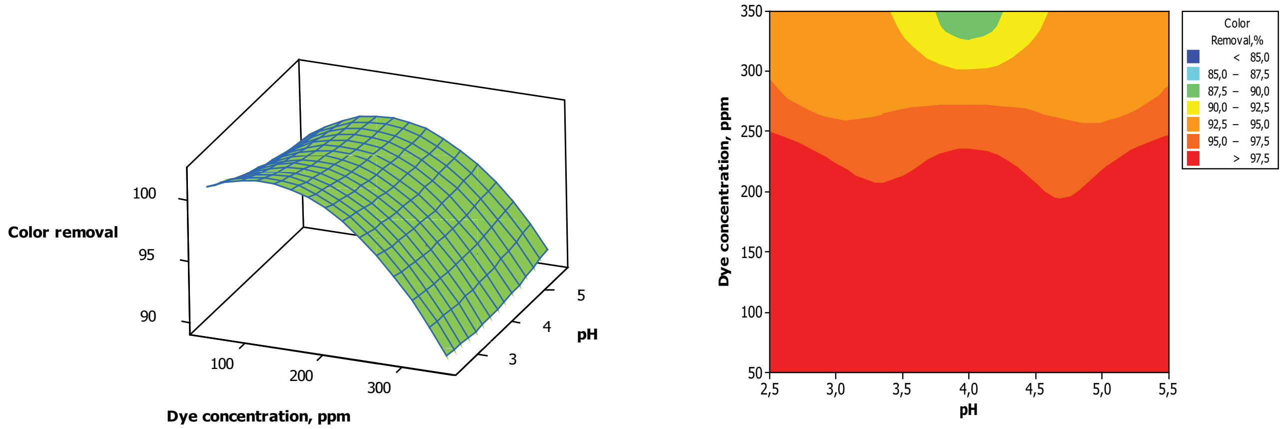

Fig. 8. Effect of RB5 dye concentration on removal efficiency (constant H_2O_2 250 ppm, Fe^{2+} 40 ppm).

3.4. Effect of dye concentration

It can be seen from Fig. 8 that increasing dye concentration reduces the removal efficiency for constant oxidant concentration. The amount of reagent required for the treatment increases with increasing pollutant concentration [15].

As a result of the optimization performed, the conditions that give the maximum color removal efficiency are shown in Table 8. A verification experiment was conducted for conditions determined and the color removal efficiency was obtained as above 99%.

Table 8
Optimum removal conditions for RB5 using Fenton oxidation process (constant temperature 30°C)

Dye concentration, mg/L	X_1	120
pH	X_2	2.5
Fe^{2+} dosage, mg/L	X_3	25
H_2O_2 dosage, mg/L	X_4	240
Color removal, %	Y	>%99

4. Conclusions

A laboratory batch study of the Fenton oxidation technique for the decolorization of synthetic RB5 solution was investigated. The effects of the discrete experiments on the color removal efficiencies were observed using an RSM and the experimental conditions were optimized.

The RSM results showed the different effects of four operating variables consisting of dye concentration, initial pH, Fe^{2+} and H_2O_2 dosages as well as their interactive and quadratic effects on color removal by Fenton. The operational conditions of the Fenton oxidation process compare properly with previously obtained decolorization data. The ratio of Fe^{2+}/H_2O_2 ions determined as optimum 1/10 according to the 5–25-fold ratio in the literature [7]. Initial pH and dye concentration exhibited a negative effect, while the dosage of H_2O_2 and dosage of Fe^{2+} had a positive effect on color removal efficiency. A verification experiment was conducted for the conditions where the maximum removal was found in the optimization result. It was determined that the color removal efficiency is 99% as a result of the verification experiment performed. This study shows that the combined effect of selected variables on the Fenton oxidation of synthetic dye solutions by using RSM can be predicted close to real results.

Table 9
Comparison of different wastewater/dye removal with other AOP methods

Wastewater/synthetic compounds	Experimental method	Remarks	References
Industrial textile wastewater	Classic Fenton (CF), Ultrasound Fenton processes (UFP)	Best decolorization percentage 95% using 0.10 g/L of Fe(II), and 2.20 g/L of H_2O_2 for 90 min at pH 3 for CF and 99% color removal 0.05 g/L of Fe(II) and 1.65 g/L H_2O_2 for 60 min at pH 3 for UFP.	[19]
Disperse Red 1 (DR1)	Photo-Fenton degradation	After 45 min of treatment, toxicity reduced to nontoxic levels, when 98% of the initial concentration of DR1 was degraded and mineralization achieved 55%.	[37]
Reactive Black 5	Electro-Fenton process, RSM optimization	Optimized conditions for max dye and COD removal were found at solution pH of 5.13, MWCNT/Fe_3O_4 concentration of 55.27 mg/L, the current density of 15.86 mA/cm^2, and electrolysis time of 57.91 min. *Magnetic multi-walled carbon nanotube.	[38]
Reactive Black 5	Electrochemical oxidation	The dimensionally stable anode and stainless steel cathodes as electrode materials used, with NaCl as supporting electrolyte. Detection and identification of by-products were identified.	[39]
Reactive Black 5	Classic Fenton, RSM optimization	Maximum decolorization percentage over 99% using 120 ppm dye concentration, 25 ppm of Fe^{2+} and 240 ppm of H_2O_2 for 90 min at pH 2.5.	Present study

Table 9 shows some examples of different wastewater treatments with various AOPs. RB5 has been used frequently in synthetic solutions to characterize textile wastewater in the literature. However, RB5 treatment with AOPs has been reported in the literature. Even so, there are not enough studies about optimization and model validation of treatment with RSM. This study is thought to contribute to this part of the literature.

When the studies are examined, it is seen that AOPs are effective in color [19] and toxicity [37] removal from synthetic or real wastewater containing dyes.

The accuracy of the proposed analysis of variance full quadratic model is acceptable, resulting in a high R^2 value of 96.19% achieved in color removal. According to our results, it is seen that the parameters which are effective in the removal of RB5 dye by Fenton oxidation can be determined by CCD. It is determined that the Fenton process is an alternative method that can be used in the treatment of wastewater containing dyes (such as the textile industry) because it provides removal of color as well as COD removal.

Symbols

DF — The degrees of freedom
Adj.SS — Adjusted sums of squares
Adj.MS — Adjusted mean squares
SE Coefficient — Standard error of the coefficient
AOPs — Advanced oxidation processes
CCD — Centeral composite design
MWCNT — Magnetic multi-walled carbon nanotube

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