

Effect of Fenton process on treatment of simulated textile wastewater: optimization using response surface methodology

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Abstract A large portion of water is consumed during various textile operations thereby discharging wastewaters with pollutants of huge environmental concern. The treatment of such wastewaters has promising impact in the field of environmental engineering. In this work, Fenton oxidation treatment was engaged to treat simulated textile wastewater. Box–Behnken design and response surface methodology were employed to optimize the efficiency of Fenton process. Iron dose, peroxide dose and pH were considered as input variables while the responses were taken as chemical oxygen demand and color removal. A total of 17 experiments were conducted and analyzed using second-order quadratic model. The quadratic models generated for chemical oxygen demand and color removal efficiencies were validated using analysis of variances, and it was found that the experimental data fitted the second-order model quite effectively. Analysis of variances demonstrated high values of coefficient of determination (R^2) for chemical oxygen demand and color removal efficiencies with values of 0.9904 and 0.9963 showing high

conformation of predicted values to the experimental ones. Perturbation plots suggested that the iron dosage produced the maximum effect on both chemical oxygen demand and color removal efficiencies. The optimum parameters were determined as Fe^{2+} dose—550 mg/L, H_2O_2 dose—5538 mg/L, pH—3.3 with corresponding chemical oxygen demand and color removal efficiencies of 73.86 and 81.35%. Fenton process was found efficient in treatment of simulated textile wastewater, and optimization using response surface methodology was found satisfactory as well as relevant. From the present study, it can also be concluded that if this method is used as pretreatment integrated with biological treatment, it can lead to eco-friendly solution for treatment of textile wastewaters.

Keywords Analysis of variances · Box–Behnken design · Color removal · Chemical oxygen demand · Azo dye

Introduction

The accelerated development of textile industries is enhancing higher rate of water pollution in the environment (Nidheesh et al. 2013). Dye molecules consist of two key segments: chromophores, helps in producing color and auxochromes which are accountable for enhancing affinity toward the fiber and render the molecule soluble in water (Nidheesh et al. 2013). The most significant chromophores are azo ($-\text{N}=\text{N}-$), carbonyl ($-\text{C}=\text{O}$), methine ($-\text{CH}=\text{}$), nitro ($-\text{NO}_2$) and quinoid groups. The most important auxochromes are amine ($-\text{NH}_3$), carboxyl ($-\text{COOH}$), sulfonate ($-\text{SO}_3\text{H}$) and hydroxyl ($-\text{OH}$) (Dos Santos et al. 2007). The auxochromes can be owned to the classes of reactive, acid, direct, basic, mordant, disperse, pigment, vat, ingrain, sulfur and solvent dye (Welham 2000).

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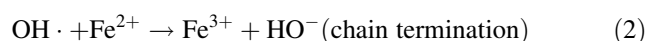
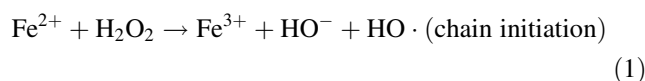
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Enormous quantities of wastewater with significant concentrations of chemical oxygen demand (COD), suspended solids, refractory organics and color are introduced to the environment by textile industries (García-Montano et al. 2006). Discharge of textile processed effluents has created unfavorable conditions in the environment (Emami et al. 2010) like reduction in solar energy penetration to the aquatic bodies, reduced reoxygenation capacity and being highly toxic toward aquatic flora and fauna (Clarke and Anliker 1980). Additionally, they are resilient to degradation due to their complex chemical structure and xenobiotic properties (Cristovao et al. 2011).

Azo dyes consist of $-N=N-$ bond and are the most commonly used dyes (Meric et al. 2004). Degradation of azo dyes which contributes about 70% of all used dyes is crucial due to their high structural diversity (Nidheesh et al. 2013). Moreover, the reductive cleavage of azo bonds is responsible for the formation of metabolites of amines, which are classified as toxic and carcinogenic (Puvaneshwari et al. 2006) and more noxious than intact dye molecules (Chung et al. 1978). Viewing the inimical effects on environment due to dyes, it becomes necessary to have an adequate treatment for textile wastewaters.

There are numerous physicochemical techniques used like adsorption by activated carbon (Nawaz and Ahsan 2014), photocatalysis and photocatalytic oxidation (Alinsafi et al. 2007), chemical coagulation (Yadav et al. 2013), ozonation (Sevimli and Sarikaya 2002) and chemical precipitation (Tunay et al. 1996) which have been reviewed for treatment of textile wastewater and their COD and color removal efficiencies are given in Table 1. However, physical and chemical treatment techniques are powerful in color removal but allow only a phase transfer of pollutant requiring additional treatment or disposal (Blanco et al. 2012). Moreover, most of the organic matter present in textile wastewater is non-biodegradable or toxic, and therefore, it becomes difficult for biological treatment to reach its required efficiency (Ugyur and Kök 1999).

In this frame, advanced oxidation processes (AOPs) are the ones involving the production of hydroxyl radical ($\cdot\text{OH}$, $E^\circ = 2.8 \text{ V vs. NHE}$), efficient enough to destroy the recalcitrant compounds to CO_2 and H_2O (Blanco et al. 2012; Mansoorian et al. 2014). Among AOPs, Fenton oxidation has come out as a promising treatment technique for textile wastewaters (Nidheesh et al. 2013). Fenton reagent is a homogenous catalytic oxidation process that uses a mixture of ferrous ion and hydrogen peroxide in an acidic medium for generation of hydroxyl radicals (Bahmani et al. 2013). Chain reactions involved in Fenton oxidation process are shown below in Eqs. 1 and 2 (Blanco et al. 2011):



The advantages of Fenton reagent are high efficiency, easy applicability, low investment cost (Rodrigues et al. 2009), lack of residues, capacity to treat complex compounds (Blanco et al. 2011) and less environmental damages (Babuponnusami and Muthukumar 2014), whereas the limitations of this process are production of sludge containing high amounts of ferric ions as well as higher operational costs due to usage of chemical reagents (Meric et al. 2004; Sun et al. 2007).

The process parameters are required to determine the performance of Fenton reaction (Zhu et al. 2011). Response surface methodology (RSM) is a useful statistical method widely used for experimental design and widely applied for optimization of wastewater treatment (Rosales et al. 2012). Rare studies for optimization of simulated textile wastewater with a mixture of 5 azo dyes with Fenton process have been performed. The most relevant part of RSM is the selection of applicable design of experiment that has higher impact on response surface and its accuracy on prediction (Sakkas et al. 2010). The application of Box–Behnken design (BBD) is a standard, stable and favored

Table 1 COD and color removal efficiencies of different physicochemical techniques

Sr. nos.	Method used	COD removal (%)	Color removal (%)	References
1	Adsorption by granular activated carbon	56	88	Nawaz and Ahsan (2014)
2	Chemical coagulation (using FeCl_3)	47.6	75	Yadav et al. (2013)
3	Ozonation	10–20	75	Sevimli and Sarikaya (2002)
4	Photocatalysis	32	51	Alinsafi et al. (2007)
5	Photocatalytic oxidation	28	42	Alinsafi et al. (2007)
6	Chemical precipitation	22	55	Tunay et al. (1996)

Table 2 Constituents of simulated textile wastewater. Isik and Sponza (2008)

Sr. nos.	Materials used	Concentration (mg/L)	Functions of material
1	Carboxymethyl cellulose	150	Sizing in reactor
2	Starch	1500	Sizing in reactor
3	Acetic Acid	500	Substrate in reactor
4	Azo dyes		Dyeing in reactor
	Direct red 80	50	
	Reactive black 5	50	
	Direct black 38	50	
	Direct blue 71	50	
	Direct fast yellow 5GL	50	
5	NaOH	660	Hydrolysis
6	H ₂ SO ₄	357	pH neutralization
7	NaCl	500	Fixing
8	Na ₂ CO ₃	1000	Fixing
9	NaHCO ₃	2000	pH buffer
10	Glucose	2000	Substrate for bacterial growth
11	NH ₄ Cl	280	Nutrient for bacterial growth
12	K ₂ HPO ₄	250	Nutrient for bacterial growth
13	MgSO ₄ ·7H ₂ O	100	Nutrient for bacterial growth
14	CaCl ₂ ·2H ₂ O	10	Nutrient for bacterial growth

design used for examining the interaction between variables. BBD is usually very competent due to reduced number of experiments (Nair et al. 2014) and due to inconsideration of points at the vertices of a cube which could be considered as an advantage as experiments carried out at these points may turn out to be either expensive or unfeasible (Montgomery 2010). As BBD designs are economical, they are widely used for research purposes.

In this study, Box–Behnken design and response surface methodology were applied to design the experiments and assess the effects of variables like pH, iron and hydrogen peroxide concentration on application of Fenton oxidation treatment to simulated textile wastewater. Two regression models were developed with the experimental data, i.e., one for COD removal and one for color removal. The significance of each variable on the efficiency of Fenton process was studied, and optimal values were acquired and ratified. This study was carried out at Sardar Vallabhbhai National Institute of Technology, Surat, Gujarat, India during August 2014–April 2015.

Materials and methods

Simulated textile wastewater

In this study, simulated textile wastewater was used as the composition of real textile wastewater changes day to day owing to different operations taking place in textile

industry. The simulated textile wastewater was prepared in agreement with the information presented in Table 2, and the characteristics obtained are shown in Table 3.

Samples of the auxiliary products and dyes as presented in Table 2 were taken from Isik and Sponza 2008. The mixture of azo dyes was prepared with concentration 50 mg/L each of Reactive Black 5, Direct Red 80, Direct Black 38, Direct Blue 71 and Direct Fast Yellow 5GL.

Chemicals

All chemicals used in the study were of highest commercially available grade. Analytical grade hydrogen peroxide (30% (w/v), Finar Limited, India) and FeSO₄·7H₂O (RFCL, India) were used to generate hydroxyl radical in aqueous solution. pH adjustment was done using reagent grade sulfuric acid and sodium hydroxide (RFCL, India) solutions. All the solutions were prepared in distilled water.

Table 3 Characteristics of simulated textile wastewater

Sr. nos.	Parameter	Values
1	pH	8.25 ± 2.5
2	COD (mg/L)	3894 ± 100
3	Absorbance at 478 nm	0.9417 ± 0.014



Fenton oxidation

Batch experiments of Fenton oxidation were carried out in glass beakers having 1 liter of operating capacity at room temperature (25–30 °C). pH of the sample was adjusted in the range of 2.5–3.5 using 0.5 M H₂SO₄. After adjusting pH, catalyst FeSO₄·7H₂O was added and reaction proceeded with further addition of H₂O₂ producing hydroxyl radicals. During the reaction, sample solution was constantly stirred using magnetic stirrer at 150 rpm for 60 min. After 60 min, residual hydrogen peroxide was eliminated by addition of excess sodium sulfite (Finar Limited, India) and by adjusting pH > 7 before analysis. Settling of samples was carried out in Imhoff cone for 2 h, and samples were analyzed thereafter.

Analytical procedures

The color of the samples was analyzed by measuring the absorbance of supernatant sample at wavelength corresponding to the maximum absorbance, i.e., 478 nm in UV–Vis Spectrophotometer (Hach DR 6000TM). As the sample absorbance varied with pH, it was adjusted similar for all supernatant samples. Analytical methods carried out for remaining parameters followed standard methods. COD of the samples was measured using Open Reflux Method (Method 5220 B). pH of the sample was determined using pH-meter.

Dye decolorization and COD removal were calculated using expressions (3) and (4):

$$R_1(\%) = 100 \times (A_i - A_t) / A_i \quad (3)$$

$$R_2(\%) = 100 \times (C_i - C_t) / C_i \quad (4)$$

where R_1 —decolorization efficiency (%), R_2 —COD removal efficiency (%); A_i and A_t , initial and final absorbance at maximum wavelength; C_i and C_t , initial and final COD (mg/L) of simulated textile wastewater.

Experimental design, analysis and statistical validation

Response surface methodology (RSM) was used for the optimization of experiments. RSM is an extensively used statistical tool applied in engineering process (Xu et al. 2013). Whenever multiple variables and their interactions affect the responses, RSM can be applied to examine the relation between independent and dependent variables along with optimization of parameters (Baş and Boyacı 2007). Under RSM, for a selected response, it is possible to restrict the number of experiments for recognition of optimal conditions (Rosales et al. 2012). Optimization by RSM involves following steps: (1) selection of independent variables and their ranges, (2) experimental design

selection, (3) estimation of mathematical coefficients using linear regression analysis technique and (4) verification of model adequacy and obtaining optimal conditions (Nair et al. 2014). Optimization of results is faster by using RSM rather than one factor at a time approach (Alim et al. 2008).

In this study, Box–Behnken design (BBD) which is widely used in RSM was employed for optimization of COD and color removal efficiencies in simulated textile wastewater. Here, a 2³ factorial design was used to perceive the influence of 3 parameters including: H₂O₂ concentration (A), Fe²⁺ concentration (B) and pH (C). These factors were chosen as they might show some promising effect on COD and color removal efficiencies. A total of 17 experiments were conducted with 5 replicates at the central point, and the codification of values was done using Eq. 5:

$$x_i = z_i - z_o / \Delta z_i \quad (5)$$

where x_i = code level, z_i = uncoded value, z_o corresponds to the uncoded value at the central point and Δz_i = step change value between low level (−1) and high level (+1) (Moghaddam et al. 2010). From preliminary experiments, the range of A, B and C was selected as shown in Table 4.

A second-order regression model was employed for analysis and proves to be a good estimation of response surface (Zhu et al. 2011) and is expressed as shown in Eq. 6:

$$y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^k \beta_{ij} X_i X_j \quad (6)$$

where y = response; x_i and x_j = input variables; β_0 = intercept constant; β_i = first-order regression coefficient; β_{ii} = second-order regression coefficient representing quadratic effect of factor i ; and β_{ij} = coefficient of interaction between two factors i and j (Xu et al. 2013).

The analysis of variances (ANOVA) was carried out using Design Expert (version 9.0.0) to study the results and to determine the implication of fitted quadratic model. The fitted model was thereafter illuminated in the form of contour and surface plots to know the interaction between the variables and responses. The quality of model was checked using co-relation coefficient (R^2) (GilPavas et al. 2012). The model was further authenticated with respect to all the three variables within the design space.

Table 4 Coded level and independent variables used in BBD

Coded level	Fe ⁺² dose (mg/L)	H ₂ O ₂ dose (mg/L)	PH
−1	450	4400	2.5
0	600	6600	3
1	750	8800	3.5



Results and discussion

Preliminary experiments

In this work, before optimization preliminary experiments were carried out to know the range in which maximum color and COD removal took place. The range obtained for Fe²⁺ concentration was 450–750 mg/L, hydrogen peroxide range was 4400–8800 mg/L, pH was varied from 2.5 to 3.5 as maximum removal of COD, and color was obtained in these ranges. Further precision of doses was done with the help of RSM.

Experimental design by BBD under RSM

According to 2³ BBD factorial design experiments were designed and carried out. Among 17 experiments, five experiments were repetition of central point (Run 2, 11, 14, 15 and 16). These runs enclosed the variables which were at central region of the cube. Proximity of the results for these runs shows the symbol of precision maintained during the experimentation work (Azami et al. 2012). The results obtained from experimental design are shown in Table 5.

Regression model and statistical testing

For determination of optimal values for decolorization and COD removal within the experimental runs, a second-

order polynomial fitted for the results of color and COD removal. The polynomials obtained are shown in Eqs. 7 and 8:

$$R_1 = 82.22 - 3.81A + 2.46B + 2.07C - 24.64A^2 - 8.79B^2 - 10.45C^2 \tag{7}$$

$$R_2 = 88.26 - 6.80A + 2.76B - 3.40AB - 29.54A^2 - 6.37B^2 - 7.12C^2 \tag{8}$$

where *R*₁ and *R*₂ accounts for COD and color removal, respectively. Tables 6 and 7 shows the ANOVA report generated for this model. In Eqs. 7 and 8, positive effect of a factor means that the response is improved when the factor level increases and a negative effect of the factor means that the response is not improved when the factor level increases (Saldaña-Robles et al. 2014). Values of probability < 0.05 indicate that model terms are significant and values > 0.1000 indicate that model terms are not significant (Rosales et al. 2012). In the case of COD removal, it can be seen that A, B, C, A², B² and C² were significant terms, and rest of the terms were not significant and therefore, not included in the equation for COD removal while for color removal, it was concluded that A, B, AB, A², B² and C² proved to be significant. Thus, statistical analysis showed that not all variables set in the grounding of model within the tested limitations and had noteworthy effect.

The impact of each factor and interactions between each other is checked by Fisher test. The better the magnitude of *F* value and likewise the lesser the ‘*p* > *F*’, the more

Table 5 Box–Behnken design matrix along with experimental and predicted values

Run	A (mg/L)	B (mg/L)	C	R ₁ COD removal (%)		R ₂ Color removal (%)	
				Experimental	Predicted	Experimental	Predicted
1	0	−1	−1	62.1	60.51	70.4	70.60
2	0	0	0	81.6	82.22	87.9	88.26
3	−1	1	0	59.4	56.98	64.7	65.31
4	1	1	0	46	45.55	45.9	44.91
5	0	−1	1	61.8	60.51	74	73.42
6	0	1	−1	60	61.29	75.8	76.38
7	−1	0	1	54.9	55.74	60	59.59
8	1	−1	0	42	44.42	46.8	46.19
9	−1	−1	0	47.8	48.25	52	52.99
10	−1	0	−1	45	46.14	58.4	57.21
11	0	0	0	83.6	82.22	89.4	88.26
12	1	0	−1	44.8	43.96	43	43.41
13	0	1	1	68	69.59	78.9	78.70
14	0	0	0	84.6	82.22	89.8	88.26
15	0	0	0	80.3	82.22	85.6	88.26
16	0	0	0	81	82.22	88.6	88.26
17	1	0	1	43.8	42.66	45	46.19

Table 6 ANOVA for response surface second-order model for COD removal

Source	Sum of squares	Degree of freedom	Mean square	<i>F</i> value	<i>p</i> value	Prob > <i>F</i>
Model	3887.53	9	431.95	80.33	<0.0001	
A	116.28	1	116.28	21.62	0.0023	
B	48.51	1	48.51	9.02	0.0198	
C	34.45	1	34.45	6.41	0.0392	
AB	14.44	1	14.44	2.69	0.1453	
AC	29.70	1	29.70	5.52	0.0511	
BC	17.22	1	17.22	3.20	0.1166	
A ²	2555.30	1	2555.30	475.21	<0.0001	
B ²	324.95	1	324.95	60.43	0.0001	
C ²	460.68	1	460.68	85.67	<0.0001	
Residual	37.64	7	5.38	–	–	
Std. dev	–	2.32	–	–	–	
Mean	–	61.57	–	–	–	
C.V (%)	–	3.77	–	–	–	
<i>R</i> ²	–	–	–	–	–	0.9904
Adjusted <i>R</i> ²	–	–	–	–	–	0.9781
Predicted <i>R</i> ²	–	–	–	–	–	0.8949
Adeq. precisor	–	–	–	–	–	22.242

Table 7 ANOVA for response surface second-order model for color removal

Source	Sum of squares	Degree of freedom	Mean square	<i>F</i> value	<i>p</i> value	Prob > <i>F</i>
Model	4782.04	9	531.34	211.39	<0.0001	
A	369.92	1	369.92	147.17	<0.0001	
B	61.05	1	61.05	24.29	0.0017	
C	13.26	1	13.26	5.26	0.0552	
AB	46.24	1	46.24	18.40	0.0036	
AC	0.040	1	0.040	0.016	0.9032	
BC	0.063	1	0.063	0.025	0.8792	
A ²	3674.78	1	3674.78	1462.02	<0.0001	
B ²	170.72	1	170.72	67.92	<0.0001	
C ²	213.30	1	213.30	84.86	<0.0001	
Residual	17.59	7	2.51	–	–	
Std. dev	–	1.59	–	–	–	
Mean	–	68.01	–	–	–	
C.V (%)	–	2.33	–	–	–	
<i>R</i> ²	–	–	–	–	–	0.9963
Adjusted <i>R</i> ²	–	–	–	–	–	0.9916
Predicted <i>R</i> ²	–	–	–	–	–	0.9744
Adeq. Precisor	–	–	–	–	–	36.863

considerable are equivalent model and individual coefficients (Montgomery 2010). From ANOVA, it was observed that the corresponding *F* values for COD and color removal efficiencies were 80.39 and 211.39 with a very low probability value (*p* value < 0.0001) which indicated there was only 0.01% chance that such model

could occur due to noise. The *F* values for COD and color removal indicate that both models were extremely significant and adequate as they were much larger than the critical *F* value of 2.42 (Rosales et al. 2012).

The overall performance of a model is generally explained by coefficient of determination (*R*²) (Nair et al.

2014). For a model to be highly competent, the value of R^2 should be nearest to 1.0. The R^2 evaluates the correlation between experimental data and predicted responses (Fathinia et al. 2010). R^2 values for COD and color removal were obtained as 0.9904 and 0.9963 which indicated that the predicted values matched the experimental ones quite realistically. The models of COD and color removal indicated that 99.04 and 99.63% of the total variability could be explained by these models leaving 0.96 and 0.37% of variability owing to random error. Figure 1 suggests that the predicted values conformed well to the experimental values of COD and color removal of simulated textile wastewater. The model prediction competency should not be examined by R^2 value alone (Sarabia and Ortiz 2009) as R^2 value increases with the increase in number of terms in model, irrespective of its statistical significance. R^2 should be related to adjusted R^2 which reflects the number of factors in experiment (Montgomery 2010). The predicted value of R^2 and the adjusted value of R^2 were in reasonable agreement for both COD and color removal because the difference between both the values was < 0.2 . The value of predicted R^2 for COD and color removal was 0.8949 and 0.9744, while the adjusted R^2 values were 0.9781 and 0.9916. As the difference between predicted and adjusted R^2 was less for both models, adequacy of model seemed to be eminently convincing with high values of adjusted R^2 confirming model of strong implication.

Another statistical tool observed for model adequacy is adequate precision. It scrutinizes the range of the predicted values at the design points to the average prediction error, in other words a signal-to-noise ratio (Mason et al. 2003).

The values of adequate precision are in range with a precision of 22.242 for COD removal and 36.883 for color removal. The obtained ratio indicates an adequate signal as values > 4 are desirable. Thus, this model can be used to navigate the design space.

The coefficient of variation is defined as the ratio of standard deviation to the mean value of observed response. This factor demonstrates the repeatability and reproducibility of the models generated (Rosales et al. 2012). Low values of C.V, i.e., 3.77 and 2.33 for COD and color removal indicated high accuracy and dependability of experiments as the values are $< 10\%$.

The sufficiency of the models was also evaluated by the residuals (difference between the observed and the predicted responses). Residuals act as components of variation unidentified by the fitted model, and so, they should have a normal distribution (Khataee et al. 2012). Normal probability plots are formed in order to check normality presumption (Nair et al. 2014). If the plots are normally distributed, the residual plots will maintain linearity with some moderate irregularity of points showing appropriate fitting of model (Carlson and Carlson 2005; Anderson and Whitcomb 2007). The points should distribute uniformly along 45° line maintaining linearity, whereas the points above and under the line indicate areas of over or under prediction (Anderson and Whitcomb 2007). Thus, a review was made for COD and color removal of simulated textile wastewater using normalized plot of residuals as seen in Fig. 2 which showed satisfying normality assumption as the points for both COD and color maintained linearity with the values.

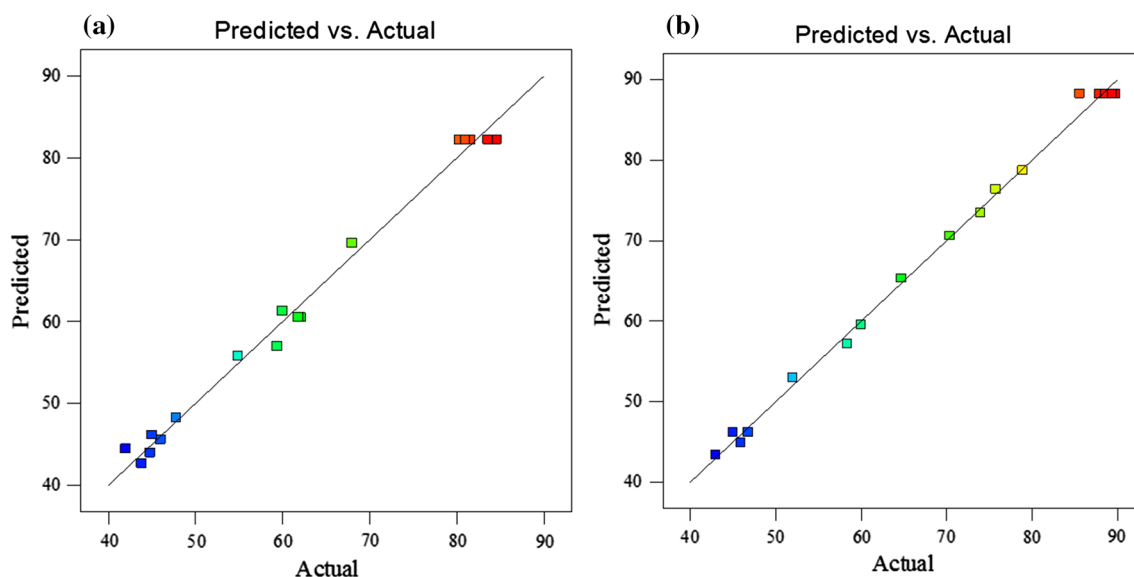


Fig. 1 Predicted versus actual plot for **a** COD removal, **b** Color removal

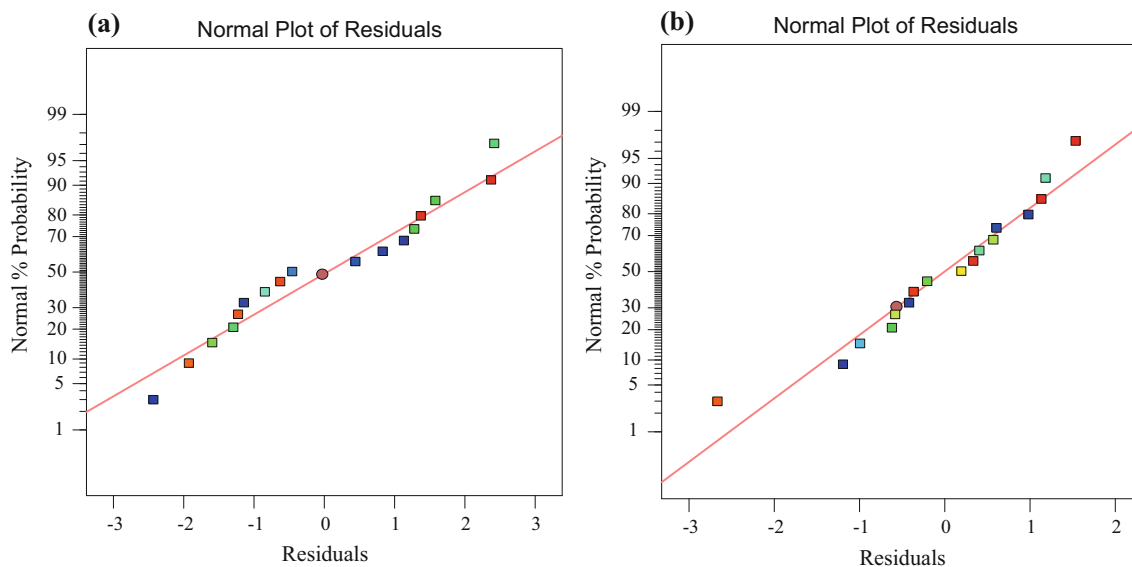


Fig. 2 Normal probability plots of studentized residual of the linear model for **a** COD removal, **b** Color removal

Chemical oxidation by Fenton

Response surface and contour plots for simulated textile wastewater treatment

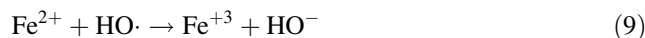
The response surface (3D) and contour plots (2D) of the model-predicted responses obtained from Design Expert software (version 9.0.0) supported in determining the interactive relationships between the process variables and treatment outputs.

Effect of Fe^{2+} concentrations on COD and color removal efficiency

Figure 3 exhibits the 3D and 2D plots for the effect of iron concentration on COD removal. As it can be seen from response surface and contour plots, the peak values for both the plots were attained at the values in middle ranges of iron. The values of COD removal increased from 50.5 to 71% for iron doses of 450–600 mg/L and then decreased from 67.8 to 46.4% for iron doses of 650–750 mg/L at hydrogen peroxide dose of 4400 mg/L. Removal of COD can be attributed to the fact that at higher concentration of iron, decomposition of hydrogen peroxide is accelerated leading to the formation of per-hydroxyl radicals ($HO_2\cdot$) (Mansoorian et al. 2014), while at lower iron concentration, the reaction with hydrogen peroxide leads to the formation of hydroxyl radicals which are more reactive than per-hydroxyl radicals. It was reported that methylene red removal was increased from 45 to 75% in the presence of iron ions (Zhou et al. 2007). Wang et al. 2010 described that iron

ions reduced COD value by increasing the concentration of iron by 0.33 mM where COD removal reached to 43 from 19%.

Color removal efficiencies were higher in the range of 500–600 mg/L with values of 71.7 and 80.1% and then decreased to 48% at 750 mg/L at hydrogen peroxide dose of 4400 mg/L as seen in Fig. 5. As the concentration of iron increases, self-scavenging effect takes place at a faster rate than the formation of hydroxyl radical leading to reduction in COD and decrease in degradation rate of pollutants as seen in Eq. 9 (Arslan-Alaton et al. 2009).



Effect of hydrogen peroxide concentration on COD and color removal efficiency

As seen in Fig. 4, COD removal efficiencies increased up to 62% at hydrogen peroxide dose of 4400–6600 mg/L and then decreased to 56.9% at dose of 8800 mg/L while color removal efficiencies were higher up to with value of 71% at dose of 7700 mg/L and decreased to 68% at dose of 8800 mg/L with constant iron dose value of 450 mg/L. Degradation rate of organic compounds increases with increased dose of hydrogen peroxide but up to a certain value until a critical H_2O_2 concentration is reached. However, when a concentration higher than critical concentration is used, the degradation was condensed due to scavenging effect as seen in Eqs. 10, 11 and 12 (Hsueh et al. 2005, Lodha and Chaudhari 2007). From Eq. 10 it can be conferred that due to the production of peroxy radical as well as the scavenging effect of hydrogen



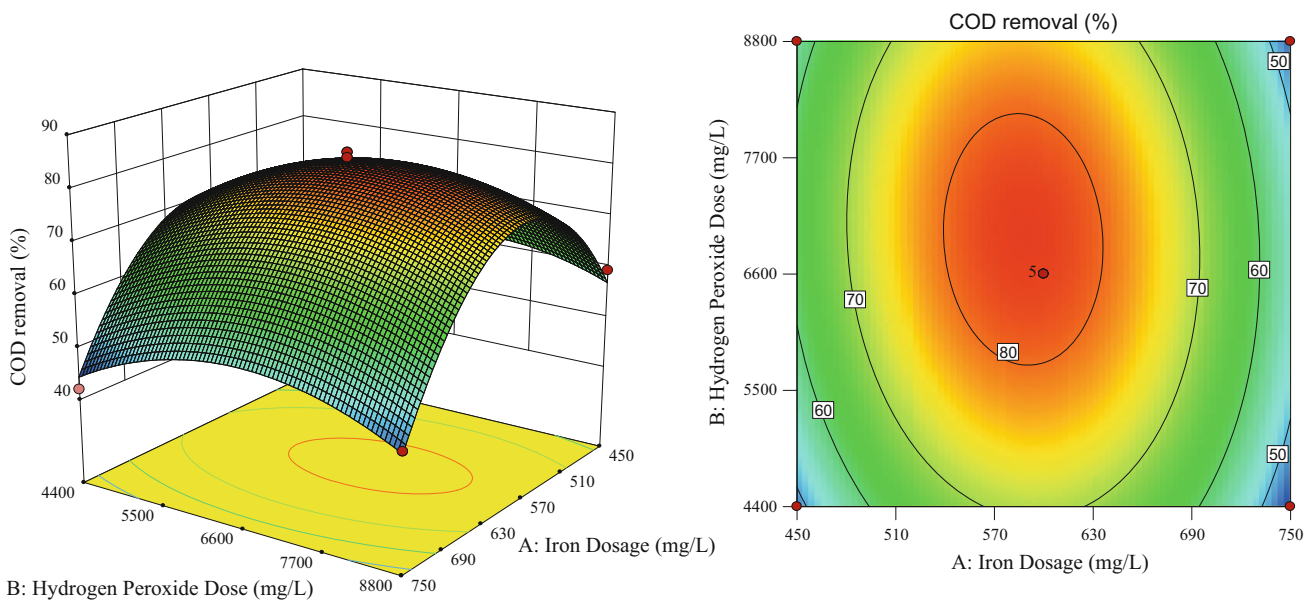


Fig. 3 Response surface and contour plots for the effect of iron and hydrogen peroxide concentration on COD removal

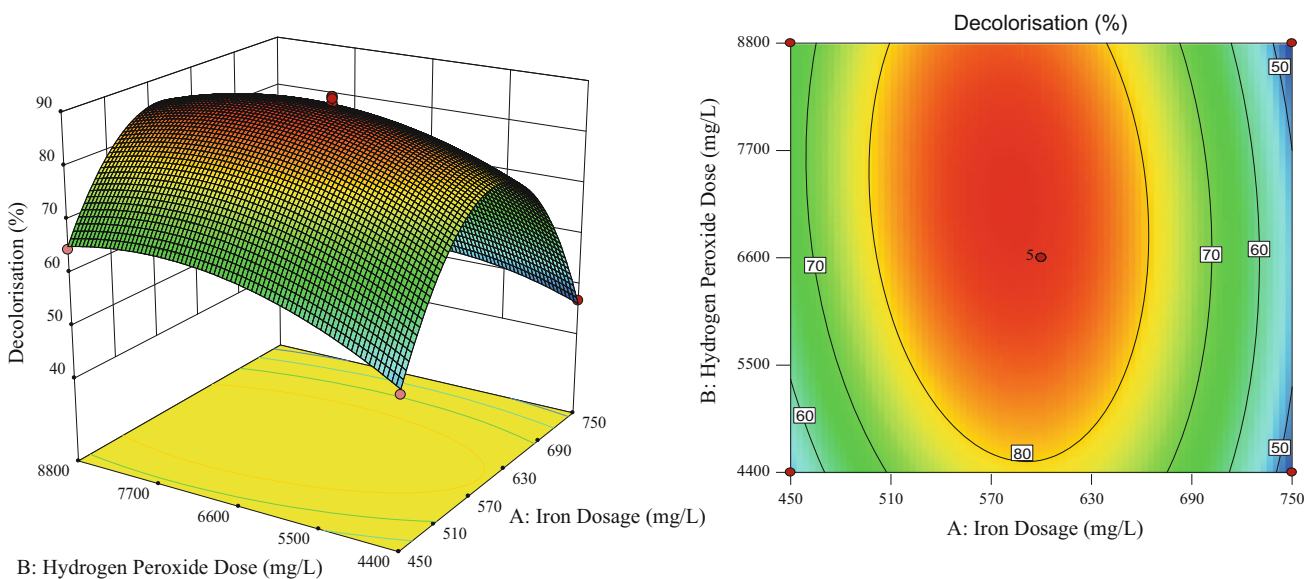


Fig. 4 Response surface and contour plots for the effect of iron and hydrogen peroxide concentration on color removal

peroxide, the removal efficiency of COD and color decreases. The unused quantity of H₂O₂ also leads to higher values of COD and might be the possible reason for more COD values and lesser removal of COD at higher concentration of H₂O₂.



Also, at higher dosages of H₂O₂, the deactivation of Fe²⁺ takes place which allows the formation of brownish yellow precipitates and thereby increasing the color of the wastewater after the critical concentration. Additionally, it was found that the ratio for influent COD and hydrogen peroxide concentration varied in the range of 0.44–0.89, where it was concluded that maximum removal for COD

and color was obtained at a ratio of 0.65–0.7 and then it decreased as the concentration of hydrogen peroxide was not enough for breaking up of recalcitrant dye molecules.

The ratio of hydrogen peroxide concentration to iron dose was seen in the range of 9.8–11.8 where it was found that as the ratio increased, the removal was seen in an ascending manner and then it decreased after a ratio of 11 which concluded that as the ratio increased more peroxy radical was produced leading to degradation of organic molecules but after the critical concentration of hydrogen peroxide was reached, the removal was lowered.

According to Mansoorian et al. (2014), the COD removal efficiency increased at H_2O_2 concentration of 2–5 mM, and then the efficiency decreased after the concentration was more than 5 mM. Also, Zhang et al. (2005) observed that efficiency of hydrogen peroxide for removal of organic materials in the leachate decreased with the increase in Fenton reagent dose.

Effect of pH on COD and color removal efficiency

As seen in Figs. 5 and 6, maximum COD and color removal were obtained in the range of 3–3.2. Efficiency for COD removal increased from 47.5 to 61% at pH from 2.5 to 3 and then decreased to 56% at pH 3.5 at iron dose of 450 mg/L. Color removal efficiency increased from 58 to 68% at pH of 2.5–3 and then decreased to 61% at pH of 3.5. The values obtained are sustained by previous studies as Lucas and Peres (2006) observed an optimum pH of 3

for the decolorization of dyes. Meric et al. (2004) depicted more than 99% color removal in the pH range of 3–3.5. Previous studies show that more hydroxyl radicals are generated in acidic range and this might be the possible reason of decolorization and COD removal. Under highly alkaline conditions, the precipitation of $\text{Fe}(\text{OH})_3$ occurs; therefore, the concentration of Fe^{+3} ions decreases in wastewater. Also, in alkaline conditions hydrogen peroxide is less stable, and therefore, lesser is the production of hydroxyl radicals which leads to the decrement in efficiency of process for color and COD removal (Rodrigues et al. 2009). At pH below 3, hydrogen peroxide will also take a proton to form oxonium ion $(\text{H}_3\text{O}_2)^+$ which produces more stable hydrogen peroxide and lower its reactivity with ferrous ions (Kavitha and Palanivelu 2005; Kwon et al. 1999). Under such conditions when pH is < 3 , reduction in the formation of hydroxyl radicals is due to decrease in soluble amount of Fe^{+3} that is in equilibrium with other iron species ($\text{Fe}(\text{OH})_2$) and $\text{Fe}(\text{OH})^{+2}$ (Lucas and Peres 2006).

Perturbation plots

Perturbation plots shows the effect when all factors at optimal experimental conditions in the design space are compared at center point. When the factor curvature is sharper, this factor is more important for the response (Saldaña-Robles et al. 2014). Figure 7 shows the perturbation plots for COD and color removal. Here, in the plots, A represents iron

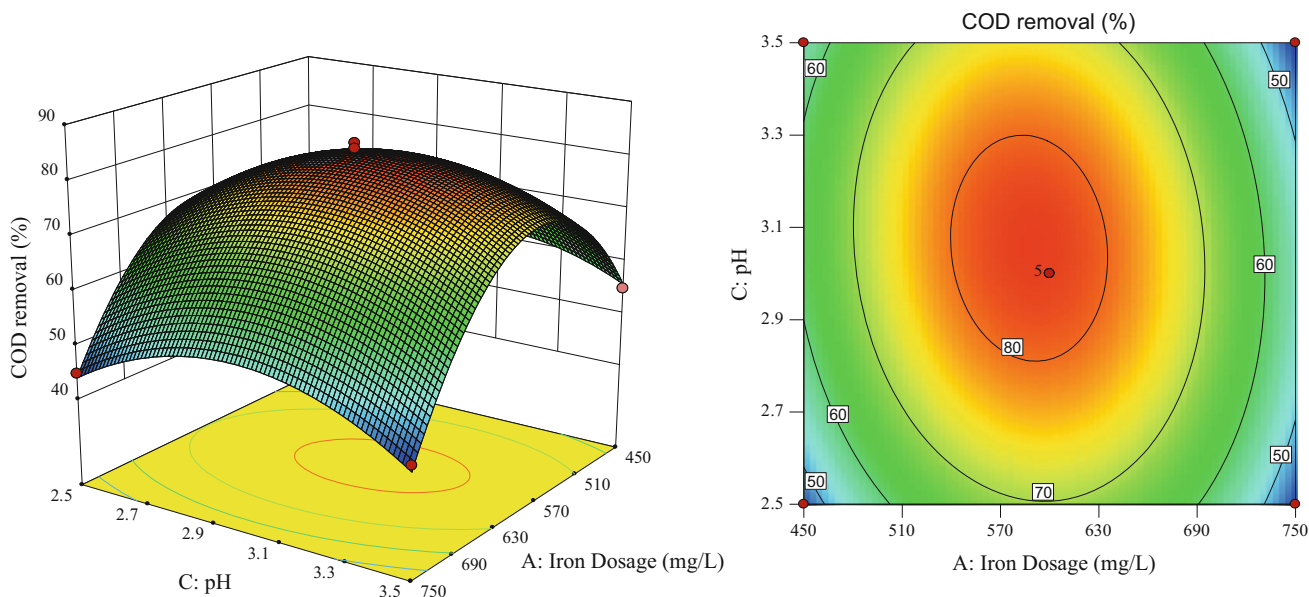


Fig. 5 Response surface and contour plots for the effect of pH on COD removal



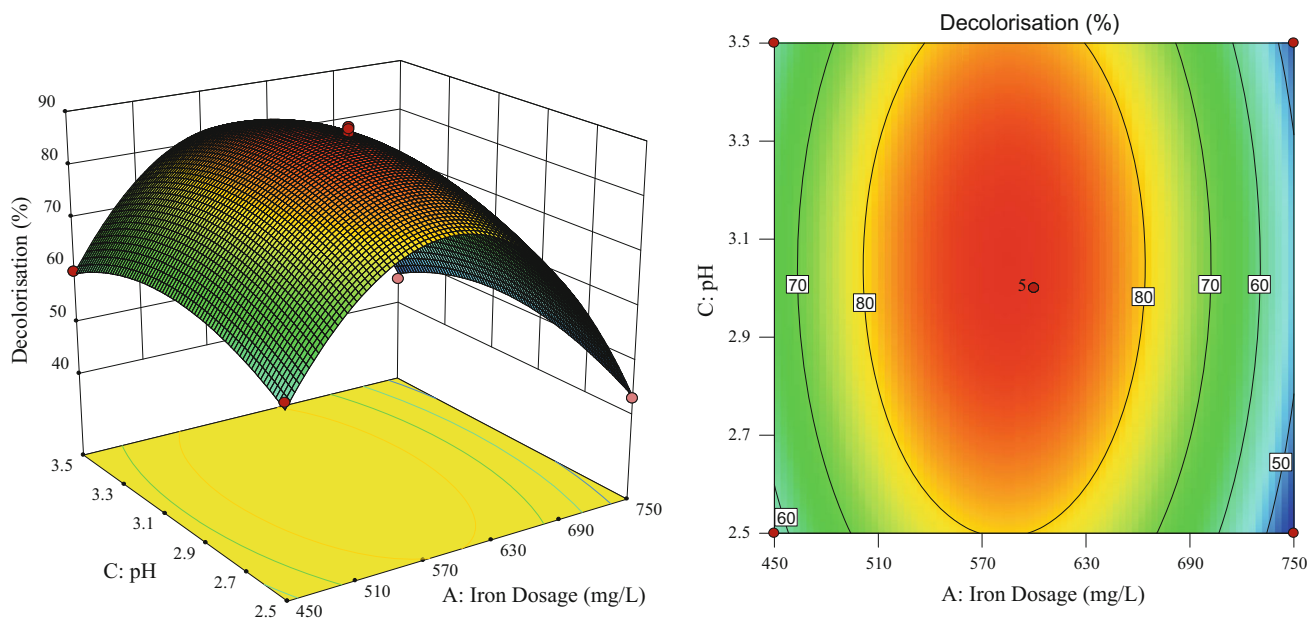


Fig. 6 Response surface and contour plots for the effect of pH on color removal

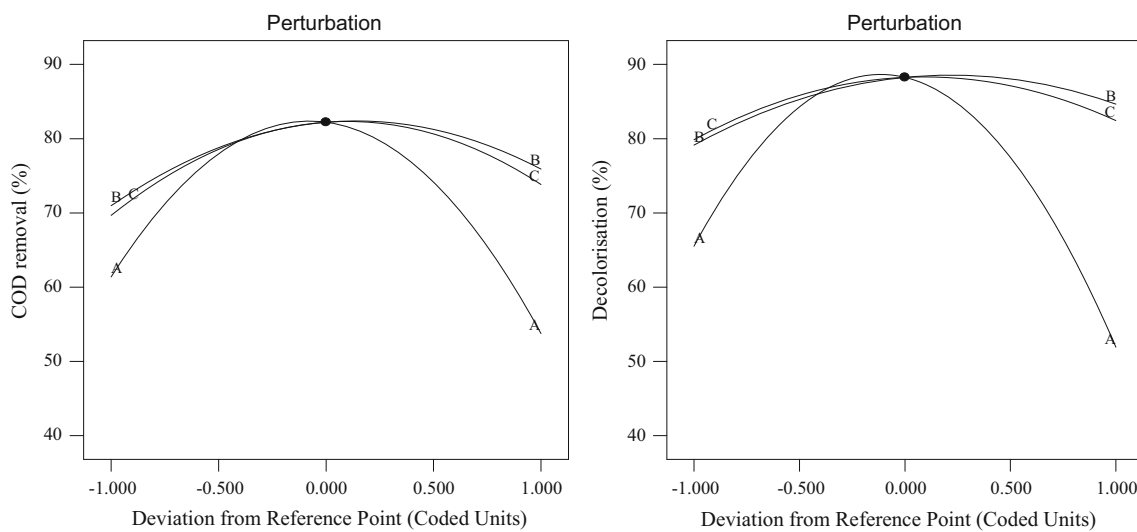


Fig. 7 Perturbation plots for COD and color removal

dose, B represents hydrogen peroxide dose, and C represents pH. It can be seen from the graph that factor A is having the steepest slope as compared to factor B and C having relatively flat slopes for both COD and color removal. A steeper slope is showing that the response is more sensitive to that factor as compared to the other two factors taken for consideration. The plots generated are nothing but “one factor at a time” experimentation where only one factor is varied keeping others constant.

Optimization of Fenton treated simulated textile wastewater for COD and color removal

In case of assorted responses, RSM appoints set of specific working conditions that functions in maximizing all responses or at least keeps them in the desired ranges (Myers and Montgomery 2002). In this study, the chosen objectives in terms of color and COD removal efficiencies were represented as “maximize” to achieve maximum

treatment while the process variables Fe^{2+} and H_2O_2 concentrations were selected to be “minimize” considering operating costs while pH variable was chosen with a condition of “maximize” with reference to less usage of chemicals. Subsequently, optimum working conditions and respective percent removal efficiencies were retrieved. The optimum values obtained with the application of these confined conditions were: Fe^{2+} dose—550 mg/L, H_2O_2 dose—5538 mg/L, pH—3.3 with COD and color removal of 73.86 and 81.35%.

An additional study was conducted applying the optimal conditions to certify the agreement of results achieved from models. It was found that the values obtained were in close agreement with the model values, i.e., COD removal –74.2% and color removal –80.4% with standard deviation of % $\pm 1.23\%$ and ± 2.48 at an interval of $\pm 5\%$. It can be known that COD and color removal response surface plots showed clear peaks which proved that the optimal conditions of Fe^{2+} dose, H_2O_2 dose and pH were within the design boundary. High R^2 values of the models indicated that RSM approach was suitable and precise for predicting Fenton parameters which was conferred well with the experimental results.

Conclusion

In this work, simulated textile wastewater was treated by Fenton method and optimization of operational parameters was studied. Box–Behnken design and response surface methodology were exercised to assess the independent and interactive effects of the parameters involved in study. The quadratic models generated showed immense significance with high values of R^2 showing that the predicted values matched the experimental ones quite fairly. Dosage of iron was the most significant factor as obtained from perturbation plots for both COD and color removal. Also, to check the normality assumption, plot of residuals were found in a straight manner showing satisfactory results for both models. Response surface and contour plots showed the effects of operational parameters in a logical manner. Based on the model prediction, the optimum conditions were obtained as Fe^{2+} dose—550 mg/L, H_2O_2 dose—5538 mg/L, pH—3.3 with COD and color removal efficiencies of 73.86 and 81.35%. Therefore, it was found relevant to use Fenton treatment for simulated textile wastewater. Viewing the results, Fenton treatment will prove as a reasonable method as a pretreatment to textile wastewater where direct biological oxidation is not possible due to the presence of recalcitrant organic molecules of dyes.

Lastly, a considerable attention can be given upon coupling of Fenton process with an optimized dosage with biological aerobic/anaerobic treatment which can lead to environmental friendly and feasible solution to such type of textile wastewaters.

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References

- Alim M, Lee J, Akoh C, Choi M, Jeon M, Shin J, Lee K (2008) Enzymatic transesterification of fractionated rice bran oil with conjugated linoleic acid: optimization by response surface methodology. *LWT Food Sci Technol* 41:764–770
- Alinsafi A, Evenou F, Abdulkarim EM, Pons MN, Zahraa O, Benhammou A, Nejmeddine A (2007) Treatment of textile industry wastewater by supported photocatalysis. *Dyes Pigm* 74(2):439–445
- Anderson M, Whitcomb P (2007) DOE simplified: practical tools for effective experimentation, 2nd edn. Productive Press, New York
- Arslan-Alaton I, Tureli G, Olmez-Hanci T (2009) Treatment of azo dye production wastewaters using Photo-Fenton-like advanced oxidation processes: optimization by response surface methodology. *J PhotoChem PhotoBiol A Chem* 202:142–153
- Azami M, Bahram M, Nouri S, Naseri A (2012) A central composite design for the optimization of the removal of the azo dye, methyl orange, from wastewater using the Fenton reaction. *J Serb Chem Soc* 77:235–246
- Babuponnusami A, Muthukumar K (2014) A review on Fenton and improvements to the Fenton process for wastewater treatment. *J Environ Chem Eng* 2:557–572
- Bahmani P, Maleki A, Ghahramani E, Rashidi A (2013) Decolorization of the dye reactive black 5 using Fenton oxidation. *Afr J Biotechnol* 12(26):4115–4122
- Baş D, Boyacı İ (2007) Modelling and optimization I: usability of response surface methodology. *J Food Eng* 78:836–845
- Bianco B, Michelis I, Veglió F (2011) Fenton treatment of complex industrial wastewater: optimization of process conditions by response surface method. *J Hazard Mater* 186:1733–1738
- Blanco J, Torrades F, Varga D, García-Montaño J (2012) Fenton and biological-fenton coupled processes for textile wastewater treatment and reuse. *Desalination* 286:394–399
- Carlson R, Carlson J (2005) Design and optimization in organic synthesis. Elsevier, Amsterdam
- Chung K, Fulk G, Egan M (1978) Reduction of azo dyes by intestinal anaerobes. *Appl Environ Microbiol* 35:558–562
- Clarke E, Anliker R (1980) Organic dyes and pigments. Handbook of environmental chemistry. Part A: anthropogenic compounds. Springer, New York, pp 181–215
- Cristovao R, Tavares A, Brigida A, Loureiro J, Boaventura R, Macedo E, Coelho M (2011) Immobilization of commercial laccase onto green coconut fiber by adsorption and its

- application for reactive textile dyes degradation. *J Mol Catal B Enzym* 72:6–12
- Dos Santos A, Cervantes F, van Lier J (2007) Review paper on current technologies for decolourisation of textile wastewaters: perspectives for anaerobic biotechnology. *Bioresour Technol* 98:2369–2385
- Emami F, Tehrani-Bagha A, Gharanjig K, Menger F (2010) Kinetic study of the factors controlling Fenton-promoted destruction of a non-biodegradable dye. *Desalination* 257:124–128
- Fathinia M, Khataee A, Zarei M, Aber S (2010) Comparative photocatalytic degradation of two dyes on immobilized TiO₂ nanoparticles: effect of dye molecular structure and response surface approach. *J Mol Catal A Chem* 333:73–84
- Garca-Montano J, Torrades F, Garca-Hortal J, Domenech X, Peral J (2006) Degradation of Procion Red H-E7B reactive dye by coupling a photo-Fenton system with a sequencing batch reactor. *J Hazard Mater* 134:220–229
- GilPavas E, Dobroz- Gómez I, Gómez- García M (2012) Decolorization and mineralization of Diarylide Yellow 12 (PY12) by photo-Fenton process: the response surface methodology as the optimization tool. *Water Sci Technol* 65:1795–1800
- Hsueh C, Huang Y, Wang C, Chen S (2005) Degradation of azo dyes using low iron concentration of Fenton and Fenton-like system. *Chemosphere* 58(10):1409–1414
- Isik M, Sponza D (2008) Anaerobic/aerobic treatment of a simulated textile wastewater. *Sep Purif Technol* 60:64–72
- Kavitha V, Palanivelu K (2005) Destruction of cresols by Fenton oxidation process. *Water Res* 39:3062–3072
- Khataee A, Safarpour M, Naseri A, Zarei M (2012) Photoelectro-Fenton/nanophotocatalysis decolorization of three textile dyes mixture: response surface modeling and multivariate calibration procedure for simultaneous determination. *Electroanal Chem* 672:53–62
- Kwon B, Lee D, Kang N, Yoon J (1999) Characteristics of p-chlorophenol oxidation by Fentons reagent. *Water Res* 33:2110–2118
- Lodha B, Chaudhari S (2007) Optimization of Fenton-biological treatment scheme for the treatment of aqueous dye solutions. *J Hazard Mater* 148:459–466
- Lucas M, Peres J (2006) Decolorization of the Azo dye reactive black 5 by Fenton and Photo-Fenton oxidation. *Dyes Pigm* 71:236–244
- Mansoorian HJ, Bazrafshan E, Yari A, Alizadeh M (2014) Removal of Azo dyes from aqueous solution using Fenton and modified Fenton processes. *Health Scope* 3(2):e15507
- Mason R, Gunst R, Hess J (2003) Statistical design and analysis of experiments. Eighth applications to engineering and science, 2nd edn. Wiley, New York
- Meric S, Kaptan D, Olmez T (2004) Color and COD removal from wastewater containing reactive black 5 using Fenton oxidation process. *Chemosphere* 54:435–441
- Moghaddam SS, Moghaddam M, Arami M (2010) Coagulation/flocculation process for dye removal using sludge from water treatment plant: optimization through response surface methodology. *J Hazard Mater* 175:651–657
- Montgomery D (2010) Design and analysis of experimenters, 7th edn. Wiley India Pvt Ltd, New Delhi
- Myers R, Montgomery D (2002) Response surface methodology: process and product optimization using designed experiments, 2nd edn. Wiley, New York
- Nair A, Makwana A, Ahammed M (2014) The use of response surface methodology for modelling and analysis of water and wastewater treatment processes: a review. *Water Sci Technol* 69(3):464–478
- Nawaz MS, Ahsan M (2014) Comparison of physico-chemical, advanced oxidation and biological techniques for the textile wastewater treatment. *Alex Eng J* 53(3):717–722
- Nidheesh P, Gandhimathi R, Ramesh S (2013) Degradation of dyes from aqueous solution by Fenton processes: a review. *Environ Sci Pollut R* 20:2099–2132
- Puvaneswari N, Muthukrishnan J, Gunasekaran P (2006) Toxicity assessment and microbial degradation of azo dyes. *Indian J Exp Biol* 44:618–626
- Rodrigues C, Madeira L, Boaventura R (2009) Treatment of textile effluent by chemical (Fenton's reagent) and biological (sequencing batch reactor) oxidation. *J Hazard Mater* 172:1551–1559
- Rosales E, Sanromán M, Pazos M (2012) Application of central composite face-centered design and response surface methodology for the optimization of electro-Fenton decolorization of Azure B dye. *Environ Sci Pollut Res* 19:1738–1746
- Sakkas V, Islam M, Stalikas C, Albanis T (2010) Photocatalytic degradation using design of experiments: a review and example of the Congo red degradation. *J Hazard Mater* 175:33–44
- Saldaña-Robles A, Guerra-Sánchez R, Maldonado-Rubio M, Peralta-Hernández J (2014) Optimization of the operating parameters using RSM for the Fenton oxidation process and adsorption on vegetal carbon of MO solutions. *J Ind Eng Chem* 20:848–857
- Sarabia L, Ortiz M (2009) Response surface methodology. In: Brown SD, Tauler R, Walczak B (eds) *Comprehensive chemometrics: chemical and biochemical data analysis*, vol 1. Elsevier, Amsterdam, pp 345–390
- Sevimli MF, Sarikaya HZ (2002) Ozone treatment of textile effluents and dyes: effect of applied ozone dose, pH and dye concentration. *J Chem Technol Biotechnol* 77(7):842–850
- Sun J, Sun S, Sun R, Qiao L, Guo H, Fan M (2007) Degradation of azo dye Acid Black 1 using low concentration iron of Fenton process facilitated by ultrasonic irradiation. *J Ult Sonochem* 14:761–766
- Tunay O, Kabdasli I, Eremetkar G, Orhon D (1996) Color removal from textile wastewaters. *Water Sci Technol* 34(11):9–16
- Ugyur A, Kök E (1999) Decolorization treatments of azo dyes wastewaters including dichlorotriazinyl reactive groups by using advanced oxidation method. *J Soc Dye Colour* 115:350–354
- Wang C, Chou W, Chung M, Kuo Y (2010) COD removal from real dyeing wastewater by electro-Fenton technology using an activated carbon fiber cathode. *Desalination* 253(1–3):129–134
- Welham A (2000) The theory of dyeing (and the secret of life). *J Soc Dye Colour* 116:140–143
- Xu H, Qi S, Li Y, Zhao Y, Li J (2013) Heterogenous Fenton-like discoloration of Rhodamine B using natural schorl as catalyst: optimization by response surface methodology. *Environ Sci Pollut Res* 20:5764–5772
- Yadav A, Mukherji S, Garg A (2013) Removal of chemical oxygen demand and color from simulated textile wastewater using a



- combination of chemical/physicochemical processes. *Ind Eng Chem Res* 52(30):10063–10071
- Zhang H, Choi H, Huang C (2005) Optimization of Fenton process for the treatment of landfill leachate. *J Hazard Mater* 125(1–3):166–174
- Zhou M, Yu Q, Lei L, Barton G (2007) Electro-Fenton method for the removal of methyl red in an efficient electrochemical system. *Sep Purif Technol* 57(2):380–387
- Zhu X, Tian J, Liu R, Chen L (2011) Optimization of Fenton and electro-Fenton oxidation of biologically treated coking wastewater using response surface methodology. *Sep Purif Technol* 81:444–450

