

Decolorization of the Anthraquinone Dye C. I. Reactive Blue 2 by Fenton Oxidation; Statistical Experimental Design

S. Papić,* M. Mužić, N. Koprivanac, I. Peternel, and M. Deanović
University of Zagreb, Faculty of Chemical Engineering and Technology,
Marulićev trg 19, 10000 Zagreb, Croatia

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This work presents the results of studies on the decolorization of water solution of anthraquinone dye C. I. Reactive Blue 2 (RB2), which was chosen as the model dye pollutant, using Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) process. Batch experiments were carried out to investigate the influence of operational parameters which affect the efficiency of Fenton process in RB2 decolorization. The final decolorization obtained with Fenton treatment at $0.0025 \text{ mol L}^{-1} \text{ H}_2\text{O}_2$ and $0.0005 \text{ mol L}^{-1} \text{ Fe}^{2+}$ ($\text{pH} = 3$; room temperature, $\vartheta = 22 \pm 1 \text{ }^\circ\text{C}$) achieves a dye removal of 100 % for initial RB2 concentration of 100 mg L^{-1} . Experimental data were analyzed with statistical experimental design method using Design of Experiments (DoE) software. Factorial design of experiments was employed to study the effect of three factors, time (2 and 60 min), Fe^{2+} concentration (0.00005 and $0.0005 \text{ mol L}^{-1}$) and H_2O_2 concentration (0.0003 and $0.0025 \text{ mol L}^{-1}$) at two levels; low and high. It was found that all three process parameters and their interaction affect the percentage of dye removal.

Key words:

Decolorization, dyeing wastewater, reactive dye, C. I. Reactive Blue 2, Fenton process, factorial design of experiments

Introduction

Reactive dyes are the most common textile dyes used due to their advantages, such as bright colors, excellent colorfastness and ease of application.^{1,2} They are capable of forming a covalent bond between the dye molecule and the fibers, which are usually cellulosic fibers. However, reactive dyes hydrolyze easily, resulting in a high portion of unfixed (or hydrolyzed) reactive dyes which have to be washed off during the dyeing process. As much as 50 % of the initial dye load is present in the dye bath effluent.³ One of the major problems concerning textile wastewaters is colored effluent. Though not particularly toxic, dyes have an adverse aesthetic effect because they are visible pollutants. The presence of color will reduce aquatic diversity by blocking the passage of light through the water. In some cases, less than 1 mg L^{-1} of dye concentration produces an obvious water colouration.⁴

The traditional methods used for the treatment of dye-containing wastewater, such as chemical coagulation/flocculation, membrane separation (ultrafiltration, reverse osmosis) or activated carbon adsorption only perform a phase transfer of the pollutant. Moreover, conventional biotreatment methods are ineffective for most synthetic dyes due to the complex polyaromatic structure and recalcitrant nature of dyes.^{5,6} Advanced oxidation processes

(AOPs) are a powerful alternative to conventional treatment methods for wastewater decontamination. These treatments are based on the in situ generation of highly reactive hydroxyl radicals as a primary oxidant species (OH^\bullet). These radicals are high oxidant species with high oxidation potential ($E = 2.8 \text{ V}$ versus NHE) that are able to degrade almost all recalcitrant organic compounds under mild experimental conditions.^{7,8} Among AOPs, the Fenton process is quite well known and has been successfully applied for the treatment of dye house effluent.^{9–20} Fenton's reagent oxidation is a homogeneous catalytic oxidation process using a mixture of hydrogen peroxide and ferrous ions. The main advantage of the Fenton process is its simplicity. The chemicals are readily available at moderate cost and there is no need for special equipment. In an acidic environment if hydrogen peroxide is added to an aqueous system containing an organic substrate and ferrous ions, a complex redox reaction will occur.^{7,20–22} The overall reaction is:



The ferrous ion initiates and catalyses the decomposition of H_2O_2 , resulting in the generation of hydroxyl radicals, OH^\bullet .

This work investigates the decolorization of aqueous anthraquinone reactive dye solution using Fenton process. The dye C. I. Reactive Blue 2 (RB2), one of the most used reactive dyes for tex-

*Corresponding author: spapic@fkit.hr

tile dyeing have been selected as a representative dye pollutant of these industrial wastewaters. Batch experiments were carried out to investigate the influence of operational parameters that affect the efficiency of Fenton process in RB2 oxidation (decolorization). Main effects and interaction effects of the three parameters (factors): time, Fe^{2+} concentration and H_2O_2 concentration were analyzed using statistical experimental design method (DoE).^{5,23,24}

Experimental section

Chemicals used in this study were supplied by Kemika, Croatia ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; H_2O_2 , 30 %; NaOH ; H_2SO_4 , > 95 %). The anthraquinone dye, C. I. Reactive Blue 2 (Cibacron Blue 3G) obtained from Ciba, Switzerland was used as received without further purification. Molecular structure of RB2 is illustrated in Fig. 1. The experimental dye solutions were prepared using distilled water. The initial concentration of RB2 for all experiments was 100 mg L^{-1} . The pH of the reaction solutions was adjusted using $1 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ and $1 \text{ mol L}^{-1} \text{NaOH}$. Batch experiments for Fenton oxidation were performed in a glass cylindrical reactor of 0.8 L capacity with the magnetic stirrer. Experiments were performed at room temperature $22 \pm 1 \text{ }^\circ\text{C}$ as follows: the required amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added into the 0.5 L of dye solution; after the pH was adjusted to 3.0 the predetermined quantity of H_2O_2 was added; the reaction mixture was stirred during 60 min period and at specific time intervals 1–2 mL of the sample was taken from the reactor using a pipette and thereafter immediately analyzed. The reaction time was recorded as the H_2O_2 was added. The pH of the solution was measured using handy-lab pH/LF portable pH-meter, Schott Instruments GmbH, Germany. The decolorization of RB2 solution was monitored by a Perkin Elmer Lambda EZ 201 UV/VIS spectrophotometer, USA, at the maximum adsorption wavelength, $\lambda_{\text{max}} = 620 \text{ nm}$.

Results and discussion

The following parameters were evaluated aiming to find the optimal conditions to promote the degradation of RB2 dye: temperature, pH, Fe^{2+} concentration, H_2O_2 concentration and reaction time. Room temperature ($22 \pm 1 \text{ }^\circ\text{C}$) was chosen for Fenton oxidation experiments. As a practical matter, most commercial applications of Fenton reagent occur at temperatures between $20\text{--}40 \text{ }^\circ\text{C}$.²⁸ As temperatures increase above $50 \text{ }^\circ\text{C}$ the efficiency of H_2O_2 utilization declines. This is due to the accelerated decomposition of H_2O_2 into oxygen and water. The pH of the solution controls the production rate of hydroxyl radicals and the concentration of ferrous ions in the solution.²⁵ The pH in the initial assays was defined as being 3, since it has been reported that Fenton reactions occur efficiently at pH in a range between 2.9 and 3.5.^{7,26,27} Different concentrations of Fe^{2+} and H_2O_2 , producing various molar ratios Fe^{2+} to H_2O_2 , were tested taking into account previous work.¹⁷ The time needed to complete a Fenton reaction will depend on many variables, most notably iron catalyst dose and wastewater strength. For simple phenol oxidation (less than 250 mg L^{-1}), typical reaction times are 30–60 minutes. For more complex or more concentrated wastes, the reaction may take several hours.²⁸ Fenton process has a potential to almost completely decolorize textile dyes solutions in relatively short time ($\approx 15 \text{ min}$).^{15,18,25,27} In these experiments, Fenton oxidation process was performing for 60 min and the decolorization of RB2 was monitored during the reaction at periodic intervals.

Effect of H_2O_2 concentration

Initial concentration of H_2O_2 plays an important role in the Fenton process. The increase in the decolorization is due to the increase in hydroxyl radical concentration by adding of H_2O_2 .

For fixed Fe^{2+} concentration ($0.0005 \text{ mol L}^{-1}$) the following H_2O_2 concentrations were tested: 0.0003; 0.0006; 0.0012 and $0.0025 \text{ mol L}^{-1}$. The effect of initial H_2O_2 concentration on the de-

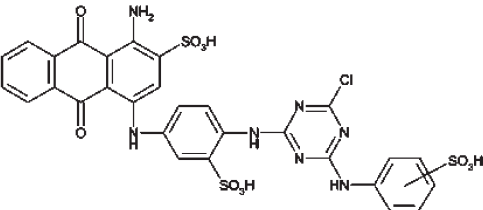
Name	Molecular Structure	λ_{max} (nm)
C. I. Reactive Blue 2		620

Fig. 1 – Molecular structure and absorption maxima of RB 2

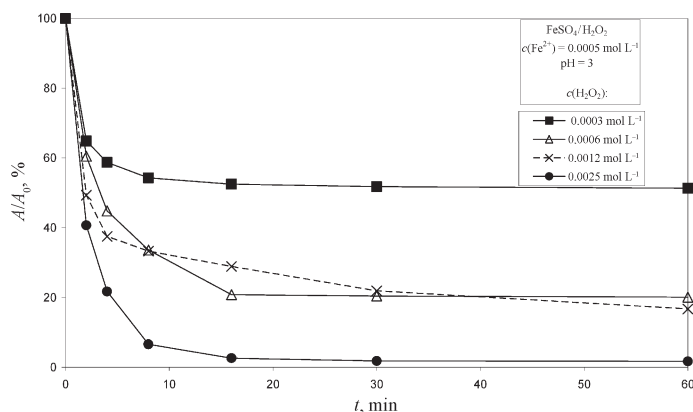


Fig. 2 – Effect of the concentration of H_2O_2 on the decolorization of RB2 by Fenton process. Experimental conditions: $[RB2] = 100 \text{ mg L}^{-1}$; $[Fe^{2+}] = 0.0005 \text{ mol L}^{-1}$; $pH = 3$; room temperature.

colorization of RB2 is shown in Fig. 2. To render the Fenton process competitive with other processes, it is essential that its applications represent a low cost operation, which basically implies better control of H_2O_2 dosage. The objective of this evaluation is to select the best operational concentration of H_2O_2 in Fenton process. The addition of H_2O_2 from $0.0003\text{--}0.0025 \text{ mol L}^{-1}$ increases the decolorization from 48 % to 99 % in 15 min. Increase from $0.0003\text{--}0.0006 \text{ mol L}^{-1}$ H_2O_2 causes the most significant change in decolorization. Color removal with $0.0006 \text{ mol L}^{-1}$ and $0.0012 \text{ mol L}^{-1}$ is almost the same. This is because at a higher H_2O_2 concentration, scavenging of OH^\bullet radicals will occur.⁷ Addition of $0.0012\text{--}0.0025 \text{ mol L}^{-1}$ H_2O_2 increases decolorization from 78 % to 99 % in 30 min. Hence, $0.0025 \text{ mol L}^{-1}$ appears as an optimum concentration of H_2O_2 .

Effect of Fe^{2+} concentration

The effect of adding Fe^{2+} ions to the decolorization of RB2 was studied. The results are shown in Fig. 3. The results indicate that the extent of decolorization increases with the increase in initial Fe^{2+} concentration. Addition of Fe^{2+} from 0.00005 to $0.0005 \text{ mol L}^{-1}$ increases color removal from 70 % to 100 % at 30 min. From these results, it is possible to say that the efficiency of the RB2 destruction increases with increasing initial Fe^{2+} concentration. Although, the increase from 0.00025 to $0.0005 \text{ mol L}^{-1}$ is very soft. With both Fe^{2+} concentrations, after 30 min of reaction the same efficiency in RB2 removal was accomplished. It may be explained by the redox reaction since OH^\bullet radicals may be scavenged by the reaction with the excess of H_2O_2 or Fe^{2+} . The lower capacity for dye degradation of Fe^{2+} at small concentrations is probably due to the lowest OH^\bullet radicals production available for oxidation. Fe^{2+} of $0.0005 \text{ mol L}^{-1}$ can be used as an optimum concentration.

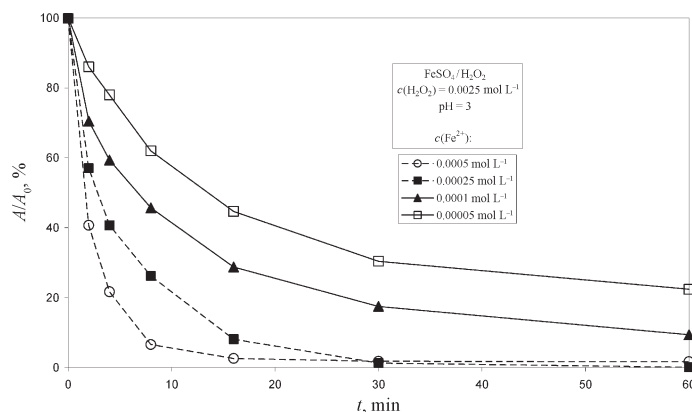


Fig. 3 – Effect of the concentration of Fe^{2+} on the decolorization of RB2 by Fenton process. Experimental conditions: $[RB2] = 100 \text{ mg L}^{-1}$; $[H_2O_2] = 0.0005 \text{ mol L}^{-1}$; $pH = 3$; room temperature.

Factorial design analysis

Experimentally achieved data concerning RB2 decolorization by Fenton process was analyzed using the statistical method design of experiments (DoE). Actual and coded values of factors and 2^3 factorial design in coded form are presented in Tables 1 and 2, respectively. The first step in the statistical analysis of experimentally achieved data on the basis of factorial plan was to estimate normalized effects of initial process parameters and their interaction on the measured value. Table 3 shows the list of individual parameters of Fenton process and their interactional effects on RB2 dye removal, while Fig. 4 shows half normal plot of effects. The points found outside the straight line indicate that initial parameters and their interactions had significant influence on the decolorization of studied RB2 water solution. The increasing distance of a particular point from the line means that the significance of the effect also increases. Values located on the line indicate that those interactions have negligible influence on dye degradation. The next step, after the main effects had been determined, was to develop a mathematical model and validate it by ap-

Table 1 – Actual and coded values of parameters in 2^3 factorial design

Parameter	Value	Level	
		low	high
time/min	Actual(t)	2.00	60.00
	Coded(A)	-1	+1
concentration of Fe^{2+} /mol L^{-1}	Actual($c(Fe^{2+})$)	0.00005	0.0005
	Coded(B)	-1	+1
concentration of H_2O_2 /mol L^{-1}	Actual($c(H_2O_2)$)	0.0003	0.0025
	Coded(C)	-1	+1

Table 2 – 2^3 factorial design in coded form

Run number	A	B	C
1	-1	+1	+1
2	-1	-1	+1
3	-1	-1	+1
4	-1	-1	-1
5	+1	+1	-1
6	-1	+1	+1
7	+1	+1	+1
8	-1	-1	-1
9	+1	-1	+1
10	+1	-1	-1
11	-1	+1	-1
12	-1	+1	-1
13	+1	-1	-1
14	+1	-1	+1
15	+1	+1	-1
16	+1	+1	+1

Table 3 – List of individual parameters and their interactional effects on absorbance

Term	Studentized Effects, –	Contribution, %
A	-32.5125	27.9
B	-30.8625	25.2
C	-37.0375	36.2
AB	7.6625	1.6
AC	-17.4125	8.0
BC	-1.9625	0.1
ABC	5.9125	0.9

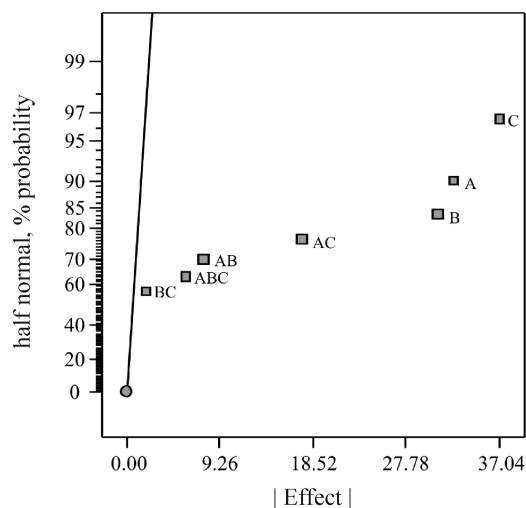


Fig. 4 – Half normal plot of effects

plying variance analysis. Model and coefficient validation are described in Table 4. Table 5 presents results of experiments and analysis: predicted, $(A/A_0)_m$, and measured, (A/A_0) , absorbance values, residuals, r , and studentized residuals, r_s . The formation of mathematical model was performed by statistical analysis of main effects by using the DesignExpert software package.

Table 4 – ANOVA results – Model and coefficient validation

Source	Sum of squares, –	Degrees of freedom, –	Mean square, –	F-value, –	P-value, –
A	4228.25	1	4228.25	1442.78	< 0.0001
B	3809.98	1	3809.98	1300.06	< 0.0001
C	5487.11	1	5487.11	1872.33	< 0.0001
AB	234.86	1	234.86	80.14	< 0.0001
AC	1212.78	1	1212.78	413.83	< 0.0001
BC	15.41	1	15.41	5.26	0.0510
ABC	139.83	1	139.83	47.71	0.0001
Model	15128.20	7	2161.17	737.44	< 0.0001
Total	15151.65	15	–	–	–
Residual	23.45	8	2.93	–	–

Table 5 – Results of experiments and analysis: predicted, $(A/A_0)_m$, and measured, (A/A_0) , absorbance values, residuals, r , and studentized residuals, r_s

Run Number	$(A/A_0)_m$, %	A/A_0 , %	r , –	r_s , –
1	40.70	38.35	2.35	1.941
2	86.00	84.75	1.25	1.033
3	83.50	84.75	-1.25	-1.033
4	96.10	96.50	-0.40	-0.330
5	51.30	52.50	-1.20	-0.991
6	36.00	38.35	-2.35	-1.941
7	1.70	2.00	-0.30	-0.248
8	96.90	96.50	0.40	0.330
9	22.40	21.25	1.15	0.950
10	80.50	79.65	0.85	0.702
11	64.90	65.85	-0.95	-0.785
12	66.80	65.85	0.95	0.785
13	78.80	79.65	-0.85	-0.702
14	20.10	21.25	-1.15	-0.950
15	53.70	52.50	1.20	0.991
16	2.30	2.00	0.30	0.248

The model described with coded factors is given by eq. (1):

$$\begin{aligned} (A/A_0)_m = & 55.11 - 16.26 \cdot A - 15.43 \cdot B - \\ & - 18.52 \cdot C + 3.83 \cdot A \cdot B - 8.71 \cdot A \cdot C - \\ & - 0.98 \cdot B \cdot C + 2.96 \cdot A \cdot B \cdot C \end{aligned} \quad (1)$$

while the model based on real factors is given by eq. (2):

$$\begin{aligned} (A/A_0)_m = & 101.63192 - 0.18137 \cdot t - \\ & - 63359.45664 \cdot c(\text{Fe}^{2+}) - 3773.07558 \cdot c(\text{H}_2\text{O}_2) + \\ & + 10.53640 \cdot t \cdot c(\text{Fe}^{2+}) - 386.18948 \cdot t \cdot c(\text{H}_2\text{O}_2) - \\ & - 1.67328 \cdot 10^7 \cdot c(\text{Fe}^{2+}) \cdot c(\text{H}_2\text{O}_2) + \\ & + 4.11877 \cdot 10^5 \cdot t \cdot c(\text{Fe}^{2+}) \cdot c(\text{H}_2\text{O}_2) \end{aligned} \quad (2)$$

F -value for mathematical model of 737.44 (Table 4) shows that the model is significant, namely the probability that this large F value is a result of an error is only 0.01 %. P values (lower than 0.05) show signification of model variables. Thereafter, influences A, B, C, AC, AB and ABC are significant while BC effect is not significant. The next step of the study was to investigate the validity of the mathematical model by normal plot of studentized residuals, r_s according to student's test (Fig. 5). It can be seen from Fig. 5 that there is no significant discrepancy of the points from linearity, so it can be concluded that the presented model is in compliance with a normal distribution and there is no problem with disparity of variance.

Validity of the model was additionally examined by establishing the correlation among normalized residual, calculated values and RB2 decolorization.

Fig. 6 shows the scatter of the points, which confirms that the proposed model is in accordance with the normal distribution and that there is no variance disparity. To be secure that no interactions between experiments occur, the correlation between normalized residuals and the sequence number of the experiment is shown in the Fig. 7. The scatter of points without order indicates that the experiments were conducted independently of one another and that the variance is constant. The influence of normalized residuals on process parameters, iron concentration, hydrogen peroxide concentration and the reaction time is described in Figs. 8, 9 and 10. It can be seen from the presented figures that the variability of the normalized residuals is lower in the case of longer reaction time as well as in the case of a lower iron and hydrogen peroxide concentrations.

The model was also tested considering its ability to describe the real decolorization process of RB2 model wastewater. It can be seen from Fig. 11 that deflection of experimentally achieved values for RB2 decolorization in comparison with calcu-

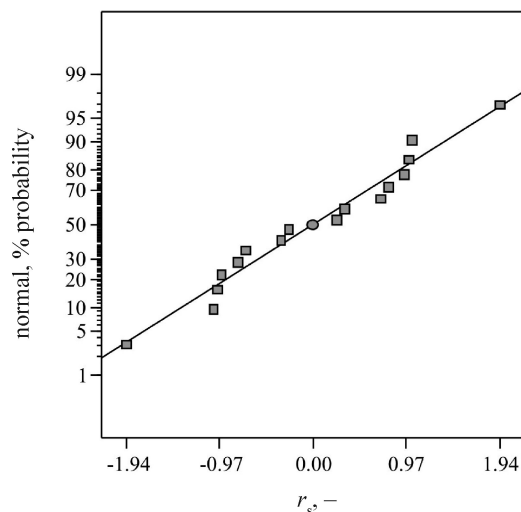


Fig. 5 – Normal plot of studentized residuals, r_s

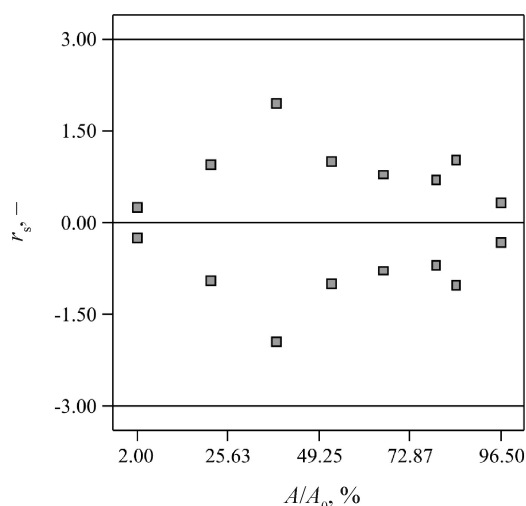


Fig. 6 – Studentized residuals, r_s , vs. predicted values of absorbance

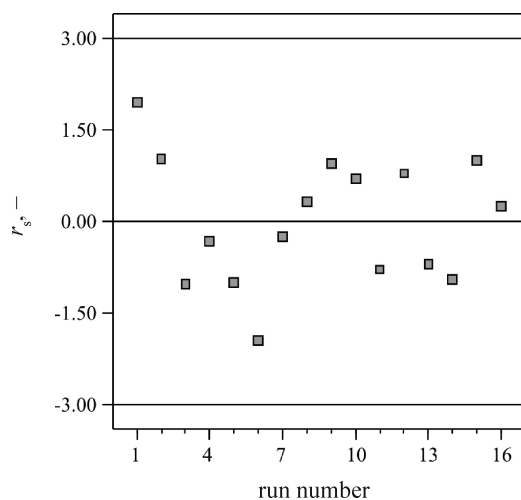
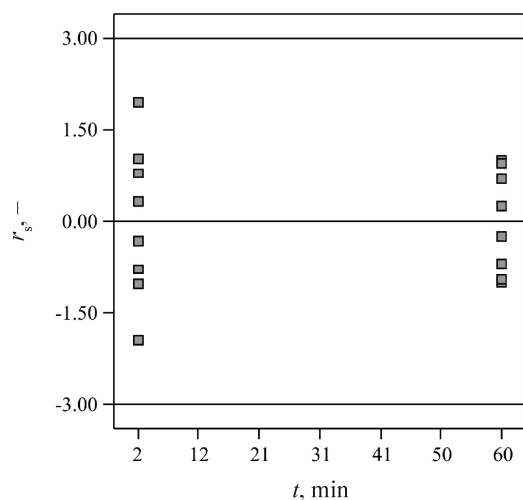
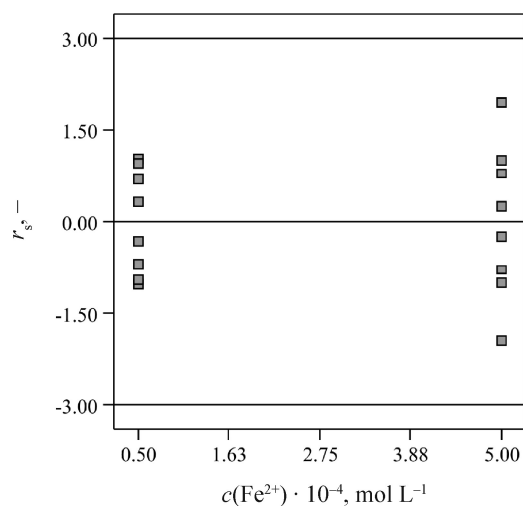
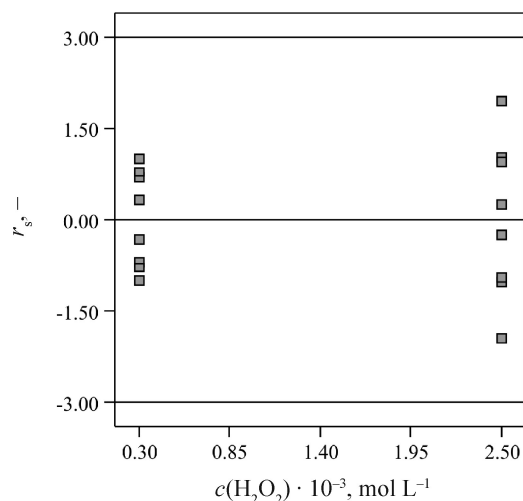
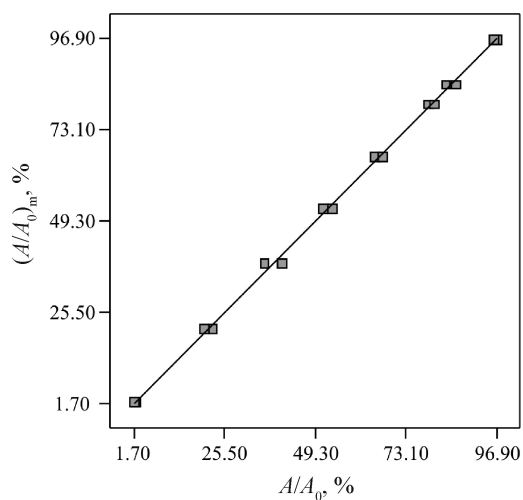
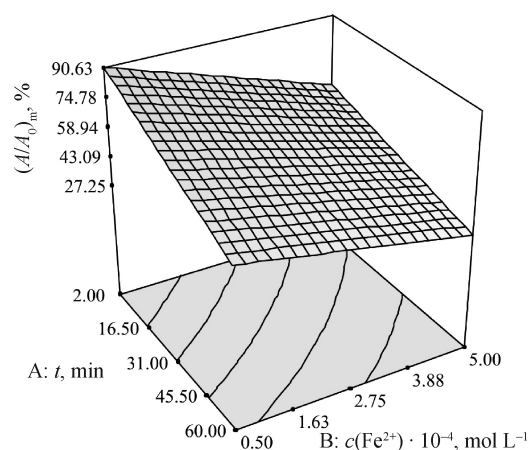


Fig. 7 – Studentized residuals, r_s , vs. run number

Fig. 8 – Studentized residuals, r_s , vs. time, t Fig. 9 – Studentized residuals, r_s , vs. concentration of Fe^{2+} , $c(Fe^{2+})$ Fig. 10 – Studentized residuals, r_s , vs. concentration of H_2O_2 , $c(H_2O_2)$ Fig. 11 – Predicted absorbance values, $(A/A_0)_m$ vs. measured absorbance values, (A/A_0)

lated extents was negligible, so it can be concluded that the proposed model describes the studied system well.

Figs. 12, 13 and 14 present correlations between calculated values of decolorization of RB2 water solution and initial process parameters on the base of response surface as a graphical model interpretation. Response surface is a curved plane in a space with designated space slope. It can be seen from the slope of the response surface that RB2 decolorization is strongly dependent on hydrogen peroxide concentration, reaction time and somewhat less on iron concentration. This is in compliance with calculated values of effects of initial process parameters on decolorization (Table 3); influence of hydrogen peroxide concentration: -37.0375 ; reaction time: -32.5125 ; iron concentration: -30.9625 .

Fig. 12 – Predicted absorbance values, $(A/A_0)_m$ vs. A: time, t , and B: concentration of Fe^{2+} , $c(Fe^{2+})$

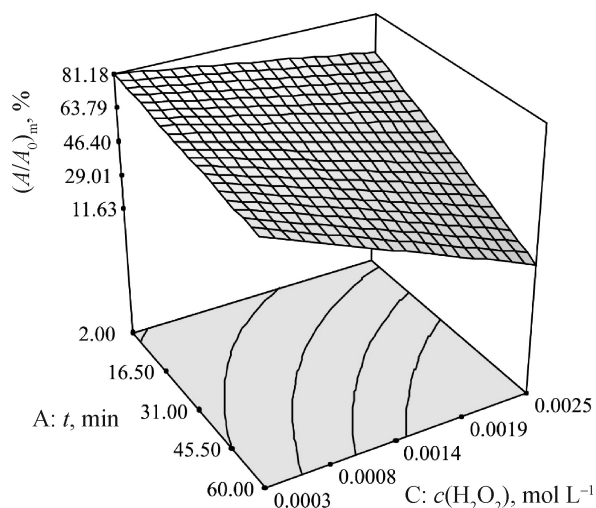


Fig. 13 – Predicted absorbance values, $(A/A_0)_{mv}$ vs. A: time, t , and C: concentration of H_2O_2 , $c(H_2O_2)$

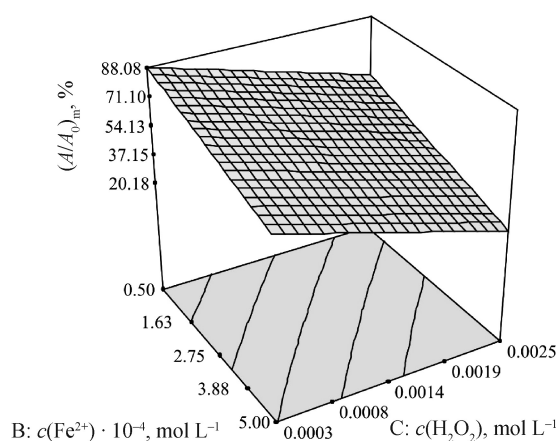


Fig. 14 – Predicted absorbance values, $(A/A_0)_{mv}$ vs. B: concentration of Fe^{2+} , $c(Fe^{2+})$ and C: concentration of H_2O_2 , $c(H_2O_2)$

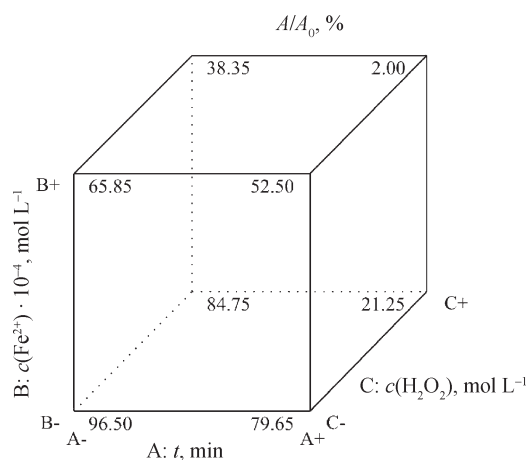


Fig. 15 – Predicted absorbance values, $(A/A_0)_{mv}$ in correlation with A: time, t , B: concentration of Fe^{2+} , $c(Fe^{2+})$ and C: concentration of H_2O_2 , $c(H_2O_2)$

Predicted values of decolorization in correlation with all process parameters at the same time were presented in a cuboidal depiction of the model (Fig. 15). It is obvious from Fig. 15 that the increase of all three parameters resulted in the increase of process efficiency in terms of decolorization.

Conclusion

In this study, decolorization of commercial anthraquinone reactive dye RB2 by Fenton oxidation was investigated. The influence of process parameters, initial H_2O_2 and Fe^{2+} concentrations and reaction time at pH 3 and room temperature were investigated and discussed on the basis of UV/VIS measurements. Complete decolorization of RB2 water solution (100 mg L⁻¹) was obtained with Fenton treatment at 0.0025 mol L⁻¹ H_2O_2 and 0.0005 mol L⁻¹ Fe^{2+} . Experimentally achieved data were analyzed using design of experiments (DoE) statistical method. Normalized effects of initial process parameters and their interactions on the RB2 decolorization were estimated. The mathematical model was developed and validated applying variance analysis. It was established that the proposed model describes the studied system well. It was shown that the increase of all three parameters (H_2O_2 concentration, Fe^{2+} concentration and reaction time) resulted in the increase of RB2 decolorization.

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