



## Decolorization of azo dye Everdirect Supra Red BWS in an aqueous solution by heat-activated persulfate: optimization using response surface methodology

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### ABSTRACT

In this study, the removal of Everdirect Supra Red BWS dye via a heat-activated persulfate process was studied. Individual and interactive effects of important process parameters, that is, persulfate concentration, initial dye concentration, process temperature and reaction time, were investigated using the response surface methodology. The high determination coefficient value ( $R^2 = 0.9948$ ) of the quadratic model showed that the model was accurate in predicting the experimental results. The experimental results corresponded well with the predicted models. Using the desirability function, the optimum conditions were found to be 2,375 mg L<sup>-1</sup> persulfate concentration, 87.51 mg L<sup>-1</sup> dye concentration, 62.5°C process temperature and 35 min reaction time, which resulted in the dye removal efficiency of 97.63%. The effects of radical scavengers on the dye degradation were also evaluated. The results indicated that SO<sub>4</sub><sup>•-</sup> was more dominant in the oxidation process. Moreover, the effect of various salts such as Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub> on the dye removal was also examined. The dye removal level slightly decreased in the presence of Na<sub>2</sub>SO<sub>4</sub> while Na<sub>2</sub>CO<sub>3</sub> did not cause a negative effect on the performance of this process.

*Keywords:* Everdirect Supra Red BWS; Persulfate; Response surface methodology; Sulfate radical

### 1. Introduction

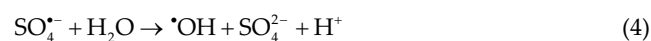
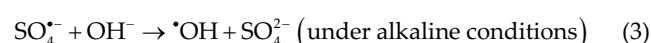
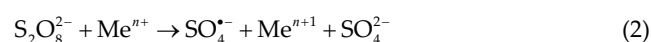
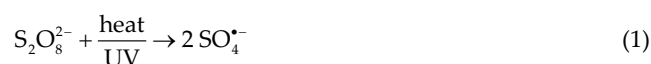
Dyes are commonly utilized in several industries such as textiles, printing, leather, paper, cosmetics and plastics [1]. It is estimated that more than 70,000 tons of dye wastewaters are discharged worldwide every year [2]. If dye-containing wastewaters are discharged into the environment without adequate treatment, they will unquestionably cause critical environmental problems. Particularly, the presence of dyes in the water environment is dangerous for both human health and aquatic life due to their potential toxic, carcinogenic and teratogenic characteristics [1]. Moreover, the entity of color in receiving water bodies is disagreeable regarding to esthetics for consumers [3]. Dyes are also rather persistent in the environment and resistant to biodegradation [2]. Thus, removal of dyes from wastewater is substantially required

prior to discharge into environment [1]. However, treatment of dyes from textile industries is difficult because of the complicated and stable structure [4]. Treatment methods such as coagulation [5,6] and adsorption [7,8] have been employed to remove dyes from wastewater. However, these methods only transport dyes from one phase to another rather than destroying them [3,9,10]. Recently, several studies have been focused on advanced oxidation processes (AOPs) for dye removal [11,12].

Among the AOPs, in recent years, persulfate technology has attracted increasing attention for treatment of wastewater containing recalcitrant and/or toxic pollutants [13]. Persulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) has an oxidation potential of 2.01 V ( $E_0$ ) [13–15], and is stable at room temperature [14]. Persulfate is activated by heat, UV-light, strong base and transition metals such as iron (e.g., Fe<sup>2+</sup>) [14,16]. When activated, it generates

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strong oxidizing sulfate radicals ( $E_0 = 2.7$  V) according to Eqs. (1) and (2) [15]. Moreover, once the sulfate radical ( $\text{SO}_4^{\bullet-}$ ) is generated, hydroxyl radical ( $\bullet\text{OH}$ ) can be generated in an indirect way, which makes a contribution to the degradation of pollutants.  $\text{SO}_4^{\bullet-}$  reacts with hydroxide, or water, and generates  $\bullet\text{OH}$  in respect to Eqs. (3) and (4) [11].  $\text{SO}_4^{\bullet-}$  is relatively more stable and selective during the treatment processes in comparison with  $\bullet\text{OH}$  (i.e., 300  $\mu\text{s}$  vs. 40  $\mu\text{s}$  for lifetime) [17].



Among the activation methods, persulfate activation by heat has been proposed as a good option to obtain high efficiency of  $\text{SO}_4^{\bullet-}$  generation and little wasted persulfate [18]. In the literature, the application of persulfate activated by heat was investigated for removing various pollutants such as perfluorooctanoic acid [19], polyvinyl alcohol [20], anti-pyrine [21], ibuprofen [22], sulfamethoxazole [23], diuron [24], carbamazepine [25], trichloroethylene [26], aniline [27],azole fungicide fluconazole [17], benzoic acid [28], mono- and dichlorobenzenes [13], methyl- and ethyl-parabens [18], sulfamethazine [29], triclosan [30] and methylene blue [11,31].

In the classical optimization method, one parameter is changed while all other parameters are kept at a constant level. The completion of the experiments using the classical method is time-consuming and tedious. In addition to this, this method does not describe the complete effects of the parameters in the process and ignores the combined interactions between parameters [32]. In order to ascertain the optimum conditions, it requires numerous experimental runs [33,34], and it may also lead to misinterpretation of results [32]. In order to overcome the classical method's limitations, some statistical experimental design methods have been used. Recently, response surface methodology (RSM) has received considerable attention for determining the effects of multiple independent variables [32]. RSM is an effective statistical technique that is commonly used for the optimization of multivariable systems [35].

RSM evaluates the relationships between the response(s) and independent variables, and depicts the effects of these variables, either alone or in combination [32]. RSM generally includes four steps: experimental design, response surface modeling, optimization and representing the direct and interactive effects. This model contains estimation of the coefficients in a mathematical model and predicting the response and checking the adequacy of the model [36]. It includes several benefits such as being more economical, requiring fewer experimental runs, studying the interaction between parameters on response, predicting the response, checking the method adequacy, and requiring a shorter time [32]. RSM-based modeling studies have been commonly used in many treatment processes such as Fenton [37],

photo-Fenton [38], photoelectro-Fenton [39], UV/ $\text{TiO}_2/\text{CeO}_2$  [40], UV/inorganic oxidants [41], persulfate/ $\text{Fe}^{2+}$ /heat [42] and adsorption [32,36,43,44] for removal of various pollutants.

Everdirect Supra Red BWS, which is an azo dye, was chosen as a model pollutant for this study because it is used in textile dyeing and it contains aromatic rings that make it difficult to treat with traditional processes [45,46]. To the best of our knowledge, there is no report on the application of persulfate activated by heat for the removal of Everdirect Supra Red BWS dye in aqueous solution till today. The main aim of this study is to determine the optimum conditions for Everdirect Supra Red BWS dye removal by heat-activated persulfate using RSM. In the heat-activated persulfate process used for Everdirect Supra Red BWS dye removal, the effects of initial dye concentration, persulfate oxidant dosage, process temperature, and contact time and the optimization were investigated through the central composite design (CCD) using RSM. The interaction among the process parameters and their contribution was assessed. The effects of radical scavengers on dye degradation were also evaluated. Moreover, the effects of various salts such as  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{CO}_3$  on the dye removal were also examined.

## 2. Materials and methods

### 2.1. Chemicals

Potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ) that was used as source of the sulfate radicals was obtained from Merck (Germany). Ethanol (EtOH) and tert-butanol (TBA) were obtained from Sigma-Aldrich (USA) and Merck (Germany), respectively. Everdirect Supra Red BWS (C.I. Direct Red 243) was supplied by a local textile factory in Turkey. The stock dye solution (1,000  $\text{mg L}^{-1}$ ) was prepared by dissolving 1,000 mg Everdirect Supra Red BWS dye in 1 L distilled water and stored in a refrigerator at 4°C. Test solutions used in the study were prepared by diluting the stock dye solution to desired concentrations. All the chemicals were employed without further purification. Distilled water was used in the preparation of all solutions throughout the study.

### 2.2. Experimental procedures

Experiments of Everdirect Supra Red BWS dye removal by heat-activated persulfate were performed in 250 mL Erlenmeyer glass flasks. 100 mL dye solutions were added in the flasks. The dye solutions in the Erlenmeyer flasks were pre-heated in a shaking water bath (GFL 1083) with reciprocating shaking motion, to predetermined temperatures prior to the addition of persulfate. Then, the required amounts of potassium persulfate that were determined based on RSM design were added to the solution as an oxidant. During the reaction, the temperature of the solutions was maintained using the water bath. Additionally, the solutions were homogeneously mixed in the water bath during the reaction. The samples were taken at the time intervals determined according to the RSM design, immediately placed in an ice bath to cease the dye oxidation process completely by chilling, and then analyzed using a UV-Vis spectrophotometer (PerkinElmer Lambda 365, USA). The initial pH in all experiments was unadjusted. Under the same conditions,

control experiments without potassium persulfate addition were also performed, and the results demonstrated that this dye could not thermally decompose. In order to determine the reactive radical species produced during the degradation of Everdirect Supra Red BWS dye under optimum conditions, EtOH and TBA were separately added into the reaction solutions using different EtOH/PS or TBA/PS molar ratio.

### 2.3. Experimental design

In the study, the CCD statistical model, one of the most effective and widely applied RSM designs, was used to examine the effects of four independent variables that contained initial dye concentration, persulfate concentration, process temperature and reaction time on Everdirect Supra Red BWS dye removal from aqueous solution by heat-activated persulfate, to evaluate the relationships among independent variables and optimize the experimental parameters. The CCD for four independent variables on five levels ( $-\alpha$ ,  $-1$ ,  $0$ ,  $1$ ,  $+\alpha$ ) was conducted by 30 experimental runs, which consisted of 16 factorial points, 8 axial points and 6 center points. The values of the independent variables and their variation limits were determined basing on experimental results obtained in preliminary studies. The ranges and the levels of the independent variables are presented in Table 1. Design-Expert Version 7 (Stat-Ease, Inc., Minneapolis, USA) statistical package was utilized to optimize the levels of the independent variables and to evaluate the interaction of process variables. Everdirect Supra Red BWS dye removal percentage was considered as a dependent variable. Additionally, Design-Expert Software was utilized for the statistical analysis, variance analysis (ANOVA) and graphical analysis of the data obtained.

The mathematical relationship between response and independent variables could be represented with the following equation [43]:

$$Y = b_0 + \sum_{i=1}^n b_i X_i + \sum_{i=1}^n b_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} X_i X_j \quad (5)$$

In this equation,  $Y$  is the predicted response (dye removal),  $b_0$  is the intercept value,  $b_i$ ,  $b_{ii}$  and  $b_{ij}$  are the coefficients for the linear, quadratic and interactive effects, respectively;  $X_i$  and  $X_j$  are the independent variables,  $n$  is the number of independent variables. Optimum values of the independent variables that ensure the maximum removal were designated by using the desirability function of Design-Expert Software.

### 2.4. Analysis methods

First, the wavelength of the maximum absorbance of Everdirect Supra Red BWS dye was determined by a UV-Vis spectrophotometer. Afterwards, the dye calibration curve was attained by utilizing the solutions with the known concentrations of the dye. The dye concentration was determined using curve of absorbance against the known dye concentration. The dye removal efficiency was determined according to Eq. (6).

$$\text{Removal (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (6)$$

where  $C_0$  (mg L<sup>-1</sup>) and  $C_t$  (mg L<sup>-1</sup>) are the dye concentration at times 0 and  $t$ , respectively.

The mineralization was evaluated by measuring the total organic carbon (TOC) with a TOC analyzer (Shimadzu, Japan). The pH of the solutions was measured by a pH meter (Orion Star A111).

## 3. Results and discussion

### 3.1. Model fitting and statistical analysis

To designate the important effects of the process variables, including persulfate concentration, initial dye concentration, process temperature and reaction time on the removal of Everdirect Supra Red BWS dye by persulfate activated with heat, a total of 30 experimental runs were conducted in accordance with the CCD experimental design. The coded values of the variables, design, the experimental (actual) and predicted results are given in Table 2. For Everdirect Supra Red BWS dye removal by heat-activated persulfate, the empirical relationship between the dependent variable (response) and independent variables in coded unit was obtained as given below:

$$\begin{aligned} \text{Removal (\%)} = & +39.78 + 8.36A - 9.47B + 19.73C + 7.40D + 0.36AB \\ & + 2.83AC + 1.53AD - 1.45BC - 0.55BD + 4.04CD \\ & - 1.61A^2 + 0.12B^2 + 5.08C^2 - 0.73D^2 \end{aligned} \quad (7)$$

where  $A$ ,  $B$ ,  $C$  and  $D$  are the coded terms for the independent variables, including persulfate concentration, initial dye concentration, process temperature and reaction time, respectively. The positive sign increases the response, while the negative sign decreases the response [47]. The persulfate concentration, process temperature, reaction time,

Table 1  
Independent variables and their levels for the CCD experimental design

Independent variables	Symbols	Range and levels				
		-2	-1	0	+1	+2
Persulfate concentration (mg L <sup>-1</sup> )	<i>A</i>	500	1,125	1,750	2,375	3,000
Initial dye concentration (mg L <sup>-1</sup> )	<i>B</i>	50	87.5	125	162.5	200
Process temperature (°C)	<i>C</i>	40	47.5	55	62.5	70
Reaction time (min)	<i>D</i>	5	15	25	35	45

Table 2  
Experimental design and results of the central composite design

Experimental run	Variables				Everdirect Supra Red BWS dye removal, %	
	A	B	C	D	Actual value	Predicted value
1	+1	-1	-1	+1	38.47	41.53
2	0	0	0	-2	22.64	22.05
3	-1	+1	+1	-1	34.29	30.54
4	-1	+1	+1	+1	48.99	49.25
5	0	0	0	0	40.14	39.78
6	0	0	0	0	39.69	39.78
7	+1	+1	+1	-1	50.00	50.60
8	0	0	0	0	40.79	39.78
9	0	0	-2	0	21.22	20.62
10	0	0	0	0	39.37	39.78
11	0	+2	0	0	18.04	21.32
12	-1	-1	+1	+1	73.16	72.92
13	+1	-1	+1	+1	97.57	97.64
14	+1	+1	-1	-1	16.9	16.45
15	0	0	0	+2	51.34	51.64
16	-2	0	0	0	14.17	16.63
17	+1	+1	+1	+1	76.12	75.42
18	0	0	0	0	39.28	39.78
19	-1	+1	-1	+1	13.42	10.26
20	-1	-1	-1	+1	27.75	28.14
21	0	-2	0	0	62.76	59.19
22	+1	+1	-1	+1	25.08	25.10
23	-1	-1	-1	-1	23.37	23.38
24	+1	-1	+1	-1	68.12	70.59
25	-1	-1	+1	-1	51.02	51.98
26	0	0	+2	0	99.24	99.55
27	0	0	0	0	39.42	39.78
28	+1	-1	-1	-1	29.94	29.94
29	-1	+1	-1	-1	6.80	7.72
30	+2	0	0	0	52.82	50.08

interaction between persulfate concentration and initial dye concentration, interaction between persulfate concentration and process temperature, interaction between persulfate concentration and the reaction time, interaction between the process temperature and reaction time had positive effect while others had negative effect.

The adequacy of the suggested quadratic model and statistical significance of the regression coefficients were examined using the analysis of variance (ANOVA). ANOVA results that are suggested by the quadratic model for Everdirect Supra Red BWS dye removal percentages are presented in Table 3. The mean squares were attained by dividing the sum of squares of each of the models and the error (residual) variance by the respective degrees of freedom (DF). The  $F$ -value of the model was determined by dividing the model mean square by residual mean square. The probability value ( $p$ -value)  $< 0.05$  expresses that the model is

significant, while the value  $> 0.1000$  specifies that the model is not significant [38]. The significance of the influence of the four independent variables was assessed by their  $F$ -value and  $p$ -value with ANOVA results for the quadratic model. In the study, the  $F$ -value and  $p$ -value were obtained to be 205.20 and lower than 0.0001, respectively. The  $p$ -value being very low ( $p$ -value  $< 0.0001$ ) confirms that the model was statistically significant for Everdirect Supra Red BWS dye removal by heat-activated persulfate.

Additionally, the importance of the fit of the suggested quadratic model was also assessed by the determination coefficient ( $R^2$ ).  $R^2$  gives the idea about the correlation between the experimental results and the predicted results. The closer the  $R^2$  value is to unity, the better the correlation between the experimental and predicted values and the better the model predicts the response [48]. The  $R^2$  value of 0.9948 indicates the accuracy of the model for Everdirect Supra Red BWS dye removal by heat-activated persulfate and that the experimental results were near the results that were predicted from the model. When the  $R^2$  value is represented as percentage, it signifies that 99.48% of the total variation for Everdirect Supra Red BWS removal by heat-activated persulfate is ascribed to the independent variables, and only 0.52% of the total variation cannot be elucidated by the model. The adjusted  $R^2$  (Adj  $R^2$ ) designates the  $R^2$  value for the sample size and the number of variables in the model. If the model includes many variables and the sample size is not very large, the adjusted  $R^2$  may be smaller than the  $R^2$  [43,48]. In this study, the adjusted  $R^2$  value of the model was obtained to be 0.99 and slightly smaller than the  $R^2$ . The predicted  $R^2$  (Pred  $R^2$ ) of 0.9705 demonstrated good agreement between the experimental and predicted values for Everdirect Supra Red BWS removal. This value was also in a good agreement with the adjusted  $R^2$  (Adj  $R^2$ ) of 0.99.

Adequate precision measures signal-to-noise ratio, and a ratio  $> 4$  is desirable [36,48]. An adequate precision of 55.284 was obtained for Everdirect Supra Red BWS removal. According to this value, the model had an adequate signal. The coefficient of variance (CV%), the ratio of the standard error of estimate to the mean value of the observed response (as a percentage), describes the reproducibility of the model. If the CV for the model is less than 10%, the model is taken into consideration as being reproducible [14,49]. The CV value of 5.58% that was obtained for Everdirect Supra Red BWS removal demonstrated that the model was confidential and accurate.

Additionally, ANOVA results were used for determining important variables. According to the ANOVA results presented in Table 3,  $A$  (persulfate concentration),  $B$  (initial dye concentration),  $C$  (process temperature) and  $D$  (reaction time) linear terms,  $A^2$  and  $C^2$  quadratic terms, and  $AC$ ,  $AD$ ,  $BC$  and  $CD$  interactive terms were the important terms of the model ( $p$ -value  $< 0.05$ ).

In order to establish the appropriateness of the model, diagnostic plots, such as the predicted values vs. the actual values, could also be utilized [14]. The predicted vs. actual value plots of the response are displayed in Fig. 1. As seen in the figure, the actual values were distributed relatively near to the predicted value line. This indicates that there was a good agreement between the actual values and predicted

Table 3  
ANOVA for response surface quadratic model

Source	Sum of squares	DF	Mean square	F-value	p value > F
Model	15,854.50	14	1,132.46	205.20	<0.0001
A-Persulfate concentration	1,678.35	1	1,678.35	304.12	<0.0001
B-Initial dye concentration	2,151.58	1	2,151.58	389.87	<0.0001
C-Process temperature	9,344.92	1	9,344.92	1,693.29	<0.0001
D-Reaction time	1,313.06	1	1,313.06	237.93	<0.0001
AB	2.10	1	2.10	0.38	0.5463
AC	128.26	1	128.26	23.24	0.0002
AD	37.33	1	37.33	6.76	0.0201
BC	33.47	1	33.47	6.06	0.0264
BD	4.93	1	4.93	0.89	0.3596
CD	261.63	1	261.63	47.41	<0.0001
A <sup>2</sup>	70.90	1	70.90	12.85	0.0027
B <sup>2</sup>	0.39	1	0.39	0.070	0.7952
C <sup>2</sup>	706.73	1	706.73	128.06	<0.0001
D <sup>2</sup>	14.78	1	14.78	2.68	0.1226

$R^2 = 0.9948$ , Adj  $R^2 = 0.99$ , Pred  $R^2 = 0.9705$ , Adeq precision = 55.284, CV% = 5.58.

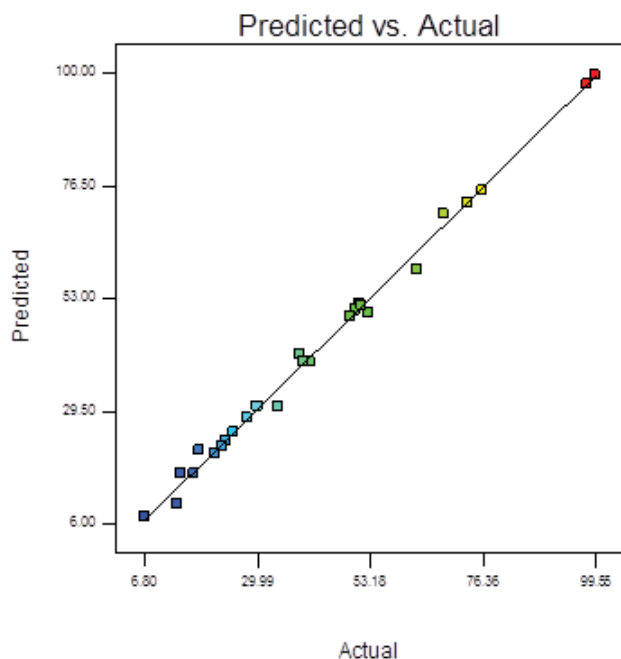


Fig. 1. Predicted vs. actual values plot for removal of Everdirect Supra Red BWS dye.

values that were obtained from the model. Therefore, the model could be applied for prediction and optimization.

### 3.2. Effects of operating parameters and their interactions on dye removal

To assess the effects of significant operating parameters on Everdirect Supra Red BWS removal efficiency, a perturbation plot was created using the Design-Expert software. The perturbation plot aids in comparing the effects of all the

parameters at a particular point in the design space [36]. As seen in Fig. 2, all the operating parameters had the significance on Everdirect Supra Red BWS removal efficiency. The increase in the persulfate concentration, process temperature and reaction time increased Everdirect Supra Red BWS removal efficiency, while the increase in the initial dye concentration reduced it.

The three-dimensional (3D) response surface and two-dimensional (2D) contour plots of the predicted responses of the model were attained by the Design-Expert software and used to evaluate the relationships between the process variables and removal efficiencies for Everdirect Supra Red BWS dye removal by heat-activated persulfate. The 3D response surface and contour plots are given in Figs. 3a–e. Fig. 3a shows the dye removal efficiency dependence on the persulfate concentration and the initial dye concentration at the temperature of 55°C and the reaction time of 25 min. Changes in the persulfate concentration and initial dye concentration within the specified range had a significant impact on the removal efficiencies. As seen in Fig. 3a, when the process temperature and the reaction time were kept at 55°C and 25 min, respectively, with the increase in the persulfate concentration, the dye removal efficiency increased, while it decreased by the increasing initial dye concentration. The observed decrease on the removal efficiency as a result of the increasing initial dye concentration could be attributed to a decrease of ratio of persulfate to dye molecules in the solution with the increase of dye concentration and more persulfate consumption in the process [11], and to be the insufficiency of persulfate amount for the dye removal. As a result, the radicals that were generated in the solution were not sufficient enough for reaction with the dye [12]. Additionally, several intermediates generated due to the degradation of the dye with the increase of dye concentration may also hinder desirable oxidation. Such a hindrance will be more distinct in the raised level of degradation intermediates generated by the increase of dye

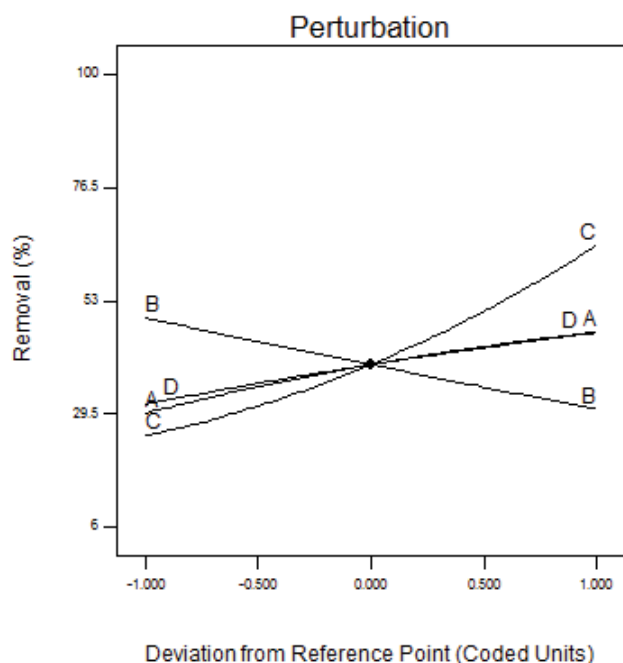


Fig. 2. Effect of the main parameters including initial persulfate dosage (a), the initial dye concentration (b), process temperature (c) and reaction time (d) on the dye removal efficiency.

concentration [11]. The increase in the persulfate concentration, determined as a significant parameter for removal of Everdirect Supra Red BWS dye, caused significant increases in Everdirect Supra Red BWS removal efficiency. This situation may be contributed more generation of sulfate and hydroxyl radicals during reaction, in accordance with Eqs. (1) and (4). Thus, a reaction between these generated radicals and dye molecules led to more degradation of Everdirect Supra Red BWS [11].

The effect of the persulfate concentration and the process temperature on the dye removal efficiency is shown in Fig. 3b. As seen in the figure, as the persulfate concentration and process temperature increased, the dye removal efficiency also increased. This result may be elucidated by the elevated thermal energy facilitating the dissolution of persulfate at higher temperatures, as described by Eq. (1), thereby generating more sulfate radicals and other potential radicals such as  $\text{HO}^\bullet$  [18]. The low efficiency obtained at low temperatures may be attributed to insufficient production of sulfate radicals. At the high reaction temperature, transformation of persulfate ions to sulfate radicals was faster [12].

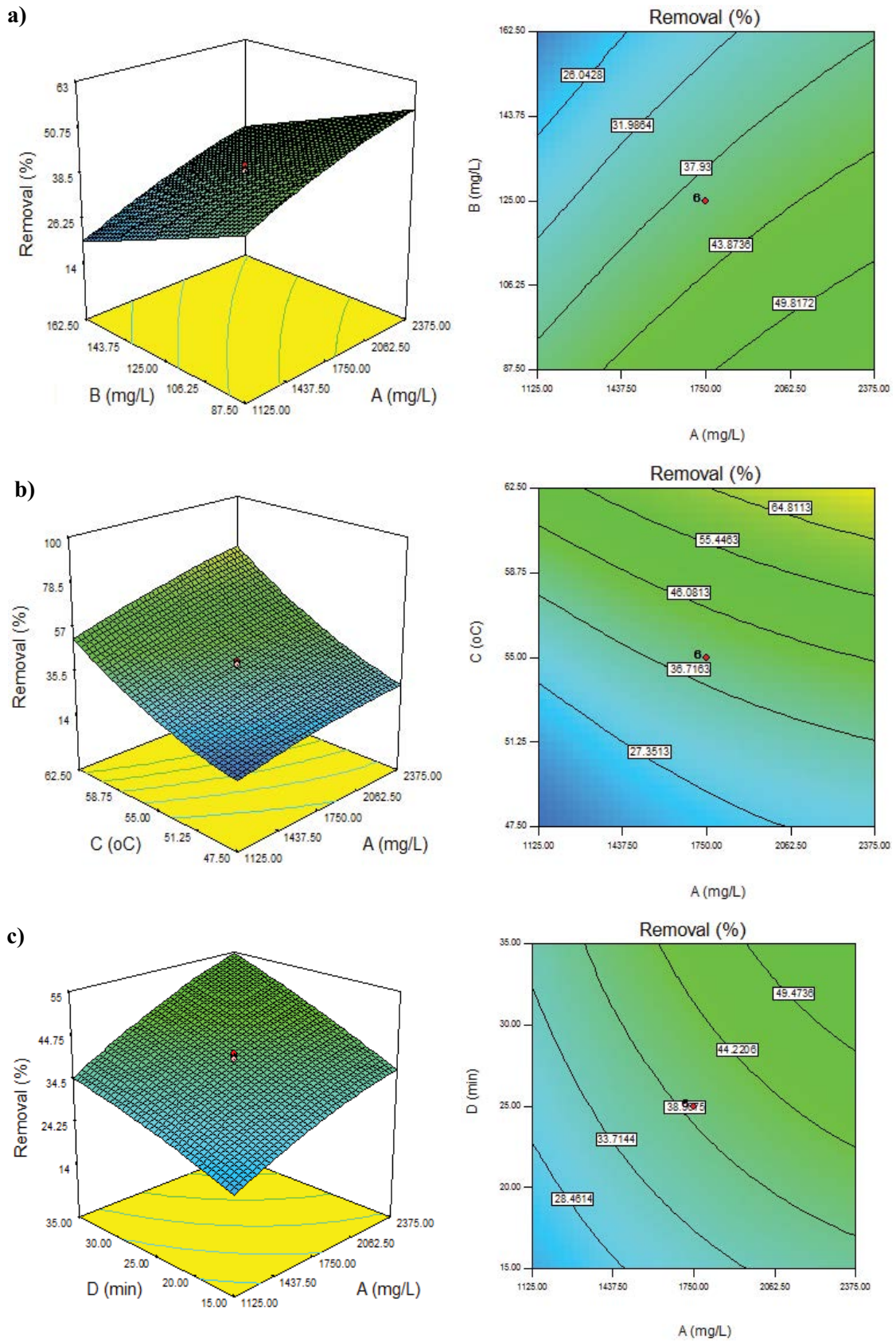
Based on Fig. 3c showing the effect of the persulfate concentration and the reaction time on dye removal efficiency, both increasing reaction time and increasing persulfate concentration increased the dye removal efficiency. Increasing reaction time and persulfate concentration provides both the collision of more radicals with the dye molecules [11], and higher contact time between dye molecules and oxidants. The effect of the initial dye concentration and the temperature and the effect of the temperature and the reaction time on the dye removal efficiency are shown in Figs. 3d and e, respectively. As it can be seen in Fig. 3d, with the increase

in the temperature, the removal efficiency increased, while on the other hand, with the increase in the initial dye concentration, the removal efficiency decreased. Under the operating conditions, the increase in both the temperature and reaction time increased the dye removal efficiency (Fig. 3e). Increase of temperature caused fast sulfate radical generation in a shorter reaction time. At a low temperature, the removal efficiency was quite low in comparison with that at a high temperature. This was due to the very slow decomposition of persulfate [18]. According to the 3D response surface and 2D contour plots, the maximum removal efficiency of Everdirect Supra Red BWS was obtained at a higher persulfate concentration, temperature and reaction time and lower dye concentration.

### 3.3. Optimization of process and model validation

In order to find the optimum conditions of Everdirect Supra Red BWS removal efficiency, optimization of the process variables was carried out by using the Design-Expert 7.0 software. In the optimization step, the desired goal for persulfate concentration, initial dye concentration, process temperature and reaction time was selected in the range while the response (dye removal efficiency) was identified as maximum to obtain the highest removal efficiency. The optimum conditions were found to be 2,375  $\text{mg L}^{-1}$  persulfate concentration, 87.51  $\text{mg L}^{-1}$  initial dye concentration, 62.5°C process temperature and 35 min reaction time (Fig. 4). Under these optimum conditions, the maximum dye removal efficiency predicted by the model was estimated as 97.63%. The desirability function value was found to be 0.983 for these optimum conditions. Several process variables and optimization results of few studies where RSM was applied in removal of dyes using persulfate activated with different activators such as UV and heat are presented in Table 4. The key design and operating factors included parameters such as reaction time, initial dye concentration, pH, temperature, distance from UV lamp, UV irradiation and persulfate concentration. In comparison with the UV-activated persulfate oxidation processes that are presented in Table 4, the heat-activated persulfate oxidation process almost exhibited similar performance for removing the dye. The results of this study showed that the heat-activated persulfate oxidation process is an effective process for removal of dyes.

To confirm the validity of the model, confirmatory experiments were conducted in replicates at the predicted optimum conditions, and the average values of the results obtained from the confirmatory experiments are presented in Fig. 5. When the dye removal efficiency obtained experimentally under the optimized working conditions was compared with the value predicted by the model, as seen in Fig. 5, the dye removal efficiency (98.72%) was close to which was foreseen by the empirical model, with a low deviation of 1.09%. The good agreement between the predicted and experimental results validated the result of response surface optimization. Consequently, the results of the confirmatory experiments demonstrated that the model was suitable and accurate in predicting Everdirect Supra Red BWS removal efficiency. Additionally, at the optimum conditions predicted



(Fig. 3. Continued)

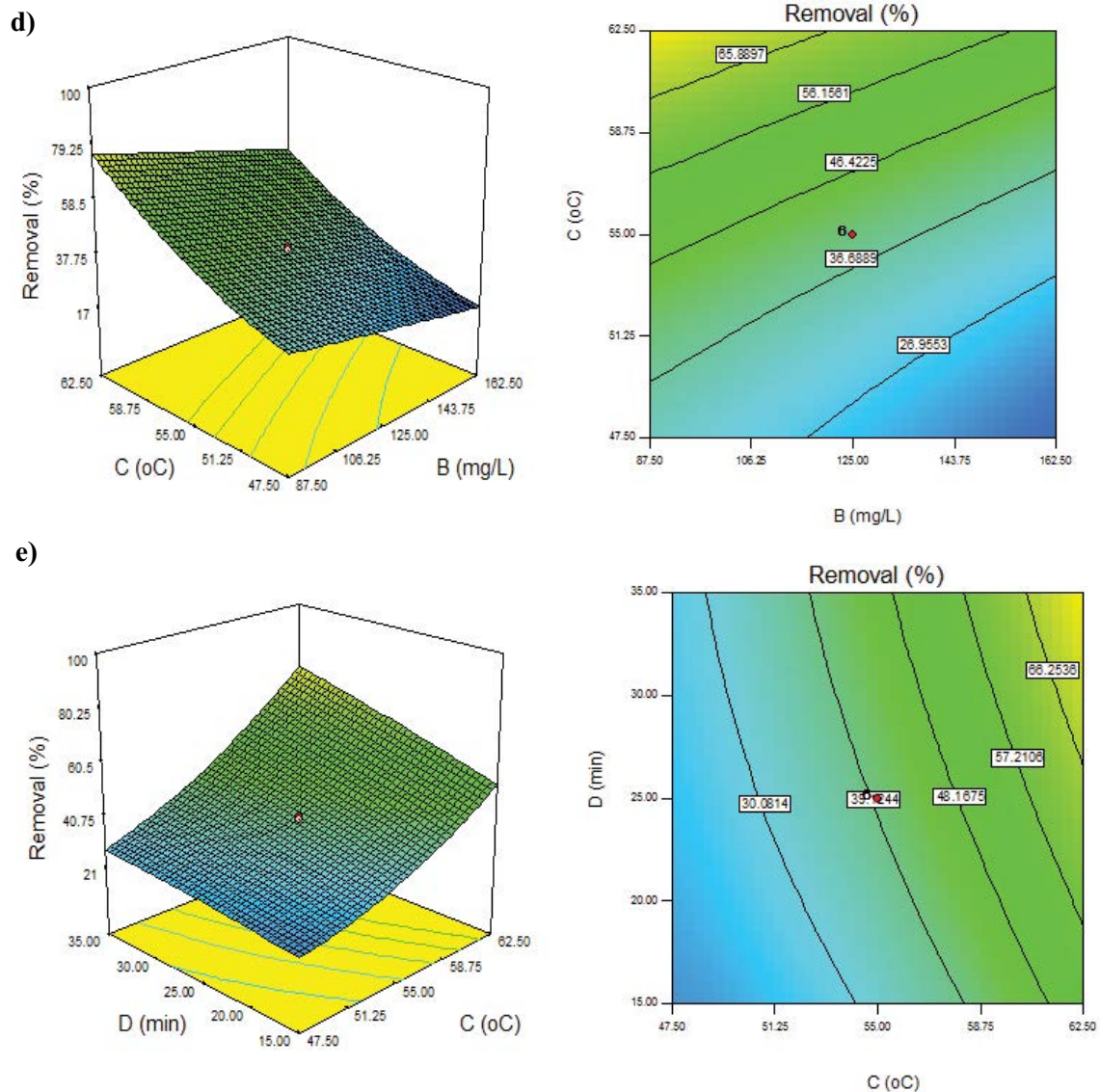


Fig. 3. Three-dimensional response surface and counter plots showing the effect of two variables on the dye removal efficiency when all other variables were kept at their center level: (a) initial persulfate dosage and initial dye concentration, (b) initial persulfate dosage and process temperature, (c) initial persulfate dosage and reaction time, (d) initial dye concentration and process temperature, and (e) process temperature and reaction time.

by the model, the pH of the solution vs. reaction time was also measured, and the results are presented in Fig. 5. Under the natural pH level of the solution without the usage of a buffer, the pH of the dye solution during the reaction time of 35 min for the heat-activated persulfate system decreased from the initial value of 6.94 to 3.10. This decrease in pH could be attributed to the production of protons and formation of acidic by-products [53].

Additionally, Everdirect Supra Red BWS loss did not appear even up to 70°C in the absence of  $S_2O_8^{2-}$  (data not shown). In the absence of  $S_2O_8^{2-}$ , the elevated temperature up to 70°C had no degrading effect on the Everdirect Supra Red BWS dye solution, indicating that the Everdirect Supra Red BWS dye does not decompose on its own even at elevated temperatures.

### 3.4. UV–vis spectrum and mineralization of dye

Under the experimental conditions of 87.5 mg L<sup>-1</sup> dye concentration, 2,375 mg L<sup>-1</sup> PS, and 62.5°C, the UV–Vis spectra changes in the dye solution as a function of reaction time are illustrated in Fig. 6. As seen in the figure, the UV–Vis spectra of the Everdirect Supra Red BWS dye solution showed peaks at 520, 400, 289, and 236 nm before treatment by the heat-activated persulfate. The peaks at 520 and 400 nm in the visible region were assigned to the conjugated structure formed by azo bond, while the peaks at 289 and 236 nm in the ultraviolet region were assigned to the aromatic rings. The peak at 236 nm disappeared completely within 10 min of reaction time. The characteristic absorption peak at 520 nm decreased over reaction time and disappeared



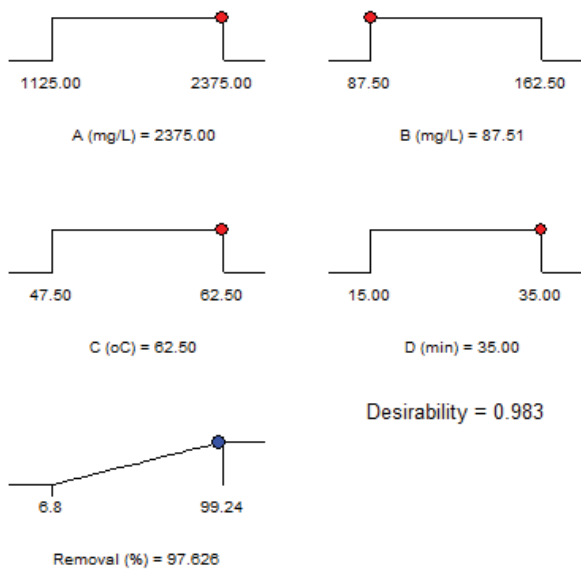


Fig. 4. Desirability ramp for numerical optimization of four independent variables.

completely within 20 min of reaction time, indicating that the chromophore group and the conjugated system of the azo dye were destroyed.

It is known that TOC removal from a degradation mixture is a very important indicator in identifying the mineralization degree of pollutants [54]. Therefore, the mineralization degree of the azo dye Everdirect Supra Red

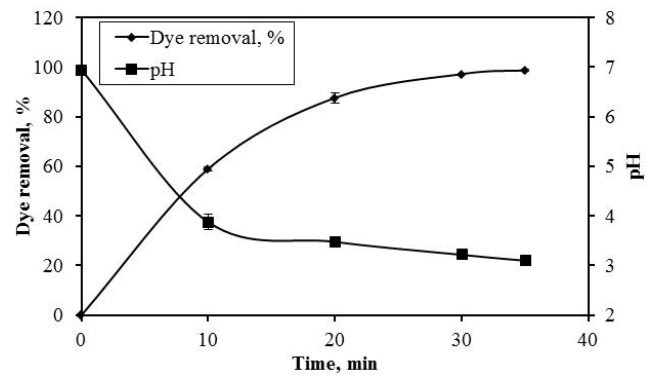


Fig. 5. Variation of the dye removal and the solution pH vs. reaction time (conditions:  $C_0 = 87.5 \text{ mg L}^{-1}$ ,  $PS = 2,375 \text{ mg L}^{-1}$ ,  $T = 62.5^\circ\text{C}$ ).

Table 4

Several process variables and optimization results of few studies that RSM was applied in removal of dyes

Process	Dye	Method	RSM	Optimization		References
			Process variables	Optimum conditions	Optimum efficiency	
UV/S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	Acid Blue 193	CCD	Initial dye concentration ( $C_0$ ), K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> concentration (KPS) UV irradiation (UVI) Process temperature ( $T$ )	$C_0 = 40 \text{ mg L}^{-1}$ KPS = 5 mM UVI = 250 W $T = 50^\circ\text{C}$	CR = 99.6%	[46]
UV/S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	Basic Red 46	CCD	Reaction time (RT) Initial dye concentration ( $C_0$ ) S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> concentration (PS) Distance from UV lamp (UVD)	RT = 10 min $C_0 = 10 \text{ mg L}^{-1}$ PS = 1.5 mmol L <sup>-1</sup> UVD = 6 cm	CR = 98%	[50]
UV/S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	Basic Blue 3	CCD	Reaction time (RT) Initial dye concentration ( $C_0$ ) S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> concentration (PS) Distance from UV lamp (UVD)	RT = 11 min $C_0 = 10 \text{ mg L}^{-1}$ PS = 1.5 mmol L <sup>-1</sup> UVD = 6 cm	CR = 98%	[51]
UV/S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	Reactive Red 45	CCD	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> concentration (KPS) pH	KPS = 15 mmol L <sup>-1</sup> pH = 5–7	CR = 100%	[52]
Fe <sup>2+</sup> /heat/S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	Basic Yellow 28	BBD	Reaction time (RT) Ferrous ion concentration (Fe <sup>2+</sup> ) S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> concentration (PS) Temperature ( $T$ )	RT = 8 h Fe <sup>2+</sup> = 1.95 mM PS = 9.87 mM $T = 65^\circ\text{C}$	TOC = 93%	[42]
Heat/S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	Everdirect Supra Red BWS	CCD	Reaction time (RT) Initial dye concentration ( $C_0$ ) S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> concentration (PS) Temperature ( $T$ )	RT = 35 min $C_0 = 87.5 \text{ mg L}^{-1}$ PS = 2375 mg L <sup>-1</sup> $T = 62.5^\circ\text{C}$	CR = 97.6%	Present study

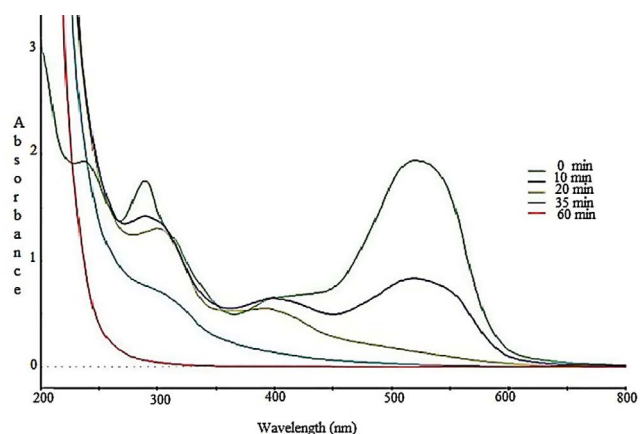


Fig. 6. UV-Vis spectrum of Everdirect Supra Red BWS (conditions:  $C_0 = 87.5 \text{ mg L}^{-1}$ ,  $PS = 2,375 \text{ mg L}^{-1}$ ,  $T = 62.5^\circ\text{C}$ ).

BWS was investigated by TOC measurements. In order to evaluate the mineralization efficiency of the azo dye Everdirect Supra Red BWS dye solution, the variation of TOC in the Everdirect Supra Red BWS dye solution over reaction time was measured. For the run performed at the dye concentration of  $87.5 \text{ mg L}^{-1}$  and PS concentration of  $2,375 \text{ mg L}^{-1}$  and at  $62.5^\circ\text{C}$ , the removal efficiency of TOC in the dye solution over time is shown in Fig. 7. As shown in the figure, after 35 min of reaction time, the decolorization efficiency reached 98.72% while the TOC removal efficiency was about only 23%, which was much lower than the dye removal rate of 98.72%. This result indicated that Everdirect Supra Red BWS dye was initially degraded by the  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  radicals generated from the heat-activated persulfate to some intermediate products, but it was difficult to mineralize it completely by the heat-activated persulfate process at a reaction time of 35 min. However, when the reaction time was extended to 60 min, the TOC removal value reached 83%. These results demonstrated that the heat-activated persulfate system could effectively remove not only color but also TOC; however, a longer time was needed to achieve a satisfactory TOC removal rate in comparison with color removal.

### 3.5. Identification of radical species

EtOH is generally an effective quencher for both  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$ , whereas TBA is an effective quencher for  $\cdot\text{OH}$  and not for  $\text{SO}_4^{\cdot-}$ . As a result, EtOH and TBA could be used to distinguish  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  based on a comparison of the degrees of pollutant degradation [18]. To understand which radical species is mainly responsible for the removal of Everdirect Supra Red BWS, a series of experiments with the addition of radical scavengers, EtOH and TBA, were conducted under the conditions of  $2,375 \text{ mg L}^{-1}$  PS and  $87.5 \text{ mg L}^{-1}$  dye concentration,  $62.5^\circ\text{C}$  and 35 min of reaction time. Additionally, the test was also carried out without the addition of radical quenchers under these conditions. In the experiments, EtOH and TBA were separately added into the reaction solutions at the alcohol/PS molar ratios of 10/1, 25/1, 50/1 and 100/1. The Everdirect Supra Red BWS removal efficiencies in the presence of EtOH

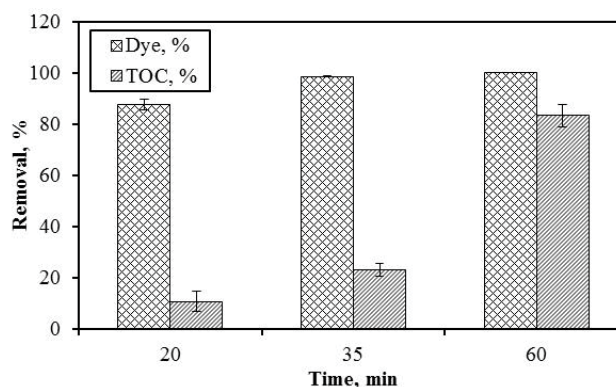


Fig. 7. Variation of the dye and TOC removal vs. reaction time (conditions:  $C_0 = 87.5 \text{ mg L}^{-1}$ ,  $PS = 2,375 \text{ mg L}^{-1}$ ,  $T = 62.5^\circ\text{C}$ ).

and TBA are presented in Fig. 8. In the absence of radical quenchers, 98.72% of the dye was removed after 35 min of reaction time (Fig. 7). As shown in Fig. 8, the dye removal rate decreased in the presence of EtOH and TBA. The dye removal efficiencies decreased by 96.01%, 93.81%, 89.56% and 80.36% at the TBA/PS molar ratios of 10/1, 25/1, 50/1 and 100/1, respectively, while the dye removal efficiencies decreased by 87.58%, 76.76%, 69.34% and 65.21% at EtOH/PS molar ratios of 10/1, 25/1, 50/1 and 100/1, respectively. As seen in Fig. 8, the presence of both EtOH and TBA inhibited the degradation of the dye. However, the inhibitory effect of EtOH was clearly greater than that of TBA. The results exhibited that both  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  were existed in the system and simultaneously had a role in the degradation of the dye, but  $\text{SO}_4^{\cdot-}$  played the dominant role. Additionally, it was determined that the dye could be removed even with the addition of EtOH. Probably, the  $\text{SO}_4^{\cdot-}$  that remained in the solution could still react with the dye [18]. According to the results that were obtained, the dominant radical species produced in the heat-activated persulfate process were the sulfate radicals.

### 3.6. Effects of salts

As it is known, textile effluents commonly contain a variety of inorganic salts such as sodium sulfate and sodium carbonate. Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) is used for the enhanced pick up of dye on cotton, while sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) provides alkaline pH for covalent fixation of the dye on cotton [12]. Since  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{CO}_3$  are likely to be present in textile effluents, the impact of these salts on Everdirect Supra Red BWS dye removal by heat-activated persulfate was also examined in this study. In order to assess the impact of these salts on the Everdirect Supra Red BWS dye removal, a series of experiments were performed by adding these salts to Everdirect Supra Red BWS dye solution at the optimized conditions, and the results were compared with those in the no salt condition. The effect of  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{CO}_3$  salts on Everdirect Supra Red BWS dye removal efficiency by the heat-activated persulfate is presented in Figs. 9a and b, respectively. Without  $\text{Na}_2\text{SO}_4$  addition, Everdirect Supra Red BWS removal efficiency was 98.72% while it decreased to 95.25% by increasing  $\text{SO}_4^{2-}$  anion to  $10 \text{ g L}^{-1}$ , but the result

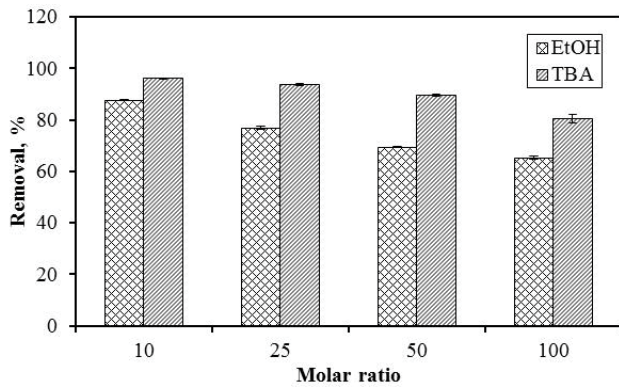


Fig. 8. Effect of various scavengers at different scavengers/PS molar ratios on Everdirect Supra Red BWS removal.

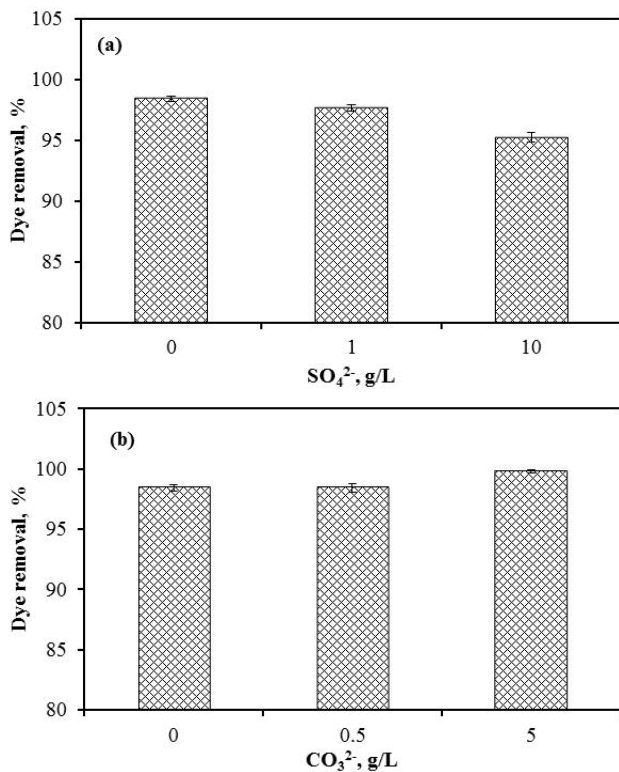


Fig. 9. Effect of (a)  $\text{SO}_4^{2-}$  anion, and (b)  $\text{CO}_3^{2-}$  anion with the different concentrations on Everdirect Supra Red BWS dye removal (conditions:  $C_0 = 87.5 \text{ mg L}^{-1}$ ,  $\text{PS} = 2,375 \text{ mg L}^{-1}$ ,  $T = 62.5^\circ\text{C}$ , time = 35 min).

was not significantly affected. The added  $\text{SO}_4^{2-}$  anions were converted to stronger  $\text{SO}_4^{\bullet-}$  radicals either by abstraction of proton from the solution (as shown in Eq. (8)) or due to interaction of the  $\text{SO}_4^{2-}$  anions with the hydroxyl radical (as shown in Eq. (9)) [12]. However, sulfate radicals may be consumed by some reactions other than with the dye, as shown in Eqs. (10)–(12) [55], and the dye removal efficiency may have decreased due to this situation.



On the other hand, the presence of  $\text{CO}_3^{2-}$  with the tested concentrations increased the Everdirect Supra Red BWS removal efficiency from 98.72% to 99.82%. The results indicated that, under the optimized conditions, Everdirect Supra Red BWS removal could not be significantly affected in the presence of  $\text{Na}_2\text{SO}_4$ , while the existence of  $\text{Na}_2\text{CO}_3$  did not cause a negative effect on the performance of this process.

#### 4. Conclusions

In this study, RSM was employed to evaluate, model and optimize the removal of Everdirect Supra Red BWS dye removal from an aqueous solution by a heat-activated persulfate process. RSM showed that increasing persulfate concentration, raising temperature or/and extending reaction time had a positive effect, while increasing initial dye concentration had an adverse effect on Everdirect Supra Red BWS removal. A high determination coefficient ( $R^2 = 0.9948$ , adjusted  $R^2 = 0.99$ ) showed good agreement between the experimental values and model predictions. Both sulfate and hydroxyl radicals were responsible for the oxidation of Everdirect Supra Red BWS by the heat-activated persulfate system. The experimental results revealed that the heat-activated persulfate oxidation process was an efficient technique for Everdirect Supra Red BWS removal from aqueous solutions. The results also demonstrated that RSM was an appropriate technique in predicting both the treatment performance of the process and the interactive effects of the process variables.

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#### References

- [1] X. Wang, P. Wang, J. Ma, H. Liu, P. Ning, Synthesis, characterization, and reactivity of cellulose modified nanozero-valent iron for dye discoloration, *Appl. Surf. Sci.*, 345 (2015) 57–66.
- [2] L. Han, S. Xue, S. Zhao, J. Yan, L. Qian, M. Chen, Biochar supported nanoscale iron particles for the efficient removal of methyl orange dye in aqueous solutions, *PLOS ONE*, 2015.
- [3] F. Ghanbari, M. Moradi, M. Manshouri, Textile wastewater decolorization by zero valent iron activated peroxymonosulfate: compared with zero valent copper, *J. Environ. Chem. Eng.*, 2 (2014) 1846–1851.

- [4] R. Abbassi, A.K. Yadav, N. Kumar, S. Huang, P.R. Jaffe, Modeling and optimization of dye removal using “green” clay supported iron nano-particles, *Ecol. Eng.*, 61 (2013) 366–370.
- [5] J. Dotto, M.R. Fagundes-Klen, M.T. Veit, S.M. Palácio, R. Bergamasco, Performance of different coagulants in the coagulation/flocculation process of textile wastewater, *J. Cleaner Prod.*, 208 (2019) 656–665.
- [6] M.S. Tunç, Ö. Tepe, Removal of Color and COD from Wastewater of a Local Textile Factory by Coagulation, ICENS International Conference on Engineering and Natural Science, Skopje, Macedonia, May 15–19 2015, pp. 364–369.
- [7] N.K. Amin, Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: adsorption equilibrium and kinetics, *J. Hazard. Mater.*, 165 (2009) 52–62.
- [8] V.K. Gupta, B. Gupta, A. Rastogi, S. Agarwal, A. Nayak, A comparative investigation on adsorption performances of mesoporous activated carbon prepared from waste rubber tire and activated carbon for a hazardous azo dye—Acid Blue 113, *J. Hazard. Mater.*, 186 (2011) 891–901.
- [9] X. Liu, Z. Chen, Z. Chen, M. Megharaj, R. Naidu, Remediation of Direct Black G in wastewater using kaolin-supported bimetallic Fe/Ni nanoparticles, *Chem. Eng. J.*, 223 (2013) 764–771.
- [10] C. Zhang, Z. Zhu, H. Zhang, Z. Hu, Rapid decolorization of Acid Orange II aqueous solution by amorphous zero-valent iron, *J. Environ. Sci.*, 24 (2012) 1021–1026.
- [11] S.A. Kordkandi, M. Forouzesh, Application of full factorial design for methylene blue dye removal using heat-activated persulfate oxidation, *J. Taiwan Inst. Chem. Eng.*, 45 (2014) 2597–2604.
- [12] N.N. Patil, S.R. Shukla, Degradation of Reactive Yellow 145 dye by persulfate using microwave and conventional heating, *J. Water Process Eng.*, 7 (2015) 314–327.
- [13] P. Dobosy, C.É. Vizsolyi, I. Varga, J. Varga, G. Láng, G. Zárar, Comparative study of ferrate and thermally activated persulfate treatments for removal of mono- and dichlorobenzenes from groundwater, *Microchem. J.*, 136 (2018) 61–66.
- [14] Q. Yang, Y. Zhong, H. Zhong, X. Li, W. Du, X. Li, R. Chen, G. Zeng, A novel pretreatment process of mature landfill leachate with ultrasonic activated persulfate: optimization using integrated Taguchi method and response surface methodology, *Process Saf. Environ. Prot.*, 98 (2015) 268–275.
- [15] K.E. Manz, K.E. Carter, Investigating the effects of heat activated persulfate on the degradation of furfural, a component of hydraulic fracturing fluid chemical additives, *Chem. Eng. J.*, 327 (2017) 1021–1032.
- [16] M.S. Tunç, O. Tepe, Removal of phenol from aqueous solution using persulfate activated with nanoscale zero-valent iron, *Desal. Wat. Treat.*, 74 (2017) 269–277.
- [17] J.-F. Yang, L.-M. Yang, S.-B. Zhang, L.-H. Ou, C.-B. Liu, L.-Y. Zheng, Y.-F. Yang, G.-G. Ying, S.-L. Luo, Degradation of azole fungicide fluconazole in aqueous solution by thermally activated persulfate, *Chem. Eng. J.*, 321 (2017) 113–122.
- [18] Y. Chen, P. Deng, P. Xie, R. Shang, Z. Wang, S. Wang, Heat-activated persulfate oxidation of methyl- and ethyl-parabens: effect, kinetics, and mechanism, *Chemosphere*, 168 (2017) 1628–1636.
- [19] Y.C. Lee, S.L. Lo, J. Kuo, Y.L. Lin, Persulfate oxidation of perfluorooctanoic acid under the temperatures of 20–40°C, *Chem. Eng. J.*, 198–199 (2012) 27–32.
- [20] S.Y. Oh, H.W. Kim, J.M. Park, H.S. Park, C. Yoon, Oxidation of polyvinyl alcohol by persulfate activated with heat, Fe<sup>2+</sup>, and zero-valent iron, *J. Hazard. Mater.*, 168 (2009) 346–351.
- [21] C. Tan, N. Gao, Y. Deng, W. Rong, S. Zhou, N. Lu, Degradation of antipyrine by heat activated persulfate, *Sep. Purif. Technol.*, 109 (2013) 122–128.
- [22] A. Ghauch, A.M. Tuqan, N. Kibbi, Ibuprofen removal by heated persulfate in aqueous solution: a kinetics study, *Chem. Eng. J.*, 197 (2012) 483–492.
- [23] C. Qi, X. Liu, C. Lin, X. Zhang, J. Ma, H. Tan, W. Ye, Degradation of sulfamethoxazole by microwave-activated persulfate: kinetics, mechanism and acute toxicity, *Chem. Eng. J.*, 249 (2014) 6–14.
- [24] C. Tan, N. Gao, Y. Deng, N. An, J. Deng, Heat-activated persulfate oxidation of diuron in water, *Chem. Eng. J.*, 203 (2012) 294–300.
- [25] J. Deng, Y. Shao, N. Gao, Y. Deng, S. Zhou, X. Hu, Thermally activated persulfate (TAP) oxidation of antiepileptic drug carbamazepine in water, *Chem. Eng. J.*, 228 (2013) 765–771.
- [26] M. Xu, H. Du, X. Gu, S. Lu, Z. Qiu, Q. Sui, Generation and intensity of active oxygen species in thermally activated persulfate systems for the degradation of trichloroethylene, *RSC Adv.*, 4 (2014) 40511–40517.
- [27] X. Xie, Y. Zhang, W. Huang, S. Huang, Degradation kinetics and mechanism of aniline by heat-assisted persulfate oxidation, *J. Environ. Sci.*, 24 (2012) 821–826.
- [28] N. Zrinyi, A.L.-T. Pham, Oxidation of benzoic acid by heat-activated persulfate: effect of temperature on transformation pathway and product distribution, *Water Res.*, 120 (2017) 43–51.
- [29] Y. Fan, Y. Ji, D. Kong, J. Lu, Q. Zhou, Kinetic and mechanistic investigations of the degradation of sulfamethazine in heat-activated persulfate oxidation process, *J. Hazard. Mater.*, 300 (2015) 39–47.
- [30] H. Gao, J. Chen, Y. Zhang, X. Zhou, Sulfate radicals induced degradation of Triclosan in thermally activated persulfate system, *Chem. Eng. J.*, 306 (2016) 522–530.
- [31] A. Ghauch, A.M. Tuqan, N. Kibbi, S. Geryes, Methylene blue discoloration by heated persulfate in aqueous solution, *Chem. Eng. J.*, 213 (2012) 259–271.
- [32] T. Shojaeimehr, F. Rahimpour, M.A. Khadivi, M. Sadeghi, A modeling study by response surface methodology (RSM) and artificial neural network (ANN) on Cu<sup>2+</sup> adsorption optimization using light expanded clay aggregate (LECA), *J. Ind. Eng. Chem.*, 20 (2014) 870–880.
- [33] M. Elibol, Optimization of medium composition for actinorhodin production by *Streptomyces coelicolor* A3(2) with response surface methodology, *Process Biochem.*, 39 (2004) 1057–1062.
- [34] A. Mohammadi, S. Nemati, M. Mosafari, A. Abdollahnejhad, M. Almasian, A. Sheikhmohammadi, Predicting the capability of carboxymethyl cellulose-stabilized iron nanoparticles for the remediation of arsenite from water using the response surface methodology (RSM) model: modeling and optimization, *J. Contam. Hydrol.*, 203 (2017) 85–92.
- [35] M. Tanyol, G. Uslu, V. Yönten, Optimization of lipase production on agroindustrial residue medium by *Pseudomonas fluorescens* (NRL B-2641) using response surface methodology, *Biotechnol. Biotechnol. Equip.*, 29 (2015) 64–71.
- [36] L.A. Kafshgari, M. Ghorbani, A. Azizi, S. Agarwal, V.K. Gupta, Modeling and optimization of Direct Red 16 adsorption from aqueous solutions using nanocomposite of MnFe<sub>2</sub>O<sub>4</sub>/MWCNTs: RSM-CCRD model, *J. Mol. Liq.*, 233 (2017) 370–377.
- [37] Y. Wu, S. Zhou, F. Qin, X. Ye, K. Zheng, Modeling physical and oxidative removal properties of Fenton process for treatment of landfill leachate using response surface methodology (RSM), *J. Hazard. Mater.*, 180 (2010) 456–465.
- [38] I. Arslan-Alaton, G. Tureli, T. Olmez-Hanci, Treatment of azo dye production wastewaters using Photo-Fenton-like advanced oxidation processes: optimization by response surface methodology, *J. Photochem. Photobiol., A*, 202 (2009) 142–153.
- [39] S. Garcia-Segura, L.C. Almeida, N. Bocchi, E. Brillas Solar photoelectro-Fenton degradation of the herbicide 4-chloro-2-methylphenoxyacetic acid optimized by response surface methodology, *J. Hazard. Mater.*, 194 (2011) 109–118.
- [40] H. Eskandarloo, A. Badiei, M.A. Behnajady, Application of response surface methodology for optimization of operational variables in photodegradation of phenazopyridine drug using TiO<sub>2</sub>/CeO<sub>2</sub> hybrid nanoparticles, *Desal. Wat. Treat.*, 54 (2015) 3300–3310.
- [41] H. Eskandarloo, A. Badiei, M.A. Behnajady, Optimization of UV/inorganic oxidants system efficiency for photooxidative removal of an azo textile dye, *Desal. Wat. Treat.*, 55 (2015) 210–226.
- [42] B. Gözmen, Ö. Sönmez, M. Turabık, Response surface methodology for oxidative degradation of the Basic Yellow 28 dye by temperature and ferrous ion activated persulfate, *Asian J. Chem.*, 25 (2013) 6831–6839.

- [43] M. Tanyol, Rapid malachite green removal from aqueous solution by natural zeolite: process optimization by response surface methodology, *Desal. Wat. Treat.*, 65 (2017) 294–303.
- [44] O. Tepe, Adsorption of Remazol Brilliant Green 6B (RBG 6B) on chitin: process optimization using response surface methodology, *Global NEST J.*, 20 (2018) 257–268.
- [45] M. Panizza, G. Cerisola, Electro-Fenton degradation of synthetic dyes, *Water Res.*, 43 (2009) 339–344.
- [46] M. Ahmadi, M.H. Ardakani, A.A. Zinatizadeh, Optimization and kinetic evaluation of Acid Blue 193 degradation by UV/peroxydisulfate oxidation using response surface methodology, *Adv. Environ. Technol.*, 2 (2015) 59–68.
- [47] M.R. Sohrabi, S. Amiri, H.R.F. Masoumi, M. Moghri, Optimization of Direct Yellow 12 dye removal by nanoscale zero-valent iron using response surface methodology, *J. Ind. Eng. Chem.*, 20 (2014) 2535–2542.
- [48] O. Tepe, A.Y. Dursun, Exo-pectinase production by *Bacillus pumilus* using different agricultural wastes and optimizing of medium components using response surface methodology, *Environ. Sci. Pollut. Res.*, 21 (2014) 9911–9920.
- [49] S. Agarwal, I. Tyagi, V.K. Gupta, A.R. Bagheri, M. Ghaedi, A. Asfaram, S. Hajati, A.A. Bazrafshan, Rapid adsorption of ternary dye pollutants onto copper (I) oxide nanoparticle loaded on activated carbon: experimental optimization via response surface methodology, *J. Environ. Chem. Eng.*, 4 (2016) 1769–1779.
- [50] A.R. Khataee, Application of central composite design for the optimization of photodestruction of a textile dye using UV/ $S_2O_8^{2-}$  process, *Pol. J. Chem. Technol.*, 11 (2009) 38–45.
- [51] A.R. Khataee, Optimization of UV-promoted peroxydisulphate oxidation of C.I. Basic Blue 3 using response surface methodology, *Environ. Technol.*, 31 (2010) 73–86.
- [52] I. Peternel, I. Grcic, N. Koprivanac, Degradation of reactive azo dye by UV/peroxodisulfate system: an experimental design approach, *React. Kinet. Mech. Catal.*, 100 (2010) 33–44.
- [53] J. Sharma, I.M. Mishra, V. Kumar, Degradation and mineralization of Bisphenol A (BPA) in aqueous solution using advanced oxidation processes: UV/ $H_2O_2$  and UV/ $S_2O_8^{2-}$  oxidation systems, *J. Environ. Manage.*, 156 (2015) 266–275.
- [54] H. Zhou, Y. Shen, P. Lv, J. Wang, J. Fan, Degradation of 1-butyl-3-methylimidazolium chloride ionic liquid by ultrasound and zero-valent iron/activated carbon, *Sep. Purif. Technol.*, 104 (2013) 208–213.
- [55] X.-R. Xu, X.-Z. Li, Degradation of azo dye Orange G in aqueous solutions by persulfate with ferrous ion, *Sep. Purif. Technol.*, 72 (2010) 105–111.