A statistical experiment design approach for advanced oxidation of Direct Red azo-dye by photo-Fenton treatment

Filiz Ay, Ebru Cokay Catalkaya, Fikret Kargi *

Department of Environmental Engineering, Dokuz Eylul University, Buca, Izmir, Turkey

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ABSTRACT

Advanced oxidation of an azo-dye, Direct Red 28 (DR 28) by photo-Fenton treatment was investigated in batch experiments using Box–Behnken statistical experiment design and the response surface analysis. Dyestuff (DR 28), H_2O_2 and Fe(II) concentrations were selected as independent variables in Box–Behnken design while color and total organic carbon (TOC) removal (mineralization) were considered as the response functions. Color removal increased with increasing H_2O_2 and Fe(II) concentrations up to a certain level. High concentrations of H_2O_2 and Fe(II) adversely affected the color and TOC removals due to hydroxyl radical scavenging effects of high oxidant and catalyst concentrations. Both H_2O_2 and Fe(II) concentration had profound effects on decolorization. Percent color removal was higher than TOC removal indicating formation of colorless organic intermediates. Complete color removal was achieved within 5 min while complete mineralization took nearly 15 min. The optimal reagent doses varied depending on the initial dyestuff dose. For the highest dyestuff concentration tested, the optimal H_2O_2/Fe(II)/dyestuff ratio resulting in the maximum color removal (100%) was predicted to be 715/71/250 $(mg\,L^{-1})$, while this ratio was 1550/96.5/250 for maximum mineralization (97.5%).

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1. Introduction

Wastewaters from textile and dye industries are highly colored with considerable amount of auxiliary chemicals. Direct discharge of textile industry wastewater into the receiving media causes serious environmental pollution by imparting intensive color and toxicity to aquatic environment [1]. The azo-dyes, characterized by having an azo group consisting of two nitrogen atoms (N=N), are the largest class of dyes used in textile industry [2]. Azo-dyes have different forms such as direct, acid, base, reactive, disperse, metal-complexed, mordant and sulfur dyes [2]. Azo-dyes are the most problematic pollutants of textile wastewaters since more than 15% of the textile dyes end up in the wastewater stream [3].

Due to the complex aromatic structure and stability of the azo-dyes, conventional biological treatment methods are not very effective for dyestuff removal [4]. A number of physical, chemical and biological methods have been used for the treatment of dyestuff containing effluents [5–8]. Among the other methods, the advanced oxidation processes are more efficient and capable of mineralizing a wide range of organic pollutants. Photochemical oxidation methods such as the photo-Fenton have been given considerable attention in recent years for the treatment of recalcitrant wastewaters. Fenton reagent was reported to be effective for degradation of the refractory organic contaminants such as chlorophenols [9,10], chlorobenzene [11], nitrophenols [12] and dye pollutants [13,14]. Fenton reagent can completely decolorize and partially mineralize the textile dyes rather rapidly [15,16]. Most of the literature studies on Fenton treatment of dyestuffs are on color removal rather than mineralization or TOC removal.

Oxidation power of Fenton reagent is due to the generation of hydroxyl radicals (OH•) during the iron catalyzed decomposition of hydrogen peroxide in acid medium. The hydroxyl radicals with a high oxidation potential (2.8 V) can completely destroy the pollutants in Fenton reagent treatments. Degradation of pollutants can be considerably improved by using UV-radiation for the generation of additional hydroxyl radicals. Photo-Fenton treatment has been effectively used for degradation of recalcitrant pollutants [17,18]. However, the optimal operating conditions and reagent concentrations need to be determined in order to reduce the cost of photo-Fenton treatment and to improve the extent of dyestuff removal. The photolytic degradation of Basic Red 2 (BR2) via UV radiation in the presence of H_2O_2 was investigated by Körbahtı and Rauf using response surface methodology (RSM) [19]. The response function for the dyestuff degradation was very sensitive to the changes in dyestuff and H_2O_2 concentrations.

Biodegradation of the azo-dye, C.I. Reactive Red 120 by the TiO_2/UV treatment was studied by Il-Hyoung and Kyung-Duk [20].

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* Corresponding author. Tel.: +90 232 412 7109.
E-mail address: fikret.kargi@deu.edu.tr (F. Kargi).

A factorial design (2^3) approach was used for the optimization of degradation conditions for color and TOC removals. Amount of TiO_2 (X_1), dye concentration (X_2) and UV intensity (X_3) were considered as the independent variables. The maximum color and TOC removals at the optimal conditions were 100 and 67.27%, respectively.
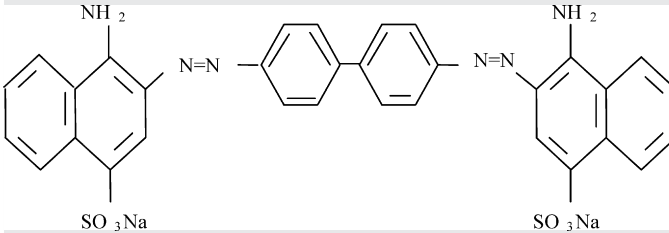
In the light of literature studies, the major objective of this study is to investigate the effects of reagent concentrations (initial dyestuff, H_2O_2 and Fe(II) concentrations) on dyestuff and TOC removal (mineralization) by the photo-Fenton treatment unlike literature studies reporting only color removal. A typical azo-dye, Direct Red 28 (DR 28) was used as the dyestuff in aqueous solution and both color and TOC removals were investigated at different reagent concentrations. Box–Behnken statistical experiment design and surface response methodology were used in the experimental study. Optimal reagent doses maximizing TOC and color removal were determined.

2. Design of experiments

The classical approach of changing one variable at a time to study the effects of variables on the objective or response functions is a time consuming method particularly for multivariable systems and also when more than one response is considered. Statistical design of experiments reduces the number of experiments to be performed, considers interactions among the variables and can be used for optimization of the operating parameters in multivariable systems. Response surface methodology is used when only several significant factors are involved in optimization. The main idea of RSM which is an efficient statistical technique for optimization of multiple variables with minimum number of experiments is to use a set of designed experiments to obtain an optimal response [21–23]. Different types of RSM designs include three-level factorial design, central composite design (CCD) [24], Box–Behnken [25] and D-optimal designs [26].

A modified central composite experimental design known as the Box–Behnken design is an independent, rotatable quadratic design with no embedded factorial or fractional factorial points where the variable combinations are at the midpoints of the edges of the variable space and at the center. Among all the RSM designs, Box–Behnken design requires fewer runs than the others (e.g., 15 runs for a three-parameter experimental design). A three-factor, three-level design would require a total of 30 runs with 3 repetitions for the central point. In statistical experiment designs, the ratio of the number of experiments to the number of coefficients in
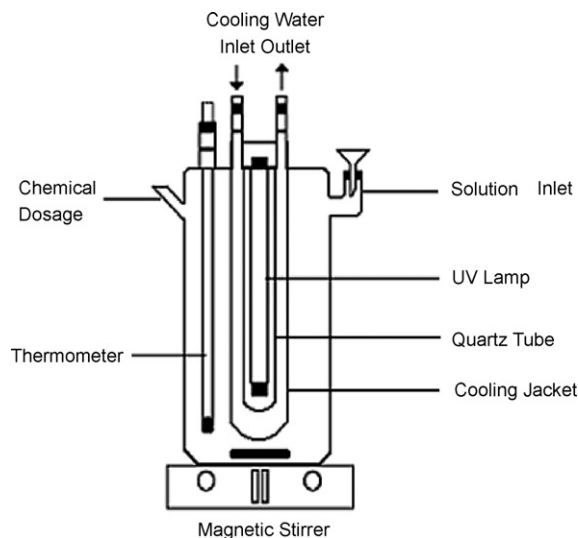

Fig. 1. Reactor used in photo-Fenton oxidations.

the quadratic model should be reasonable. In most of the experiment designs this ratio is within the range of 1.5–2.6 and is 1.67 for the Box–Behnken experiment design (BBD) with three variables. A comparison between the BBD and other response surface designs (central composite, Doehlert matrix and three-level full factorial design) has demonstrated that the BBD and Doehlert matrix are slightly more efficient than the central composite design, but much more efficient than the three-level full factorial designs [27]. By careful design and analysis of experiments, Box–Behnken design allows calculations of the response function at intermediate levels and enables estimation of the system performance at any experimental point within the range studied [28].

3. Materials and methods

3.1. Chemicals

The azo-dye (Direct Red 28, DR 28) was used in the experimental studies since it is a widely used textile dyestuff in Turkish textile industry. The dyestuff was obtained from the EKOTEN Textile Industry in Torbali, Izmir, Turkey. Characteristics of the DR 28 are presented in Table 1. Ferrous ($FeSO_4 \cdot 7H_2O$) used as source of Fe(II) was analytical grade and purchased from the Merck Co. (Germany). Hydrogen peroxide solution (30%, w/w) in stable form, H_2SO_4 (98–99%) and NaOH were all provided from the Merck. Concentrated stock solution of Fe(II) (5000 mg L^{-1}) was prepared for further use after dilutions and was stored at dark to prevent oxidation of Fe(II). The pH of aqueous solutions was adjusted using either dilute sodium hydroxide or sulfuric acid. All other chemicals were of analytical grade and used without further purification. Water used for reagent solutions was purified using a Mili-Q system (Milipore filtration).

3.2. Reactor configuration

Fig. 1 depicts a schematic diagram of the laboratory-scale photochemical reactor used in the experimental studies. All photo-oxidation experiments were performed in the completely mixed, cylindrical photo-reactor made of glass with a total volume of 2.2 L operated in batch mode. The reactor was covered with an aluminum foil to avoid any light leakage to the outside. The reactor was placed on a magnetic stirrer and contained ports for reagent addition,

Table 1
Characteristics of the azo-dye, Direct Red 28 (DR 28)

Direct Red 28	
Color index number	22120
Synonyms	Kongo Red
Molecular formula	$C_{32}H_{24}N_6O_6S_2$

Molecular weight (g mol^{-1})	696.67
λ_{max} (nm)	497
Purity (%)	~85

sample removal and temperature measurement. The UV irradiation source placed in a quartz tube was a 16 W low-pressure mercury vapor lamp with maximum emission at 254 nm. The intensity of the UV radiation was measured using the ferrioxalate actinometry method and found to be 4.98×10^{-6} Einstein s^{-1}. The lamp was surrounded with a water-cooling jacket to remove the heat and to maintain a constant temperature. The lamp tube was immersed in the reaction solution.

3.3. Experimental procedure

Photo-Fenton experiments were carried out at room temperature ($23 \pm 2\,^{\circ}$C) using different hydrogen peroxide and ferrous ion doses at the pH 3 which is reported to be a suitable pH for photo-Fenton treatment [29]. Dyestuff solution with desired concentration of the dyestuff ($10–250$ mg L^{-1}) was placed in the reactor and predetermined amounts of oxidant ($100–2000$ mg L^{-1} H$_2$O$_2$) and the catalyst ($0–100$ mg L^{-1} Fe(II)) were injected to the reactor at the beginning of each experiment. The iron salt was mixed well with the dyestuff solution before addition of hydrogen peroxide. Hydrogen peroxide and ferrous ion doses used in this study were within the ranges reported in literature.

Box–Behnken statistical experiment design and the RSM [30] were used to investigate the effects of the three independent variables on the response functions and to determine the optimal conditions maximizing the percent color and TOC removals. The optimization procedure involves studying the response of the statistically designed combinations, estimating the coefficients by fitting the experimental data to the response functions, predicting the response of the fitted model and checking the adequacy of the model. The independent variables were the dose of dyestuff (X_1), hydrogen peroxide (X_2), and ferrous ion (X_3). The low, center and high levels of each variable are designated as -1, 0, and $+1$, respectively, as shown in Table 2. The dependent variables (or objective functions) were the percent color (Y_1) and TOC (Y_2) removals.

3.4. Analytical methods

Samples withdrawn from the reactor at certain time intervals were analyzed immediately to avoid further reactions. Samples (20 ml) of raw and treated dyestuff solutions were analyzed for TOC and color intensity after centrifugation. pH levels were also recorded. Color and TOC analysis were carried out immediately in order to avoid hydrogen peroxide interference.

A pH meter (WTW Scientific, Germany) was used to monitor the pH. A spectrophotometer of Novaspec II (Pharmacia Biotech.) was used to measure the absorbance at 497 nm which was the wavelength for the maximum absorbance of DR 28. A DOHRMAN DC 190 TOC Analyzer (USA) was used to determine the total organic carbon (TOC) content of the samples. For the TOC measurements, potassium phthalate solution was used as the calibration standard with the concentrations between 0 and 200 mg L^{-1}.

Table 2
The levels of variables in Box–Behnken statistical experiment design

Variable	Symbol	Coded variable level		
		Low	Center	High
		-1	0	$+1$
Dyestuff dose (mg L^{-1})	X_1	10	130	250
Hydrogen peroxide dose (mg L^{-1})	X_2	100	1050	2000
Ferrous ion dose (mg L^{-1})	X_3	0	50	100

4. Results and discussion

The values of the dependent and independent variables and the experimental data are presented in Table 3 for every experiment. The center point (0, 0, 0) was repeated three times and nearly the same results were obtained indicating the reproducibility of the data. The observed and predicted percent removals for color and TOC are compared in Table 4.

4.1. The response function coefficients

The application of RSM offers an empirical relationship between the response function and the independent variables. The mathematical relationship between the response function (Y) and the independent variables (X) can be approximated by a quadratic polynomial equation as follows:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3$$
$$+ b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \tag{1}$$

The coefficients of the response functions for different dependent variables were determined correlating the experimental results with the response functions by using a Stat-Ease Design Expert 7.0 regression program. The response functions with the determined coefficients for percent color (Y_1) and TOC (Y_2) removals are presented by Eqs. (2) and (3).

$$Y_1 = 38.99 - 0.14X_1 + 0.014X_2 + 1.90X_3 + 1.67 \times 10^{-5}X_1X_2$$
$$+ 1.72 \times 10^{-3}X_1X_3 - 1.66 \times 10^{-4}X_2X_3 - 7.03 \times 10^{-6}X_1^2$$
$$- 2.27 \times 10^{-6}X_2^2 - 0.013X_3^2 \quad (R^2 = 0.98) \tag{2}$$

$$Y_2 = -33.62 + 0.41X_1 + 0.029X_2 + 2.19X_3 - 5.78 \times 10^{-5}X_1X_2$$
$$+ 1.16 \times 10^{-5}X_1X_3 - 5.09 \times 10^{-5}X_2X_3 - 1.05 \times 10^{-3}X_1^2$$
$$- 6.77 \times 10^{-6}X_2^2 - 0.015\,X_3^2 \quad (R^2 = 0.98) \tag{3}$$

On the basis of the coefficients in Eqs. (2) and (3), it can be said that percent color removal decreases with the dyestuff concentration (X_1) while increasing with peroxide (X_2) and Fe(II) (X_3) doses. Fe(II) dose has a more profound effect on decolorization as compared to peroxide. TOC removal or percent mineralization increases with the dyestuff, peroxide and Fe(II) doses with a more profound effect by the Fe(II) dose.

The analysis of variance (ANOVA) tests were also conducted for each response and presented in Tables 5 and 6 indicating the fact that the predictability of the model is at 95% confidence level. Response function predictions were in good agreement with the experimental data ($R^2 > 0.99$). The variables for which the computed F-values were much greater than that of the tabulated $F_{0.01(14,14)}$-value of 3.70 had significant effect on the response function. The F-test in the ANOVA analysis is used for comparing model variance with residual (error) variance. If the variances are almost the same, the ratio will be nearly one indicating that it is less likely any of the factors have a significant effect on the response. If the Prob > F-value is very small (less than 0.05) then lack of fit is significant. P-values in the test indicate probability of seeing the observed F-value if the null hypothesis is true. Small probability values call for rejection of the null hypothesis.

Table 3
Results of the Box–Behnken experiments

Run number	Actual and coded levels of variables			Experimental percent removals	
	X_1, Dye (mg L^{-1})	X_2, H$_2$O$_2$ (mg L^{-1})	X_3, Fe(II) (mg L^{-1})	Y_1, color	Y_2, TOC
1	−1 (10)	−1 (100)	0 (50)	98.86	39.45
2	1 (250)	−1 (100)	0 (50)	95.48	90.52
3	−1 (10)	1 (2000)	0 (50)	95.63	65.52
4	1 (250)	1 (2000)	0 (50)	99.88	90.21
5	−1 (10)	0 (1050)	−1 (0)	55.00	0.00
6	1 (250)	0 (1050)	−1 (0)	15.20	11.00
7	−1 (10)	0 (1050)	1 (100)	98.14	53.25
8	1 (250)	0 (1050)	1 (100)	99.72	92.17
9	0 (130)	−1 (100)	−1 (0)	19.34	1.54
10	0 (130)	1 (2000)	−1 (0)	46.24	11.00
11	0 (130)	−1 (100)	1 (100)	99.70	90.21
12	0 (130)	1 (2000)	1 (100)	95.00	90.00
13	0 (130)	0 (1050)	0 (50)	99.61	92.82
14	0 (130)	0 (1050)	0 (50)	99.61	92.82
15	0 (130)	0 (1050)	0 (50)	99.61	92.82

4.2. Color removal

Color removal is related to removal of color imparting functional groups from the dyestuff (i.e., removal of azo-groups), but not necessarily complete degradation or mineralization of the dyestuff. Response functions with determined coefficients were used to estimate variations of color and TOC removals with the independent variables under different conditions.

Fig. 2 shows the effect of initial H$_2$O$_2$ concentration on percent color removal at different dye concentrations after 5 min of reaction time when Fe(II) was 37 mg L^{-1}. Percent color removal

Table 4
Comparison of the observed and predicted color and TOC removals

Run number	Predicted percent removals		Observed percent removals	
	Y_1, Color	Y_2, TOC	Y_1, Color	Y_2, TOC
1	100.00	44.74	98.86	39.45
2	87.97	89.35	95.48	90.52
3	100.00	66.69	95.63	65.52
4	97.62	84.92	99.88	90.21
5	49.93	0.00	55.00	0.00
6	19.90	10.07	15.20	11.00
7	93.44	54.18	98.14	53.25
8	100.00	99.56	99.72	92.17
9	22.15	3.63	19.34	1.54
10	43.79	17.22	46.24	11.00
11	100.00	83.99	99.70	90.21
12	92.19	87.91	95.00	90.00
13	99.61	92.73	99.61	92.82
14	99.61	92.73	99.61	92.56
15	99.61	92.73	99.61	92.82

increased with increasing initial hydrogen peroxide concentration at all dyestuff concentrations. However, at low dyestuff concentrations below 50 mg L^{-1}, color removal slightly decreased with increasing H$_2$O$_2$ concentrations above 1500 mg L^{-1} H$_2$O$_2$ due to hydroxyl scavenging effect of high concentrations of H$_2$O$_2$. Previous studies have reported that increases in the H$_2$O$_2$ concentration improved the degradation of organic compounds in photo-Fenton reactions up to a certain limit due to additional production of HO$^\bullet$ [31,32]. However, adverse effects were also observed when excess doses of H$_2$O$_2$ were present [33,34]. The accepted explanation is the scavenging of HO$^\bullet$ by H$_2$O$_2$ and consequent formation of the less reactive radical HO$_2$$^\bullet$, as presented by the following equations:

$$OH^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet \qquad (4)$$

$$OH^\bullet + HO_2^\bullet \rightarrow H_2O + O_2 \qquad (5)$$

Percent color removal decreased with increasing dyestuff concentrations at all H$_2$O$_2$ concentrations due to limitations by H$_2$O$_2$ doses at high dyestuff concentrations. At an H$_2$O$_2$ concentration of 500 mg L^{-1}, percent color removal was nearly 95% when dyestuff was 10 mg L^{-1} which decreased to 68% when dyestuff concentrations increased to 250 mg L^{-1}. At constant dyestuff and Fe(II) doses of 130 and 40 mg L^{-1} and variable H$_2$O$_2$ doses of 100, 1000 and 2000 mg L^{-1} percent dye removals were 85.3, 91.6 and 94.4%, respectively, indicating limitations by H$_2$O$_2$. The optimal reagent doses varied depending on the initial dyestuff dose. At a dyestuff dose of 10 mg L^{-1}, the optimal H$_2$O$_2$/Fe(II)/dyestuff ratio yielding the highest color removal (100%) was 515/45/10 mg L^{-1}, while at a high dyestuff dose of 250 mg L^{-1} this ratio was

Table 5
ANOVA test for response function Y_1 (%color removal)

Source	Sum of squares	d.f.	Mean square	F-ratio	P-value
Model	13097.07	9	1455.23	29.51	0.0008
X_1 (Pest.)	174.38	1	174.38	3.54	0.1188
X_2 (H$_2$O$_2$)	68.27	1	68.27	1.38	0.2923
X_3 (Fe(II))	8242.00	1	8242.00	167.14	<0.0001
$X_1 X_2$	14.55	1	14.55	0.30	0.6103
$X_1 X_3$	428.08	1	428.08	8.68	0.0320
$X_2 X_3$	249.64	1	249.64	5.06	0.0743
X_1^2	0.038	1	0.038	0.0007676	0.9790
X_2^2	15.46	1	15.46	0.31	0.5997
X_3^2	3898.50	1	3898.50	79.06	0.0003
Residual	246.55	5	49.31		
Lack of fit	246.55	3	82.18		
Pure error	0.000	2	0.000		
Total (corr)	13343.63	14			

Table 6
ANOVA test for the response function Y_2 (%TOC removal)

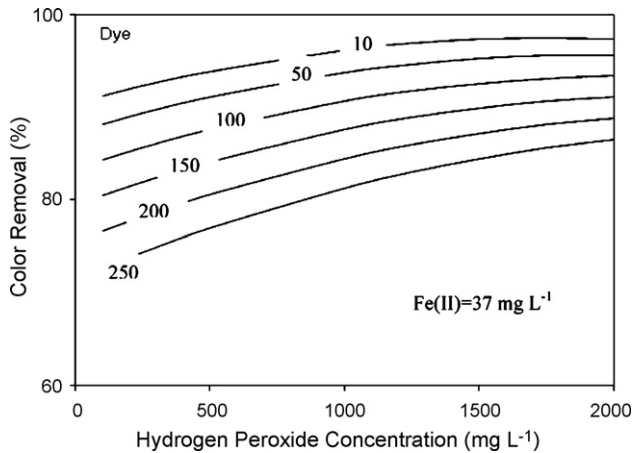| Source	Sum of squares	d.f.	Mean square	F-ratio	P-value
Model	19956.87	9	2217.43	43.35	0.0003
X_1 (Pest.)	1974.43	1	1974.43	38.60	0.0016
X_2 (H$_2$O$_2$)	153.21	1	153.21	3.00	0.1441
X_3 (Fe(II))	11407.30	1	11407.30	222.99	<0.0001
$X_1 X_2$	173.98	1	173.98	3.40	0.1245
$X_1 X_3$	194.88	1	194.88	3.81	0.1084
$X_2 X_3$	23.38	1	23.38	0.46	0.5290
X_1^2	852.56	1	852.56	16.67	0.0095
X_2^2	137.97	1	137.97	2.70	0.1615
X_3^2	5453.87	1	5453.87	106.61	0.0001
Total error	255.78	5	51.16		
Lack of fit	255.73	3	85.24	3783.00	0.0003
Pure error	0.045	2	0.023		
Total (corr)	20212.64	14			

Fig. 2. Variation of percent color removals with H_2O_2 concentration at different initial dyestuff doses by the photo-Fenton method (reaction time 5 min).

Fig. 4. Variation of percent TOC removals with H_2O_2 concentration at different initial dye doses by the photo-Fenton method (reaction time 15 min).

715/71/250 mg L^{-1} yielding 100% color removal. High dyestuff doses required higher peroxide and Fe(II) doses for complete color removal.

Effects of Fe(II) and dyestuff concentrations on percent dyestuff removal by photo-Fenton treatment are depicted in Fig. 3 at an H_2O_2 concentration of 1000 mg L^{-1}. Percent color removal increased with increasing Fe(II) doses at all dye concentrations up to 60 mg L^{-1}. Further increases in Fe(II) concentrations resulted in negligible changes or slight decreases in percent color removal probably due to adverse effects of high Fe(II) doses. Optimal Fe(II) concentration was nearly 50 mg L^{-1} for dyestuff concentrations below 100 and 60 mg L^{-1} for dyestuff concentrations above 100 mg L^{-1}. Percent color removal decreased with increasing initial dyestuff concentrations at all Fe(II) doses below 60 mg L^{-1} due to limitations by Fe(II) at high dyestuff concentrations. At a H_2O_2 dose of 1000 mg L^{-1}, percent color removals were 36.9, 99.5 and 100% with an initial dyestuff dose of 130 mg L^{-1} and Fe(II) doses of 0, 50 and 100 mg L^{-1}, respectively, indicating Fe(II) limitations at low Fe(II) doses. In the absence of Fe(II) or with only UV-hydrogen peroxide treatment color removal was very low (34.5%) indicating the importance of Fe(II) in the photo-Fenton treatment.

These results are in agreement with the literature reports, where a beneficial effect of increasing Fe(II) was observed in photo-degradation of dyes [35]. However, high iron concentrations can also scavenge OH$^\bullet$ yielding lower levels of oxidation. Apparently

the use of high catalyst doses inhibited the removal of color due to formation of radical scavengers. Moreover, there is a need for strict pH control to avoid precipitation of iron hydroxides which can prevent penetration of light due to high turbidity or optical density of the solution slowing down the generation of Fe(II) and consequently the degradation reaction [33]. At high dyestuff concentrations such as 250 mg L^{-1}, complete decolorization was realized at hydrogen peroxide dose of 1000 mg L^{-1} and Fe(II) concentrations above 60 mg L^{-1} after 5 min reaction time while lower concentrations of Fe(II) did not result in complete dyestuff degradation.

The ANOVA analysis indicated that all three variables dyestuff, H_2O_2 and Fe(II) doses and the interactions (X_1, X_3, X_1X_3, X_2X_3, X_3^2) were significant and played important roles in decolorization by the photo-Fenton treatment as summarized in Table 5.

4.3. Total organic carbon removal: mineralization of the dyestuff

Decolorization of the dyestuff does not always result in complete degradation to CO_2 and H_2O. Some colorless reaction intermediates may be formed during degradation of dyestuffs. Therefore, it is important to know the degree of mineralization or total organic carbon removal during decolorization of azo-dyes. In our study, complete mineralization of the dyestuff was achieved after 15 min of reaction time while decolorization was realized in 5 min. The difference between percent color and TOC removals is a measure of formation of colorless organic intermediates contributing to TOC, but not to color measurements. The photo-Fenton reaction scheme can be summarized as follows,

$$\text{Dyestuff} + H_2O_2$$
$$+ \text{Fe(II)} + \text{UV} \rightarrow \text{colorless intermediates} + \text{nitrate} \qquad (6)$$

$$\text{Dyestuff} + H_2O_2 + \text{Fe(II)} + \text{UV} \rightarrow CO_2 + H_2O \qquad (7)$$

The first reaction is for color removal and the second is for TOC removal or mineralization. In decolorization reaction azo-groups were removed from the dyestuff without much TOC removal and some colorless organic intermediates were formed. In mineralization reaction the dyestuff is degraded to CO_2 and H_2O.

Fig. 4 depicts variation of percent TOC removal (mineralization) with H_2O_2 doses at different dyestuff concentrations (10–250 mg L^{-1}) at a constant Fe(II) dose of 50 mg L^{-1}. At dyestuff concentrations below 100 mg L^{-1} percent TOC removal increased with H_2O_2 concentrations and this increase was steeper at low
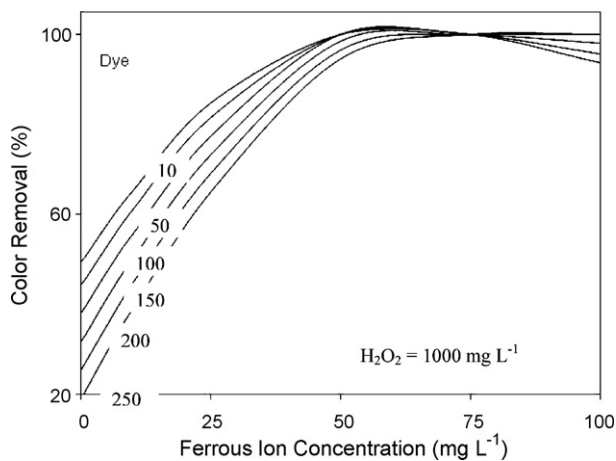

Fig. 3. Variation of percent color removals with Fe(II) dose at different initial dye concentrations by the photo-Fenton method (reaction time 5 min).
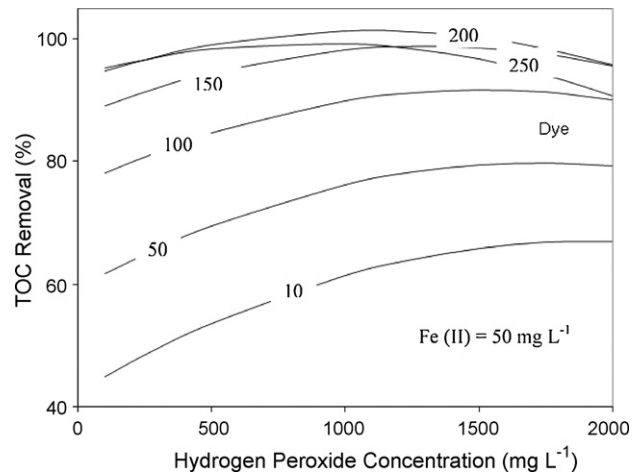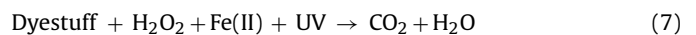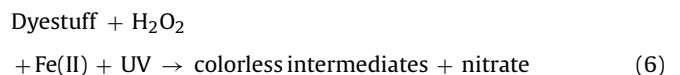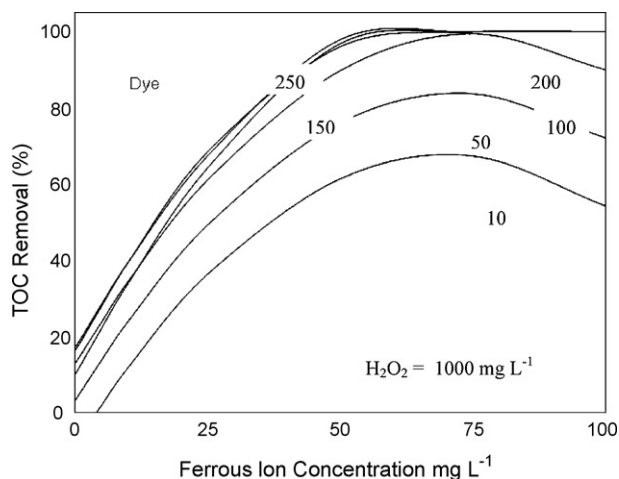
Fig. 5. Variation of percent TOC removals with Fe(II) concentration at different dye doses by the photo-Fenton method (reaction time 15 min).

H_2O_2 doses. However, at dyestuff doses above 100 mg L^{-1}, percent TOC removal increased with H_2O_2 doses up to nearly 1000 mg L^{-1} indicating limitations by H_2O_2 concentration. TOC removal decreased with further increases in H_2O_2 doses due to hydroxyl radical scavenging effect of high H_2O_2 doses. Percent TOC removal or mineralization steadily increased with increasing dyestuff concentrations up to 200 mg L^{-1} due to limitations by low dyestuff concentrations while the peroxide and Fe(II) doses were high. Decrease in percent TOC removal for dyestuff concentrations above 200 mg L^{-1} is due to limitations by the peroxide and Fe(II) which were probably below the required levels.

H_2O_2 concentrations above 1500 mg L^{-1} resulted in decreases in percent TOC removal indicating adverse effects of high H_2O_2 concentrations. At high hydrogen peroxide concentrations, H_2O_2 served as a free-radical scavenger reducing the hydroxyl radical concentration. At constant dyestuff and Fe(II) doses of 130 and 50 mg L^{-1} and variable H_2O_2 doses of 100, 1000 and 2000 mg L^{-1} percent TOC removals were 80.5, 92.5 and 89%, respectively, indicating limitations by H_2O_2 concentrations at peroxide doses below 1000 mg L^{-1} and adverse effect of peroxide above 1000 mg L^{-1}.

Initial dyestuff and Fe(II) concentrations were the most important factors affecting the percent TOC removal by the photo-Fenton oxidation. Mineralization efficiencies obtained at high dyestuff concentrations were higher than those of low dyestuff doses due to limitations by the dyestuff at low doses. Fig. 5 depicts variations of percent TOC removal with Fe(II) concentration at different dyestuff doses and constant H_2O_2 dose of 1000 mg L^{-1}. Mineralization or TOC removal was mainly influenced by the Fe(II) concentration as indicated by the coefficient for this parameter (X_3) in Eq. (3). Percent mineralization (TOC removal) increased with increasing Fe(II) doses up to nearly 60 mg L^{-1} due to limitations by the Fe(II) ions and then decreased with further increases in Fe(II) due to adverse effects of high Fe(II) doses yielding an optimal Fe(II) dose of nearly 60 mg L^{-1} under the specified experimental conditions. Excessive ferrous ions in the system resulted in decreases in mineralization yield due to radical scavenging effects

of high Fe(II) doses. When dyestuff concentration was 130 mg L^{-1}, percent TOC removals were 15.2, 92.5 and 93.5%, respectively, at Fe(II) doses of 0, 50 and 100 mg L^{-1} and hydrogen peroxide dose of 1000 mg L^{-1} indicating marginal effects of Fe(II) on TOC removal above 50 mg L^{-1}. At a dyestuff dose of 10 mg L^{-1}, the optimal H_2O_2/Fe(II)/dyestuff dose yielding the highest TOC removal (72%) was 1845/70/10 mg L^{-1}, while at a high dyestuff dose of 250 mg L^{-1} this ratio was 1550/96.5/250 mg L^{-1} yielding 97.5% TOC removal.

The ANOVA analysis indicated that all three variables dyestuff, H_2O_2 and Fe(II) doses and the interactions ($X_1, X_3, X_1X_3, X_1^2, X_2^2, X_3^2$) played important roles for the mineralization of dye or TOC removal (Table 6). In a literature study, the same dyestuff (DR 28) was degraded by photo-Fenton treatment using a different experimental approach, by considering different reagent doses and reaction times. For the treatment of 100 mg L^{-1} dyestuff (DR 28) with the 100% TOC removal efficiency, the selected oxidant, catalyst doses and the reaction times were reported to be H_2O_2 = 850 mg L^{-1}, Fe(II) = 25 mg L^{-1} and reaction time = 90 min, respectively [36]. Our study covered for a larger range of dyestuff, H_2O_2 and Fe(II) doses using a statistical experiment design and the results were evaluated for both TOC and color removals. Moreover, complete TOC removal was achieved in 15 min indicating the effectiveness of our approach.

The optimal peroxide and Fe(II) doses resulting in the highest TOC and color removals by the photo-Fenton treatment varied depending on the initial dyestuff dose. The optimal reagent doses were determined by using an optimization program and the results are presented in Table 7 for the highest initial dyestuff dose of 250 mg L^{-1}. Complete mineralization required more peroxide and Fe(II) as compared to the color removal since mineralization required further oxidation over removal of azo-groups imparting the color. At a an initial dyestuff dose of 100 mg L^{-1} the optimal peroxide/Fe(II)/dyestuff doses were 625/58/100 mg L^{-1} for 100% color removal and 1355/72/100 mg L^{-1} for 97.2% TOC removal (mineralization). Also, the reagent requirements for the maximum color and TOC removal increased with increasing initial dyestuff dose.

As compared to the Fenton reagent treatment for DR 28 which was investigated in previous study [37], the photo-Fenton treatment provided considerable improvements in color and TOC removals requiring lower levels of reagents for the same degree of TOC and color removals. At a dyestuff dose of 245 mg L^{-1}, the photo-Fenton treatment required 1000 mg L^{-1} peroxide 55 mg L^{-1} Fe(II) for 96% TOC removal while the Fenton treatment alone required 1720 mg L^{-1} peroxide and 80 mg L^{-1} Fe(II) for the same degree of TOC removal.

Apparently, some colorless soluble organic intermediates were formed during photo-Fenton treatment which contributed to TOC content of the final solution. TOC removal or mineralization was realized when the colorless intermediates were degraded to CO_2 and H_2O as described by Eq. (7). The difference between the percent color and TOC removals is a measure of colorless intermediate formation. Fe(II) dose was the major parameter affecting the color removal since decolorization required removal of azo-groups, but not complete oxidation. TOC removals were more profoundly affected by the oxidant (H_2O_2) and the catalyst (Fe(II)) doses since mineralization involved oxidation of the colorless intermediates. Low H_2O_2 doses may be satisfactory for decolorization, but not for complete mineralization.

Table 7
Optimum reagent doses maximizing the color and TOC removals for the highest dyestuff dose

Response	Dyestuff, X_1, mg L^{-1}	H_2O_2, X_2, mg L^{-1}	Fe(II), X_3, mg L^{-1}	Percent removal
Color removal	250	715	71	100
TOC removal (mineralization)	250	1550	96.5	97.5

5. Conclusions

Box–Behnken statistical experiment design and the response surface methodology were proven to yield statistically reliable results for oxidation of dyestuffs by the photo-Fenton treatment. Predictions obtained from the response functions were in good agreement with the experimental results indicating the reliability of the methodology used. The RSM also provided a better understanding for the roles of Fe(II) and H_2O_2 doses on degradation of the dyestuff for a large range of concentrations. Fe(II) doses were found to be more effective than peroxide for decolorization.

Percent color removals were higher than TOC removals indicating formation of some colorless intermediates. At a constant dyestuff concentration percent color removal increased with increasing H_2O_2 and Fe(II) concentrations up to a certain level above which color removals decreased due to scavenging effects of H_2O_2 and Fe(II) on hydroxyl radicals. The optimal reagent doses varied with the initial dyestuff doses. High initial dyestuff doses required higher peroxide and Fe(II) doses for complete decolorization and mineralization. At the highest initial dyestuff dose of $250\,mg\,L^{-1}$, the optimal peroxide/Fe(II)/dyestuff ratio was predicted to be $715/71/250\,mg\,L^{-1}$ for 100% color removal, while this ratio was $1550/96.5/250\,mg\,L^{-1}$ for 97.5% TOC removal. Complete mineralization required higher reagent doses and was also slower as compared to decolorization. This is due to the fact that decolorization did not require complete oxidation, but only removal of azo-groups imparting the color.

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