



## Determination of optimum conditions for color and COD removal of Reactive Blue 19 by Fenton oxidation process

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### ABSTRACT

In this study, Taguchi method was used to determine the optimum parametric conditions such as initial pH,  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  concentrations, initial dye concentration, slow mixing rate (SMR) and rapid mixing rate (RMR) for Fenton oxidation process performance. The main objective of the study is to provide maximum color and chemical oxygen demand (COD) removals by using optimal levels for Fenton reaction parameters. The orthogonal array  $L_{25}$  was selected as experimental matrix to determine of the optimum parametric levels. It was also, the contribution ratios of each factor were determined by the analysis of variance analysis, separately. Thus, the most effective parameter manages to the process was determined in terms of color and COD removals. Consequently, the optimum color removal conditions for the initial pH,  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  concentrations, initial dye concentration, SMR and RMR are 3, 500 mg/l, 150 mg/l, 250 mg/l, 60 rpm, 90 rpm, respectively, and 3, 400 mg/l, 150 mg/l, 250 mg/l, 60 rpm and 15 rpm for the initial pH,  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  concentrations, initial dye concentration, SMR and RMR to the COD removal, respectively. Under these optimum conditions, 98.90% color and 100% COD removals were achieved by Fenton oxidation process.

*Keywords:* Fenton oxidation; Reactive Blue 19; COD removal; Color removal; Taguchi; Optimization

### 1. Introduction

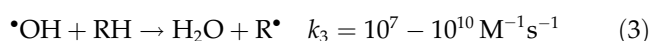
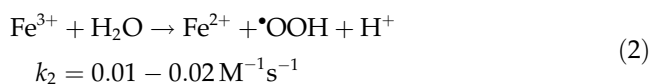
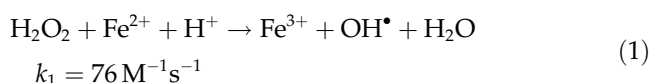
Synthetic dyes are widely used in textile, cosmetics, paper, food, leather, plastic and printing industries because of their fastness and their colors in variety compared to natural dyes. There are more than 100,000 dyes and the annual production of synthetic dyes is approximately one million tons [1]. Among them, the reactive azo dyes are highly recalcitrant to conventional wastewater treatment processes.

In fact, as much as 90% of reactive dyes can remain unaffected after activated sludge treatment [2]. Also, these dye wastewaters are characterized by a high color and chemical oxygen demand (COD) content with pH ranging from 2 to 12 [3]. Many synthetic dyes and their degradation by-products pose a threat to ecosystems due to the wide range of hazardous properties [4]. There are numerous methods to treat dye wastewater, such as physical adsorption, electrochemical oxidation, chemical oxidation,

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chemical coagulation/precipitation, and biological anaerobic/aerobic decomposition [5,6].

Recently, advanced oxidation processes (AOPs) have been widely used to remove toxic and persistent pollutants [7]. Fenton's oxidation is one of these AOPs with high efficiency and low capital costs. It is a mixture of  $H_2O_2$  and ferrous salts, and capable of generating aggressive hydroxyl radicals at ambient temperature. The generated radicals are able to oxidize a wide range of chemicals in aquatic medium, theoretically all organic compounds containing hydrogen (RH) [8]. In the Fenton process, the hydroxyl radical ( $\bullet OH$ ) is easily produced by the iron (II) catalyst and hydrogen peroxide ( $H_2O_2$ ) as follows [6,7]:



The regeneration of Fe(III) to Fe(II) through the reduction by  $H_2O_2$  or  $HO_2$  formed from  $H_2O_2$  also occurs in this reaction system. Therefore, as long as  $H_2O_2$  is available, the redox cycle of iron ions is basically continuous between Fe(II) and Fe(III), thus forming a hydroxyl radical. It is essential to promote this cycle in order to degrade organic compounds efficiently [9]. The Fenton's reagent has not only advantages of both oxidation and coagulation processes, but it can also increase the oxygen level in the water by the process time. As a result, Fenton process could provide effective color removal for all dye wastewater. At the same time, hydrogen peroxide is a widely used pretreatment reagent in dying process and so, the method is economically more advantageous in the treatment of this type of wastewater than others [10].

There are several parameters which have major effects on the Fenton process performance such as, pH,  $Fe^{2+}$  and  $H_2O_2$  concentrations, wastewater concentration, reaction temperature etc. [11–14]. It is essential to optimize the process conditions for an effective Fenton process performance as well as in many processes. Classical optimization techniques is based on changing one independent factor at a time

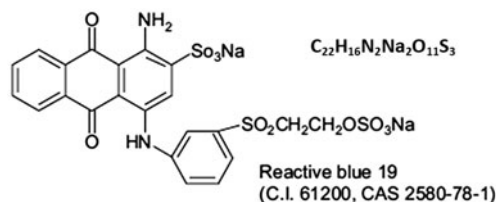


Fig. 1. Color index number, chemical formula, and chemical structures of RB 19.

keeping all others remain constant, which enables to assess the impact of those particular parameters on the process performance. Classical procedures are time consuming and impractical, and require more experiment and cannot provide information about the mutual interactions of the parameters [15].

The Taguchi method of orthogonal array (OA) consists of a set of independent variables (factors) over a specific section of interest (levels). The application of Taguchi method provided a number of conditions depending on the level assigned to each factor, leading to a successful optimization [16].

The scope of this study is the methodological application of Taguchi DOE for optimization of Fenton process variables for color and COD removal from the synthetic dye solution (Reactive Blue 19). In this experiment, six important influencing factors of Fenton process performance such as pH,  $Fe^{2+}$  and  $H_2O_2$  concentrations, dye concentration, slow mixing rate (SMR) and rapid mixing time (RMR) have been optimized.

## 2. Materials and methods

### 2.1. Reagents

Commercially available Reactive Blue 19 (RB 19) dye was obtained from Sirma Chemistry manufacturing company (Istanbul in Turkey) and used without further purification. The color index number, commercial name, and chemical structure of the dyestuff are shown in Fig. 1 and their characteristics are explained in detail in Table 1. Distilled water was used to

Table 1  
Main characteristics of RB 19

Parameters	Value
pH	6.15
<sup>a</sup> COD (mg/L)	88.89
<sup>b</sup> Conductivity ( $\mu S/cm$ )	47.8
<sup>a</sup> Color (abs)	1.336
$\lambda_{max}$ (nm)	610

<sup>a</sup>100 mg/L dye concentration.

<sup>b</sup>1000 mg/L dye concentration, 20.8 °C.

Notes:  $\lambda_{max}$ : wavelength at maximum absorbance.

prepare the desired concentration of dyestuff solutions.  $\text{H}_2\text{O}_2$  (Merck, 30% w/w) and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (Merck) were prepared at a pre-determined concentration in Fenton's oxidation process. The pH of the sample was adjusted to desired pH value (2.0–6.0) using 1 N  $\text{H}_2\text{SO}_4$  and 1 N NaOH.

### 2.2. Analytical methods

COD was measured spectrophotometrically according to Standard Methods (2120 C. Spectrophotometric Method) by APHA, AWWA, and WEF [17]. All optimization experiments (i.e. pH, coagulant dosage) of textile wastewater were carried out with jar test apparatus (Velp VC6S). The residual  $\text{H}_2\text{O}_2$  concentration was measured with  $\text{H}_2\text{O}_2$  test strips in this study. According to Talinli and Anderson, the residual  $\text{H}_2\text{O}_2$  in the Fenton process can consume  $\text{K}_2\text{Cr}_2\text{O}_7$  and lead to increase of COD [18]. Accordingly, Kang et al. and Meriç et al. reported that 1 mg/L  $\text{H}_2\text{O}_2$  is equal to 0.43 mg/l COD [19,20]. So, the same correction value was used in our study. A spectrophotometer (Hach Lange DR2500) was employed to measure color value of the dyestuff. The wavelength at maximum absorbance of dye wastewater was determined as 610 nm by spectrum scanning between 300 and 800 nm. The pH was measured with a multi parameter (Hach-Lange HQ40D). All experiments were performed in duplicate.

### 2.3. Fenton process procedure

The Fenton process experiments were conducted by jar test according to Kang et al. and Kuo's methods

with some modifications [19,21]. The Fenton process experiments were carried out at ambient temperature and the process procedure consisting of the following steps;

- Preparation of dye wastewater at different concentrations
- Adjusting the initial pH to the pre-determined values according to the Taguchi DOE
- Addition of pre-determined amounts of iron and hydrogen
- 2 min rapid mixing and then 20 min slow mixing at the pre-determined rates.
- Settling for 1 h
- Readjusting of the supernatant pH up to 7.5
- Finally, supernatant centrifuge for 10 min at 4,000 rpm for COD and color analyses.

Color and COD removal efficiencies were calculated according to Eq. (6);

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

Here,  $A_o$  is the initial COD or color value before being treated and  $A_f$  is the final COD or color value after being treated for the dye solution.

A statistical analysis of the data of dye wastewater treatment efficiency and the optimum operating conditions obtained from the peer reviewed publications on applications of the Fenton process to treatment of dye wastewater are presented in Table 2.

Table 2  
Fenton process applications in the literature

Reference	Dye	pH	T (°C)	Mixing time (min)	$\frac{\text{Fe}^{2+}}{\text{H}_2\text{O}_2}$ (Molar ratio)	COD (%)	Color (%)
[22]	Reactive Blue 114	3	20	20	0.1	–	86
[24]	Reactive Yellow 3	3	23	90	0.025	78 (TOC)	95
	Reactive Blue 2						
	Reactive Violet 2						
[23]	Reactive Blue 4	3	20	30	0.2	30	93
[25]	Reactive Black 5	3	–	30	0.18	63	>99
	Reactive Blue 3					89	
[21]	Reactive dyes	3.5	50	30	0.42	88	97
[26]	Reactive Red	5	20	–	0.10	54.2	91.2
	Reactive Yellow	4	20	–	0.08	52.6	18.1
[27]	Reactive Black 5	3	–	30	0.2	21.6 (TOC)	97.5
[19]	R94H reactive dye	4	–	5	0.25		95
[28]	Reactive Yellow 84	3	–	30	0.37	70–80.3	92–95.8
	Reactive Blue 49				0.2		
[29]	Reactive Black 5	3	40	20	0.25	71	99

Note: – No data.

Table 3  
The effective parameters on Fenton process performance

Factors	Levels				
	1	2	3	4	5
A: Initial pH	2	3	4	5	6
B: Initial dye concentration (C <sub>0</sub> ) (mg/l)	100	200	300	400	500
C: Reagent dosage (mg Fe <sup>2+</sup> /l)	0	150	250	300	500
D: Reagent dosage (mg H <sub>2</sub> O <sub>2</sub> /l)	0	150	250	300	500
E: Rapid mixing rate (RMR)	60	90	120	150	200
F: Slow mixing rate (SMR)	15	30	45	60	90

The literature survey extracts information from some of the literature available about effective factors on the system performance such as initial pH, dye concentration, rapid mixing rate, SMR, Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> concentrations, and their levels were chosen in this study and given in the Table 3.

#### 2.4. Statistical analysis

To simplify and standardize experimental design and to minimize the number of factor combinations required to test the factor effects, the Taguchi method uses a special design of orthogonal arrays to study the entire factor space with only a small number of experiments [30]. In this study, MINITAB release 13.20 computer software package was used to establish experimental matrix according to parameters and its levels, and, evaluation by analysis of variance (ANOVA) analysis of the obtained results. In this regard, The Fenton oxidation experiments were performed according to the L<sub>25</sub> OA due to the best fitted design for six factors and five levels. All experiments were carried out as shown in experimental plan in Table 4.

Taguchi recommends analyzing the mean response for each run in the inner array and analyzing the variation using an appropriately chosen signal-to-noise ratio (S/N), which is derived from a quadratic loss function and can be calculated by Eq. (7) [31]:

Table 4  
Experimental design for Fenton process according to L<sub>25</sub> OA

Exp. no	Parameters and levels						Color removal (%)			COD removal (%)		
	A	B	C	D	E	F	I	II	Aver.	I	II	Aver.
1	1	1	1	1	1	1	15.89	16.09	15.99	16.41	7.97	12.19
2	1	2	2	2	2	2	74.09	73.36	73.72	33.96	47.96	40.96
3	1	3	3	3	3	3	71.08	80.88	75.98	48.91	48.19	48.55
4	1	4	4	4	4	4	73.85	77.77	75.81	48.03	48.72	48.38
5	1	5	5	5	5	5	93.44	92.34	92.89	49.66	51.67	50.67
6	2	1	2	3	4	5	21.37	29.47	25.42	9.02	10.63	9.82
7	2	2	3	4	5	1	38.50	41.39	39.95	44.13	41.88	43.00
8	2	3	4	5	1	2	99.42	99.48	99.45	98.19	96.07	97.13
9	2	4	5	1	2	3	99.68	99.68	99.68	87.42	88.68	88.05
10	2	5	1	2	3	4	89.92	90.52	90.22	15.74	20.02	17.88
11	3	1	3	5	2	4	8.74	9.18	8.96	5.08	0.00	2.54
12	3	2	4	1	3	5	97.13	96.89	97.01	81.68	85.79	83.73
13	3	3	5	2	4	1	97.89	97.26	97.57	84.71	87.14	85.92
14	3	4	1	3	5	2	74.29	48.81	61.55	52.85	52.52	52.68
15	3	5	2	4	1	3	97.48	97.93	97.70	91.85	94.05	92.95
16	4	1	4	2	5	3	3.12	4.75	3.94	0.00	0.00	0.00
17	4	2	5	3	1	4	99.43	99.42	99.43	91.21	84.22	87.72
18	4	3	1	4	2	5	85.20	88.95	87.08	60.00	63.81	61.90
19	4	4	2	5	3	1	98.28	98.88	98.58	59.88	58.34	59.11
20	4	5	3	1	4	2	96.12	96.09	96.10	77.06	73.97	75.51
21	5	1	5	4	3	2	2.37	4.14	3.26	0.00	0.00	0.00
22	5	2	1	5	4	3	35.85	40.41	38.13	18.72	19.00	18.86
23	5	3	2	1	5	4	40.28	38.54	39.41	23.99	22.66	23.32
24	5	4	3	2	1	5	99.14	99.14	99.14	57.72	57.88	57.80
25	5	5	4	3	2	1	98.46	99.11	98.79	80.48	82.54	81.51

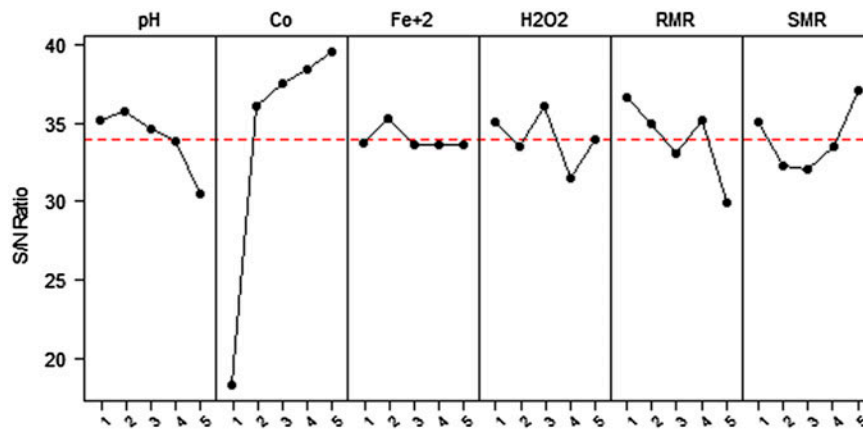


Fig. 2. Main effects of experimental parameters on the  $S/N$  ratio for color removal.

$$SNL = -10 \text{Log}_{10} \left( \frac{1}{n} \sum_{i=1}^n \frac{1}{Y_i^2} \right) \quad (7)$$

Here, SNL is performance characteristic,  $n$  is the number of repetitions done for an experimental combination and  $Y_i$  is the performance value of the  $i$ th experiment. In the Taguchi method, the experiment corresponding to optimum working conditions might not have been done during the whole period of the experimental stage [32]. The “larger the better” response is considered with the aim to maximize the removal [31].

It is expressed in Eq. (8) that the performance value corresponding to the optimum working conditions can be predicted by utilizing the balanced characteristic of OA [33].

$$Y_i = m + X_i + e_i \quad (8)$$

Here,  $m$  is the overall mean of performance value,  $X_i$  is the fixed effect of the parameter level combination used in the  $i$ th experiment and  $e_i$  is the random error in the  $i$ th experiment [33].

If the experimental results are in percentages, the omega transformation of the percentage values expressed in Eq. (9) should be used before calculating and then the relevant values are obtained by the reverse transformation as described by Taguchi [34]:

$$\Omega(\text{db}) = -10 \text{Log} \left( \frac{1}{p} - 1 \right) \quad (9)$$

Here, the term of  $\Omega$  (db) is decibel value of percentage value subject to omega transformation and “ $p$ ” indicates the percent value ( $0 < p < 1$ ) [35].

### 3. Results and discussion

#### 3.1. Taguchi results

The color and COD removal experiments of synthetic dye solutions were performed using Fenton process according to the design of experiments based on Taguchi method. In order to evaluate the influence of each factor on color and COD removal, the  $S/N$  ratios for each factor should be computed. The  $S/N$  ratio for a single factor can be calculated by averaging the value of  $S/N$  ratios at different levels. The mean  $S/N$  ratio for every factor was calculated and plotted in a graphical form. The peak points in these plots correspond to the optimum condition. The optimum conditions for color and COD removal for Fenton process are shown in Figs. 2 and 3, respectively.

As seen from Figs. 2 and 3, the factor of  $C_0$  has the biggest variation around the mean  $S/N$  value, that is, it can be said that  $C_0$  is the system controlling factor for both color and COD removals.

##### 3.1.1. Effect of pH

To determine optimum removal efficiencies of dye solution with the initial pH of 2.0, 3.0, 4.0, 5.0 and 6.0 were chosen in the  $L_{25}$  design. Figs. 2 and 3 show that optimum pH value for the best color and COD removals by Fenton process are second level (pH 3). It is known that suitable pH value is 3 for Fenton reactions [22,36–38]. In the Fig. 4 the pH variations can be seen depending on different experimental conditions.

It is also seen from the Figs. 2 and 3, when the initial pH is increased,  $S/N$  ratio (removal percentages) is decreased. The reason for this, ferrous ions are unstable at higher pH values, and also, hydrogen peroxide tends to decompose to give oxygen and water in the basic solutions and loss their oxidation capacity

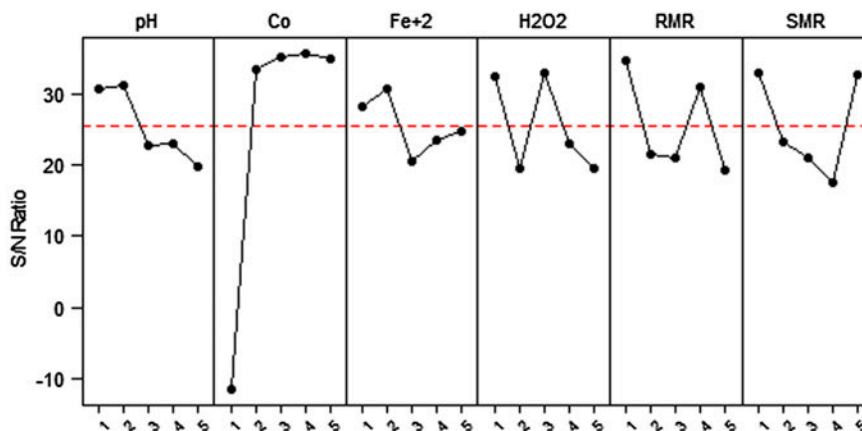


Fig. 3. Main effects of experimental parameters on the S/N ratio for COD removal.

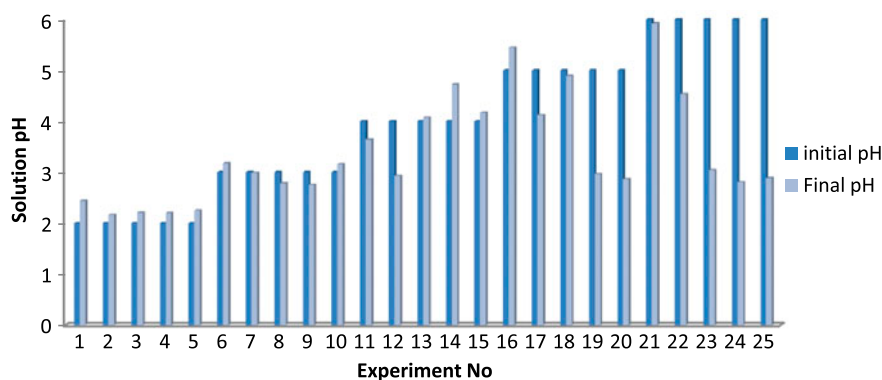


Fig. 4. The variations in the solution pH at different experimental conditions.

[21]. According to Ma and Xa, it is worth noting that on the basis of their results, COD removal decreases slightly at pH 4 because of the increasing rate of autodecomposition of H<sub>2</sub>O<sub>2</sub>, deactivation of iron ion into iron oxyhydroxides, the increased scavenging effect of HO<sup>•</sup> resulting in the decreased oxidation potential of HO<sup>•</sup> [39].

### 3.1.2. Effect of initial dye concentration

The investigated second parameter is initial dye concentration (C<sub>0</sub>) with effect on color and COD removal. In order to investigate the effect of C<sub>0</sub> on the dye degradation rate, the C<sub>0</sub> value varied from 100 to 500 mg/L. As shown in Fig. 2, color removal increases with increasing C<sub>0</sub> values. On the other hand, COD removal increased up to 3rd parametric level (300 mg/l), and then almost remained stable according to Fig. 3. Chang et al. reported that high dye concentrations are beneficial to allow more dye molecules reacting with the hydroxyl radicals in accordance with the Eq. (10) [40]:



Conversely, too high dye concentrations may affect oxidation efficiencies negatively and so, oxidation efficiency decreased as the initial dye concentration increased [40].

### 3.1.3. Effect of Fe<sup>2+</sup> concentration

The third parameter investigated in the scope of the study is the effect of Fe<sup>2+</sup>. It is known that Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> molar ratio is an important parameter in Fenton's reactions because it directly influences the yield of HO<sup>•</sup> generation [41]. In the Figs. 2 and 3, it is shown that 150 mg Fe<sup>2+</sup>/l (2nd level) is the optimum concentration for both color and COD removal. In higher concentration of Fe<sup>2+</sup>, removal efficiencies decreased and remained stable. Fe<sup>2+</sup> ions provide the rapid decomposition of H<sub>2</sub>O<sub>2</sub> to form HO<sup>•</sup>. This is because use of as many Fe<sup>2+</sup> ions as possible would initially be considered advantageous. Conversely, in case of using excessive amount of Fe<sup>2+</sup> ions, they have

tendency of scavenge effect on generated HO• ions [7,42]. Therefore, increasing the concentration of ferrous ions may not result in increase as expected in the removal of COD and color from the wastewater [7].

### 3.1.4. Effect of H<sub>2</sub>O<sub>2</sub> concentration

Another parameter effective on Fenton process is H<sub>2</sub>O<sub>2</sub> concentration. Experiments were conducted at different concentrations varying from 0 to 500 mg H<sub>2</sub>O<sub>2</sub>/l to determine optimum concentration. As shown in Figs. 2 and 3, it is clearly seen that third parametric level is optimum for both color and COD removal. At higher concentrations, removal efficiencies decreased. Medien and Khalil explained this situation by the fact that H<sub>2</sub>O<sub>2</sub> decomposes into O<sub>2</sub> and H<sub>2</sub>O. As a result, a rapid increase in solution temperature, decreases the oxidative power of the Fenton reagent because of dramatic fall in the concentration of H<sub>2</sub>O<sub>2</sub> [43]. On the other hand, addition of H<sub>2</sub>O<sub>2</sub> higher than optimal Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> molar ratio may cause interference with the measurement of COD. The residual H<sub>2</sub>O<sub>2</sub> in the solution reacts with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, and finally causes increase in inorganic COD [18,19].

### 3.1.5. Effects of mixing rates

If the optimum levels for SMR and RMR are evaluated according to the Figs. 2 and 3, it can be seen that best color and COD removal efficiencies were obtained at minimum parametric levels for RMR (the 1st parametric level). The results can be explained as follows; floc size was inversely proportional to the hydraulic gradient. Generally, the floc size decreases with the average hydraulic gradient (*G*). Increased floc size is a result of the increased floc strength. This is because floc size is a balance between growth and breakage [44]. Likewise, the best COD removal result was obtained at the 1st parametric level for SMR, but different from this, the 5th parametric level provided the best color removal efficiency for SMR.

### 3.2. ANOVA results and contribution ratios

Using statistical ANOVA could be seen whether the process parameters were statistically significant or not. Beside this, the effects of process parameters on the removal efficiencies can be evaluated by the *F*-test. The *F*-value for each process parameter is simply a ratio of mean of the squared deviations to the mean of squared error. Generally, the higher *F* values means that the greater the effect on the performance criteria value due to the change of the process parameter.

Table 5

Results of the analysis of variance for the color removal efficiencies

Source	DF	Seq SS	Adj MS	<i>F</i>
pH	4	2603.5	650.9	36.9
C <sub>o</sub>	4	44290.7	11072.7	627.66
Fe <sup>2+</sup>	4	2639.7	659.9	37.41
H <sub>2</sub> O <sub>2</sub>	4	954.2	238.6	13.52
RMR	4	6810.1	1702.5	96.51
SMR	4	2071.7	517.9	29.36
Error	25	441	17.6	
Total	49	59810.9		

With the performance characteristics and ANOVA analyses, the optimal combination of process parameters can be predicted [45]. The results of variance analysis are given in Tables 5 and 6.

When the *F* values are evaluated, it can be seen that the highest *F* value is belongs to C<sub>o</sub>. Accordingly, the most effective parameter is C<sub>o</sub> in this system. If the other parameters are ordered in terms of their *F* values, the ranking is RMR > Fe<sup>2+</sup> > pH > SMR > H<sub>2</sub>O<sub>2</sub> for both color and COD removals, respectively.

Quantitative evaluation can be achieved using percentage contribution (P%) [46]. It is calculated by dividing the source's net variation by SS<sub>T</sub>, which is given as follows (Eq. (11)):

$$P (\%) = \frac{SS_A - (DF \times MS_e)}{SS_T} \times 100 \quad (11)$$

Here, the term SS<sub>A</sub> is the sum of square value of the parameter, DF is the degree of freedom, MS<sub>e</sub> is the error of mean of square value and SS<sub>T</sub> is the total of sum of square value. The contribution ratios for all factors for color and COD removals are given in Figs. 5 and 6, respectively.

Table 6

Results of the analysis of variance for the COD removal efficiencies

Source	DF	Seq SS	Adj MS	<i>F</i>
pH	4	5162.3	1290.6	146.93
C <sub>o</sub>	4	25464.9	6366.2	724.77
Fe <sup>2+</sup>	4	6450.1	1612.5	183.58
H <sub>2</sub> O <sub>2</sub>	4	1882.8	470.7	53.59
RMR	4	7360.4	1840.1	209.49
SMR	4	2549.7	637.4	72.57
Error	25	219.6	8.8	
Total	49	49089.8		

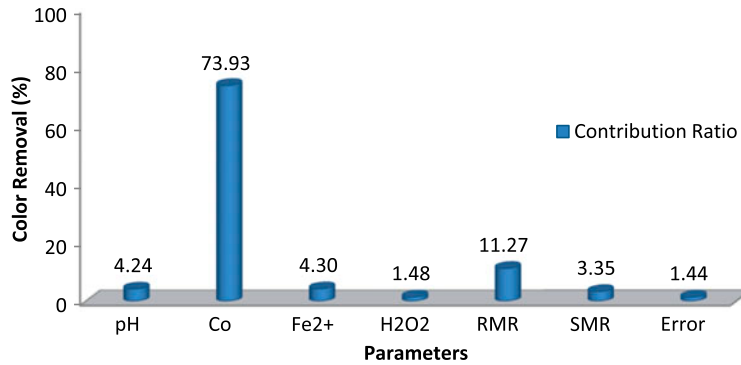


Fig. 5. The contribution ratios of each factor for color removal.

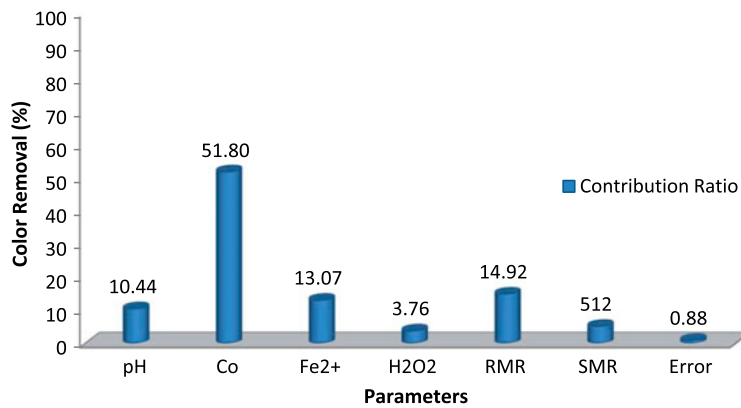


Fig. 6. The contribution ratios of each factor for COD removal.

The contribution ratios show the effect sizes of each factor as numerical. Hereunder, the  $C_o$  is the control parameter of Fenton oxidation system due to having the largest contribution ratio. This means, the system can be largely controllable by the  $C_o$  parameters to remove both color and COD. On the other hand, percent margins of error can be seen in Figs. 5 and 6, also. However, small percentages mean that errors are insignificant for the system.

### 3.3. Confirmation test

After determination of the optimum conditions of each factor, the final step is to predict and verify the improvement using the optimum removal conditions. The prediction error is the difference between the observed  $Y_i$  and the predicted  $\hat{Y}_i$ . The confidence interval calculation is as follows [47];

$$Se = \pm 2 \sqrt{\left[ \frac{1}{n_0} \right] \sigma_e^2 + \left[ \frac{1}{n_r} \right] \sigma_e^2} \quad (12)$$

$$\sigma_e^2 = \frac{\text{sum of squares due to error}}{\text{degrees of freedom for error}} \quad (13)$$

$$\frac{1}{n_0} = \frac{1}{n} + \left[ \frac{1}{n_{A_i}} - \frac{1}{n} \right] + \left[ \frac{1}{n_{B_i}} - \frac{1}{n} \right] + \left[ \frac{1}{n_{C_i}} - \frac{1}{n} \right] \dots \quad (14)$$

Here,  $S_e$  is the two-standard deviation confidence limit,  $n$  is the number of rows in the matrix experiment,  $n_r$  is the number of repetitions in the confirmation experiment and  $n_{A_i}$ ,  $n_{B_i}$ ,  $n_{C_i}$ , ... are the replication numbers for the parameter levels  $A_i$ ,  $B_i$ ,  $C_i$ , ... If the prediction error is outside these limits, the possibility that the additive model is not adequate should be suspected [47].

The confirmation test shows that experimentally obtained results are within the confidence intervals (Table 7), namely, the Taguchi method can be applied successfully with “5% error” for the determination of optimum color and COD removal by Fenton oxidation process.



Table 7

Optimum experimental conditions, predicted and observed removal efficiency values

		Parameters						Predicted	Observed	Confidence interval
		A	B	C	D	E	F			
Color removal	Level	2	5	2	3	1	5	99.87	98.90	87.71–100
	Value	3	500	150	250	60	90			
COD removal	Level	2	4	2	3	1	1	99.49	100.00	93.27–100
	Value	3	400	150	250	60	15			

#### 4. Conclusions

In this study, optimum conditions of Fenton oxidation process were determined by Taguchi method. The selected parameters are the initial pH,  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  concentrations, initial dye concentration, SMR and rapid mixing time (RMR). The following results can be concluded from the present work.

- The most effective parameter on Fenton process performance in terms of both color and COD removals is the initial dye concentration ( $C_0$ ). The contribution ratios are 73.90 and 51.80% for the color and COD removals, respectively. That is, Fenton process performance can be controlled by the controlling of the initial dye concentration.
- The optimum color removal conditions for the initial pH,  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  concentrations, initial dye concentration, SMR and rapid mixing time (RMR) are 3, 500 mg/l, 150 mg/l, 250 mg/l, 60 rpm, 90 rpm, respectively.
- In a similar manner order made above, the optimum parametric values for the COD removal are 3, 400 mg/l, 150 mg/l, 250 mg/l, 60 rpm and 15 rpm for the initial pH,  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  concentrations, initial dye concentration, SMR and rapid mixing time (RMR), respectively.
- The interactive effects of parameters are negligible because the results of the confirmation experiments are in confidence interval and have proved that there is no need to perform all 7,776 experiments ( $6^5=7,776$ ) to optimize the system parameters affecting on both color and COD removal.
- In addition, another important parameter affecting the Fenton process performance is the  $\frac{\text{Fe}^{2+}}{\text{H}_2\text{O}_2}$  molar ratio which is determined as 0.15 for both color and COD removals at this optimum conditions. The obtained result is accordance with the literature (can be seen in Table 2).

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