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Removal of Terasil Red R dye by using Fenton oxidation: a statistical analysis

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ABSTRACT

The Fenton oxidation is one of the advanced oxidation processes (AOPs) that produce hydroxyl radicals with the aid of ferrous ions as catalyst. This treatment method was used to study the treatment efficiency of 100 mg/L synthetic dye wastewater comprises of a disperse dye commercially named as Terasil Red R. The treatment efficiency was determined in terms of percentage chemical oxygen demand (COD) removal and percentage color removal. Statistical design of experiment was employed to obtain optimal operating parameters. The optimal parameters were pH 3.5 and H_2O_2/Fe(II) molar ratio of 4. With this optimal condition, the Fenton oxidation was capable to achieve 93% of COD removal and more than 99% of color removal. The process was optimized with 3^2 factorial design and the interaction (dependent) between pH and molar ratio were found to be significant from the analysis of variance (ANOVA).

Keywords: COD and color removal; Factorial design; Fenton oxidation; Optimization; Terasil Red R

1. Introduction

Wastewater that contains dye can be toxic and poses potentially carcinogenic characteristics to the environment. Besides as dye is able to disturb the photosynthetic activities of aquatic plants by absorbing or blocking penetration of sunlight, thus it can be a major threat to the ecosystem [1]. There is a necessity to treat the effluents from dye production and application industries. Dye residues from textile and printing industries are an important source of water contamination, as the effluents discharged by dye processing plants contain high amounts of dyes [2]. These residues cause environmental damage to living organisms by interfering with the re-oxygenation of water bodies, as well as blocking sunlight penetration; the aquatic activities are affected as the consequences [3]. Disperse dyes are nonionic, they do not contain either acidic or basic group in the molecule, have very low solubility or almost insoluble in water at room temperature. Their disperse colloidal form are suitable for dyeing and printing hydrophobic fibers and fabrics, for example, they are usually used to dye cellulose acetate, nylon, polyester fibers from aqueous suspensions [4].

Regulatory authorities are, therefore, becoming more stringent on industrial wastewater treatment,

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waste minimization, and water conservation nowadays. These industries are required to dispose the used or unused chemicals in a proper manner and to keep the concentration of the effluents at minimum level in order to comply with environmental laws and legislations. Different treatment methods have been employed to treat dye wastewater [5]. However, due to the limitation of conventional treatment methods, Fenton oxidation being one of the advanced oxidation processes (AOPs) is able to present as an alternative to remove dye wastewater loads. Fenton oxidation is relatively cheap, easily operated and maintained compared with other treatment methods, since iron is abundant and nontoxic [6].

Fenton oxidation system uses hydrogen peroxide (H_2O_2) and ferrous ion (Fe^{2+}) to generate hydroxyl radicals with strong oxidizing ability to degrade organic pollutants as shown in Eqs. (1)–(5):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-} \tag{1}$$

Ferrous ions initiate and catalyze the decomposition of H_2O_2, generating the hydroxyl radicals ($OH^{\cdot}$):

$$OH^{\cdot} + Fe^{2+} \rightarrow OH^{-} + Fe^{3+} \tag{2}$$

$$OH^{\cdot} + RH \rightarrow H_2O + R^{\cdot} \tag{3}$$

Hydroxyl radicals may react with ferrous ions to form ferric ions (Fe^{3+}) or react with organic pollutant (RH) and continue with further oxidation:

$$OH^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \tag{4}$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \tag{5}$$

Hydroxyl radicals may react with hydrogen peroxide as well to produce other radicals or combine with each other to produce hydrogen peroxide. Moreover, the newly formed ferric ions (Fe^{3+}) may catalyze hydrogen peroxide, ferrous ions, and radicals are produced during the reactions shown in Eqs. (6)–(8):

$$H_2O_2 + Fe^{3+} \leftrightarrow H^{+} + FeOOH^{2+} \tag{6}$$

$$FeOOH^{2+} \rightarrow HO_2^{\cdot} + Fe^{2+} \tag{7}$$

$$HO_2^{\cdot} + Fe^{2+} \rightarrow O_2 + Fe^{3+} + H^{+} \tag{8}$$

The reaction rate in Eq. (1) is much faster than that in Eq. (6) as ferrous ions are consumed quickly but reproduce slowly. Thus, as there is large amount of ferrous ions, large amount of hydroxyl radicals are formed and lead to fast oxidation rate of organic compounds [7].

The overall Fenton reaction can be simplified into Eq. (9) by accounting for the dissociation of water. The products from oxidation are usually low molecular weight oxygenated compounds that are easily biodegradable [8–10], or, the organic compounds are reduced to carbon dioxide and water.

$$Fe^{2+} + H_2O_2 + 2H^{+} \rightarrow 2Fe^{3+} + 2H_2O \tag{9}$$

The aim of this study is to determine the efficiency of chemical oxygen demand (COD) and color removal. Several parameters are having great influence on dye removal efficiency, such as pH, concentration of hydrogen peroxide, concentration of ferrous ion, and initial concentration of dye solution. These parameters were investigated to establish the optimal conditions for effectiveness of this system through factorial design.

2. Materials and methods

2.1. Chemicals

Terasil Red R (CI Disperse Red 324), a commercial disperse dye powder was procured from CIBA and was used directly without further purification. Characteristics of Terasil Red R were given in Table 1. Hydrogen peroxide, H_2O_2 (35%), was obtained from R&M chemicals; ferrous (II) sulfate heptahydrate, $FeSO_4.7H_2O$, was obtained from Merck, and NaOH and H_2SO_4 were obtained from Systerm ChemAR. Distilled water was used for the preparation of all dye solutions, stock solutions, and dilution of acid and base in this study.

2.2. Methods

All experiments were conducted by using a standard Jar Test apparatus. The dye solutions were

Table 1
General characteristics of Terasil Red R dye solution

Characteristics	Value
Class	CI Disperse Red 324
Concentration	100 mg/L
Volume	100 mL
pH*	6.08
COD*	118 ± 2.050 mg/L
Colour point*	3,290 ± 20.432 PtCo

*Average value of 20 samples.

fixed at 100 mg/L with 100 mL working volume in each run. H_2SO_4 and NaOH were used for pH adjustment prior to the addition of Fe(II) and H_2O_2.

Desired amount of Fe(II) was added into the synthetic dye wastewater, the beaker was then placed in the Jar Test apparatus. Hydrogen peroxide (H_2O_2) was added slowly into the solution while it was being stirred. After 30 min stirring at 100 rpm, the sample was allowed to settle for 30 min. Mixing time and speed had no influence in this treatment method as reported. Filter paper (Whatman No. 4, pore size 20–25 m) was used to filter the sample. The filtrate was used for COD and color point measurements. Color point measurement is reported as true color according to the spectrophotometric-single wavelength method using DR 2800 HACH spectrophotometer adopted from Standard Methods, Method No. 2120C, in which true color of samples and platinum cobalt standards follows Beer's Law. COD was determined using the closed reflux, colourimetric method according to procedures in Standard Methods, Method No. 5220D. Samples were placed in ampules followed by the addition of COD digestion solution and inverted several times to ensure complete mixing before being placed in COD reactor which was preheated to !50˚C. Samples were kept refluxed for 2 h. After 2 h, samples were left to cool to room temperature before the measurementof COD absorption at 620 nm wavelength by a DR 2800 HACH spectrophotometer was conducted [11].

The COD removal efficiency can be calculated using the equation below:

$$\text{COD (mg/L)} = (\text{Instrument reading}) \times (\text{Dilution factor})$$

$$\text{Percentage of COD removal} = M_i - M_f/M_i \times 100$$

where M_i = Initial COD content (mgO_2/L), M_f = Final COD content (mg O_2/L).

The efficiency of color removal from the dye water can be calculated using the formula below:

$$\text{Color (unit PtCo)} = (\text{Instrument reading}) \times (\text{Dilution factor})$$

Dilution factor = volume of sample + volume of distilled water/volume of sample

$$\text{Percentage of color removal} = C_i - C_f/C_i \times 100$$

where C_i = initial color concentration (PtCo), C_f = final color concentration (PtCo).

2.3. Factorial design

Three-level factorial design was employed to study the effect of two factors pH and molar ratio and their joint effect on the two responses; percentage of color removal and percentage of COD removal, this design is called 3^2 factorial design [12]. This design is capable to generate the smallest number of treatment combinations with which factors can be studied in a complete factorial arrangement. Thus, valid results can be obtained at a reduced time and cost, compared with results obtained from conventional approach [13]. The experiment was run with two replicates and the total number of runs was 18. Factorial design allows identifying the significant effect on each response since the effect of each factor is to be estimated at different levels of other factors. Furthermore; factorial design allows the experimenter to study the interaction between different factors which is ignored by using one factor at a time. The results obtained from 3^2 factorial designs were analyzed using design expert software version 6.0.10 to identify the significant effect of different factors and then optimize the process.

2.4. Analyses

Results of the experimental designs were analyzed by using Design Expert statistical software to estimate the response of each dependent response variable and to obtain the mean square, degree of freedom and other statistical parameters of the model. The optimized condition was obtained from the generated regression equation. Quality of fit was expressed by the coefficient of determination R^2, and statistical significance was analyzed by the analysis of variance (ANOVA). The level of significance at 5% probability level was given by P less than 0.05. The effect of experimental factor is considered to be significant when P-value is small (<0.0001).

3. Results and discussion

3.1. Effect of pH

The effect of pH was studied by keeping H_2O_2 and Fe(II) constant at their respective optimal concentrations. The effect of pH toward treatment efficiency in terms of percentage of COD removal and percentage color removal is presented in Fig. 1. There is about 5% COD removal at pH 2. The COD removal increases and achieves maximum value (85%) at pH 3.5 and decreases drastically after pH 9, as shown in Fig. 1. Color removal is reported to be 99% from pH 2.5 to pH 9. Relatively low color removal is reported at pH 2 and pH 10, which are 27 and 14%,

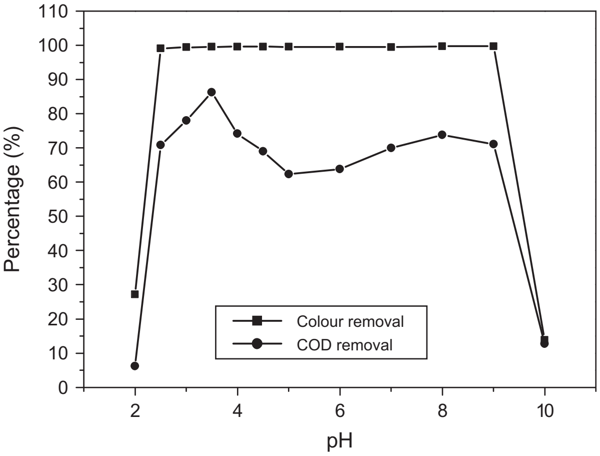

Fig. 1. COD removal (%) and color removal (%) against pH.

respectively. Relatively higher COD removal is achieved at lower pH because hydrogen ion (H^+) is required in the decomposition of hydrogen peroxide [7]. The best treatment is achieved at pH 3.5, where there is abundance of ferrous ion. Treatment efficiency is low at low pH (pH 2), this could be due to hydrogen peroxide is not fully decomposed by ferrous ion and no hydroxyl radical is produced. Thus, the dye is hardly decomposed due to the unavailability of hydroxyl radical. Hydrogen peroxide could stay stable in this condition probably because of the formation of an oxonium ion $(H_3O_2^+)$ by solvating a proton. Hydrogen peroxide becomes electrophilic and more stable with the presence of oxonium ion, as a presumably result, reactivity with ferrous ion is reduced significantly [14]. Besides, Eq. (10) suggests that hydroxyl radical scavenging of ions could cause the low treatment efficiency at pH 2 and below. This reaction between hydroxyl radical and hydrogen becomes important at low pH [15].

$$OH^{\cdot} + H^+ + e^- \rightarrow H_2O \qquad (10)$$

Apart from these, inhibition of hydroxyl radical formation at low pH, could be due to the small amount of formation of soluble iron (Fe^{3+}) which is responsible for the continuity of the oxidation process, occurring in the formation of $Fe(OH)^{2+}$ and $Fe(OH)_2^+$ [16]. The solubility of Fe^{3+} in solution decreases exponentially from pH 2.6 to 3.2 at ambient temperature. Thus, the regeneration of ferrous ion by the reaction of ferric ion with hydrogen peroxide is inhibited [17].

On the other hand, significant decrease in treatment efficiency at pH 9 and above is seen in Fig. 1. This is probably due to the decrease in free iron species in the solution, precipitation of ferric ion to $Fe(OH)_3$, which hinder the reaction between ferric ion and hydrogen peroxide and therefore inhibit the regeneration of ferrous ion. Moreover, $Fe(OH)_3$ is able to catalyze the decomposition of hydrogen peroxide to oxygen and water in which results in low production of hydroxyl radical. Besides there is a possibility of formation of highly stable Fe(II) complexes and ferric hydroxy complexes from ferric ions when the pH is higher than 9, which interfere with the reaction of ferrous ion and hydrogen peroxide. Apart from the pH effects on ferrous ion, hydrogen peroxide is unstable in alkaline condition and may decompose to oxygen and water, where it loses its oxidation ability and leads to low treatment efficiency [18–20].

3.2. Effect of H_2O_2 dosage

Fig. 2 shows that percentage of COD removal and color removal vs. dosage of hydrogen peroxide.

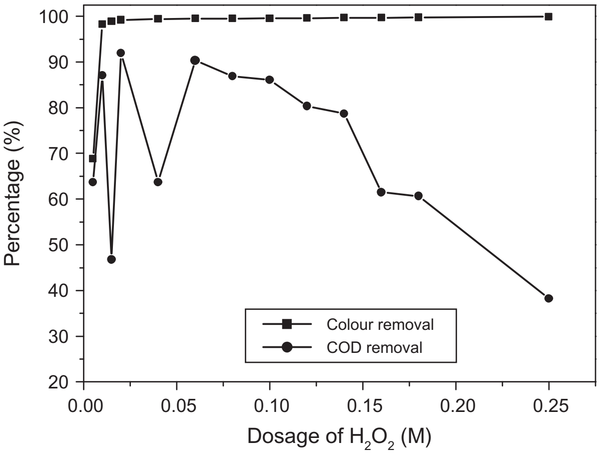

Fig. 2. COD removal (%) and color removal (%) against H_2O_2 dosage at pH 3.5.

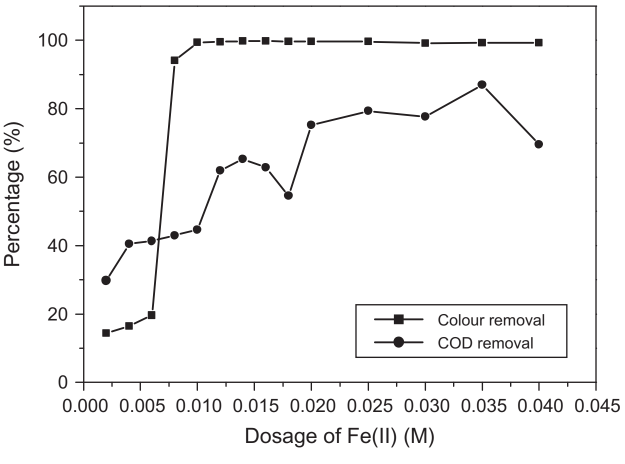

Fig. 3. COD removal (%) and color removal (%) against Fe(II) dosage at pH 3.5.

Dosage of ferrous ion was fixed at 0.015 M, while the initial concentration of dye was 100 mg/L. Dosage of hydrogen peroxide as one of the operating parameters in Fenton oxidation has a significant effect on the dye removal efficiency. Apparently, the best dosage for the color removal of Terasil Red R dye solution is 0.02 M of H_2O_2, which achieves more than 90% of COD removal and more than 99% of color removal. At dosage of H_2O_2 lower than 0.02 M, there is only 45–90% of COD removal and 68–98% of color removal. However, COD removal decreases when H_2O_2 dosage is higher than 0.02 M. Color removal remains constant (>99%) from 0.06 to 0.25 M of H_2O_2 dosage.

Color removal efficiency is low at low H_2O_2 dosage as insufficient hydroxyl radicals are generated, and the oxidation is slow. Further increase in H_2O_2 dosage decreases the treatment efficiency in which it could be attributed to the scavenging nature of hydrogen peroxide toward hydroxyl radical. Hydrogen peroxide may undergo further decomposition upon neutralization; however, large amount of H_2O_2 would require necessary time for sufficient removal prior to final discharge [21]. It is noticeable that color removal is generally higher than COD removal from Fig. 2. This could be attributed to the organic compounds are decomposed to smaller organic compounds in their structure but they still contribute to the COD, although the dye solution is decolourized by the cleavage of azo double bonds or aromatic linkages, as a result of Fenton oxidation [22].

Table 2
Input factors of 3^2 factorial design in Fenton oxidation

Experiment	Experimental factors	
	pH	Molar ratio H_2O_2/Fe(II)
1	3.50	6
2	3.50	4
3	4.50	4
4	2.50	4
5	4.50	4
6	2.50	6
7	4.50	2
8	2.50	6
9	4.50	6
10	3.50	6
11	3.50	4
12	3.50	2
13	4.50	2
14	3.50	2
15	4.50	6
16	2.50	4
17	2.50	2
18	2.50	2

3.3. Effect of Fe(II) dosage

The effect of Fe(II) dosage was studied by varying the dosage from 0.002 to 0.040 M, while other parameters were fixed, H_2O_2 dosage at 0.015 M and the initial concentration of dye at 100 mg/L. Fig. 3 shows the COD removal and color removal of Terasil Red R dye solution vs. different Fe(II) dosage. Relatively low treatment efficiency is found at low dosage of Fe(II) (0.002–0.010 M), which only achieves 42–44% of COD removal and 15–94% color removal. The treatment efficiency increases with further increase in Fe(II) and reaches the highest COD removal at 0.035 M of Fe(II) in which it is able to reduce 87% of COD and remove 99% of color. However, the COD removal starts to decrease after 0.035 M of Fe(II) and color removal values remain constant at 99% from 0.0010–0.040 M of Fe(II).

The treatment efficiency of Terasil Red R is relatively low at low dosage of Fe(II). This is probably due to insufficient of Fe(II) ions and causing low production of hydroxyl radicals available for Fenton reaction. Treatment efficiency increases with Fe(II) dosage, because as the amount of Fe(II) and Fe(III) ions increase, the catalytic effect on H_2O_2 also

Table 3
The result of ANOVA for COD removal

Source	SS	DF	MS	*F* value	Prob > *F*
Model	7200.63	8	900.08	705.66	<0.0001
pH	5508.85	2	2754.43	2159.45	<0.0001
Molar ratio	168.35	2	84.17	65.99	<0.0001
pH x molar ratio	1523.44	4	380.86	298.59	<0.0001
Error	11.48	9	1.28		
Total	7212.11				

Note: SS: sum of squares; DF: degrees of freedom; MS: mean square; *F* value: *F*-test value and Prob > *F*: probability of observed *F* value.

Table 4
The result of ANOVA for color removal

Source	SS	DF	MS	*F* value	Prob > *F*
Model	12823.23	8	1602.90	683.66	<0.0001
pH	7313.18	2	3656.59	1559.59	<0.0001
Molar ratio	1850.43	2	925.22	394.62	<0.0001
pH × molar ratio	3659.62	4	914.91	390.22	<0.0001
Error	21.10	9	2.34		
Total	12844.33	17			

Note: SS: sum of squares; DF: degrees of freedom; MS: mean square; *F* value: *F*-test value and Prob > *F*: probability of observed *F* value.

increases [15,23]. As the dosage of Fe(II) increases higher than 0.035 M, a large amount of Fe(II) ions leaches out easily in the form of $Fe(OH)_2$ in acidic environment, therefore, causing COD removal to decrease. Besides excess Fe(II) may tend to scavenge the hydroxyl radicals formed, thus, decreases the treatment efficiency. The excess amount of Fe(II) in the presence of organic dye, and ferrous ion is utilized as a major reactant, not as a catalyst in the Fenton reaction [24].

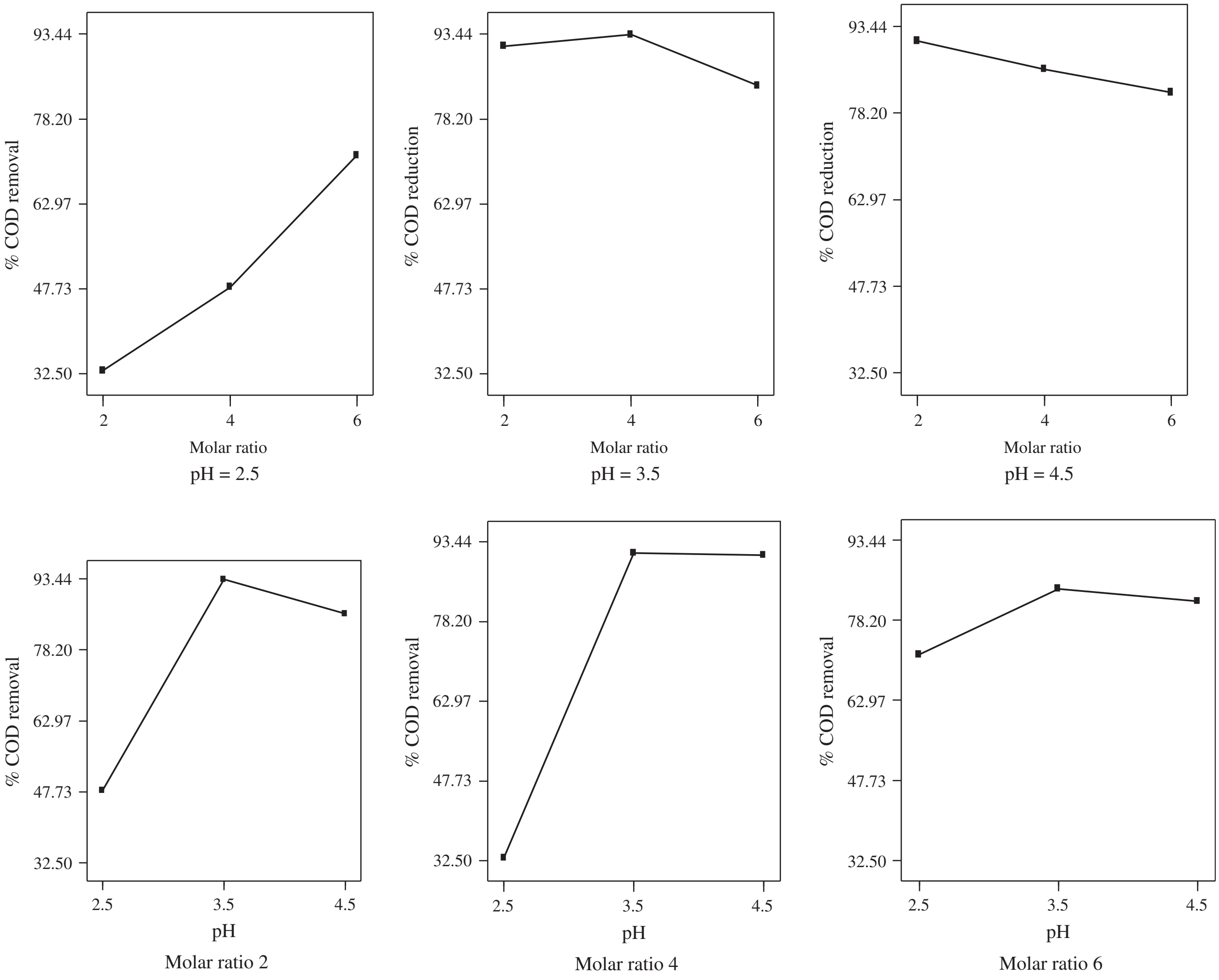

Fig. 4. The behavior of pH and molar ratio individually on COD removal (%).

3.4. Process optimization

In Fenton oxidation, the effect of two factors pH and molar ratio on the two responses, removal efficiencies for COD and color were studied. The levels of each factor are given in Table 2. The range of each factor was chosen based on preliminary experiments as discussed previously. The results obtained from 3^2 factorial design with 18-run were analyzed using ANOVA. The results of ANOVA exhibited that the effect of pH and molar ratio was significant on COD and color removal efficiency as shown in Tables 3 and 4. Furthermore, the analysis showed that the interaction between pH and molar ratio was significant which indicates that the effect of each factor depends on the presence of other factor. Regression model was fitted to the data. Regression models for COD removal and color removal are given in Eqs. (11) and (12), respectively.

$$\begin{aligned}\%\ \text{COD removal} = 75.59 &- 24.66A[1] + 14.03A[2] \\ &- 3.84B[1] + 0.20B[2] \\ &- 14.03A[1]B[1] + 5.51A[2]B[1] \\ &- 3.07A[1]B[2] + 3.54A[2]B[2]\end{aligned} \tag{11}$$

$$\begin{aligned}\%\ \text{color removal} = 85.29 &- 28.51A[1] + 14.17A[2] \\ &- 9.75B[1] - 4.23B[2] \\ &- 19.31A[1]B[1] + 9.67A[2]B[1] \\ &- 8.51A[1]B[2] + 4.27A[2]B[2]\end{aligned} \tag{12}$$

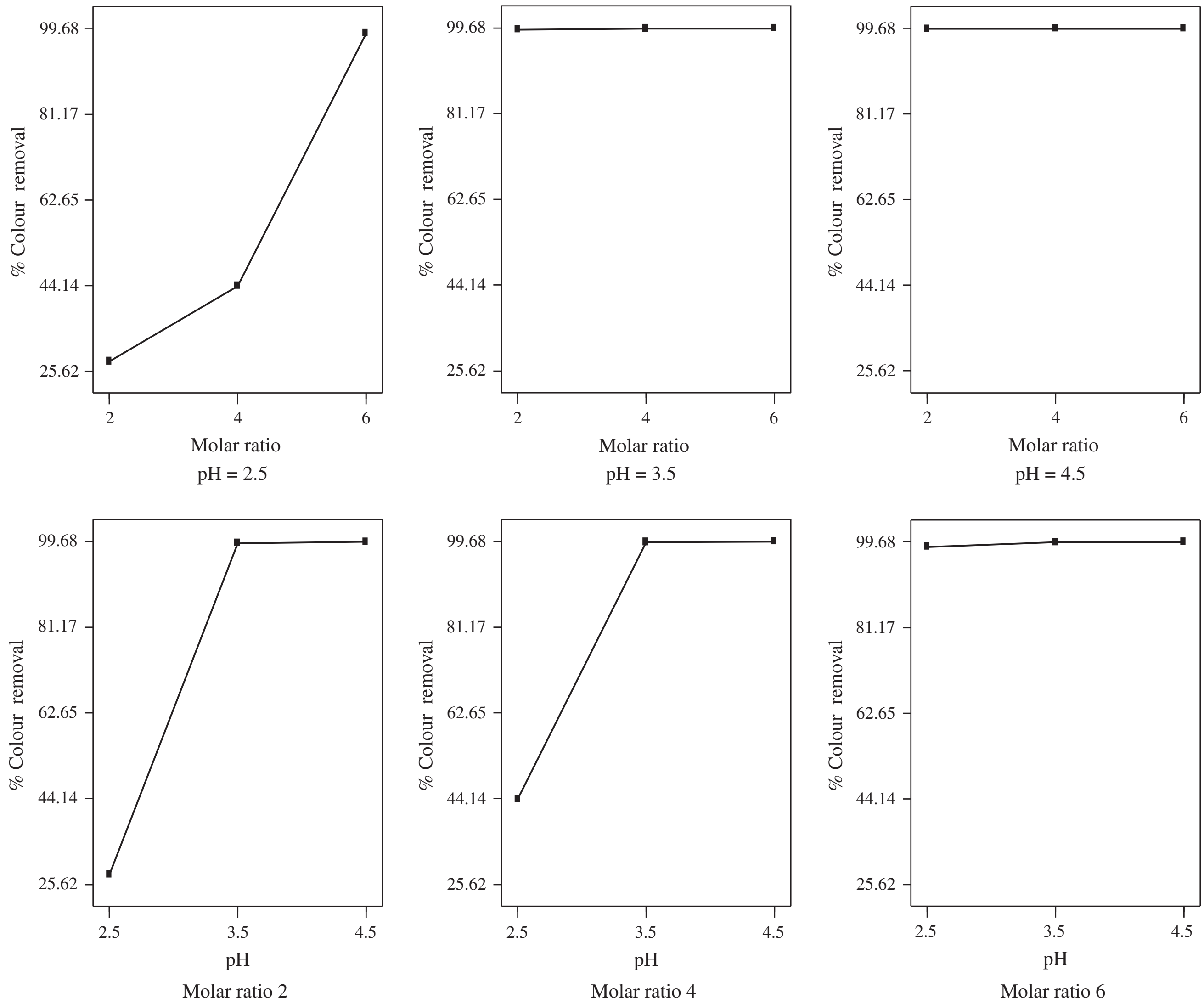

Fig. 5. The behavior of pH and molar ratio individually on colour removal (%).

where A is pH and B is molar ratio; [1] and [2] denote codes of "dummy variables"where pH at low level, $A1 = 1$; $A2 = 0$; pH at intermediate level, $A1 = 0$; $A2 = 1$; pH at high level, $A1 = 0$; $A2 = 0$. For molar ratio 2, $B1 = 1$; $B2 = 0$; molar ratio 4, $B1 = 0$; $B2 = 1$; molar ratio 6, $B1 = 0$; $B2 = 0$.

Regression models in Eqs. (11) and (12) are satisfied since the values of coefficient of determination (R^2) are high and close to 1. The values of R^2 for COD removal and color removal are 0.998 for both models which indicates that more than 99% of the total variation is explained by the model and less than 1% due to unknown source. The behavior of each factor individually is graphed as given in Figs. 4 and 5 for pH and molar ratio. Interaction plot between pH and molar ratio are given for COD removal and color removal in Fig. 6.

At pH 3.5, COD removal achieves 91% at molar ratio 2, 93% at molar ratio 4 and 84% at molar ratio 6, while color removal is almost constant above 99% for molar ratio 2, 4 and 6, as shown in Figs. 4 and 5. This phenomenon can be explained by the Fenton's reaction mechanisms proposed by several researchers [25–28]. When $H_2O_2/Fe(II)$ molar ratio is low, the reaction rate follow second order and the stoichiometry of $2Fe(II) \approx H_2O_2$. As the molar ratio increases, the reaction kinetics approaches as zero order. However, at high molar ratio, one or more side reactions would occur (Eqs. (13) and (14)) and causes to the changes in their mechanism [29], thus the reaction becomes independent of hydrogen peroxide:

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + H^+ + O_2 \tag{13}$$

$$Fe^{2+} + HO_2^{\cdot} \rightarrow Fe^{3+} + HO_2^- \tag{14}$$

From Fig. 4, the highest COD removal is achieved at pH 3.5. However, low removal is found at lower pH and higher pH. The interaction between pH and molar ratio is given in Fig. 6 by showing the behavior of each factor in the presence of other factors. The COD removal and color removal is plotted vs. pH 2.5, 3.5, and 4.5 at molar ratio 2, 4, and 6, respectively. In Fig. 6, and it is noted that relatively low treatment efficiency is achieved at low pH and low molar ratio. There are around 25 and 45% of color removal at pH 2.5 for molar ratio 2 and 4, respectively. The % color removal increases with pH, which reaches more than 99% at pH 3.5 and pH 4.5.

Using factorial experiment can help the researchers to find the best setting (levels) for the selected factors.

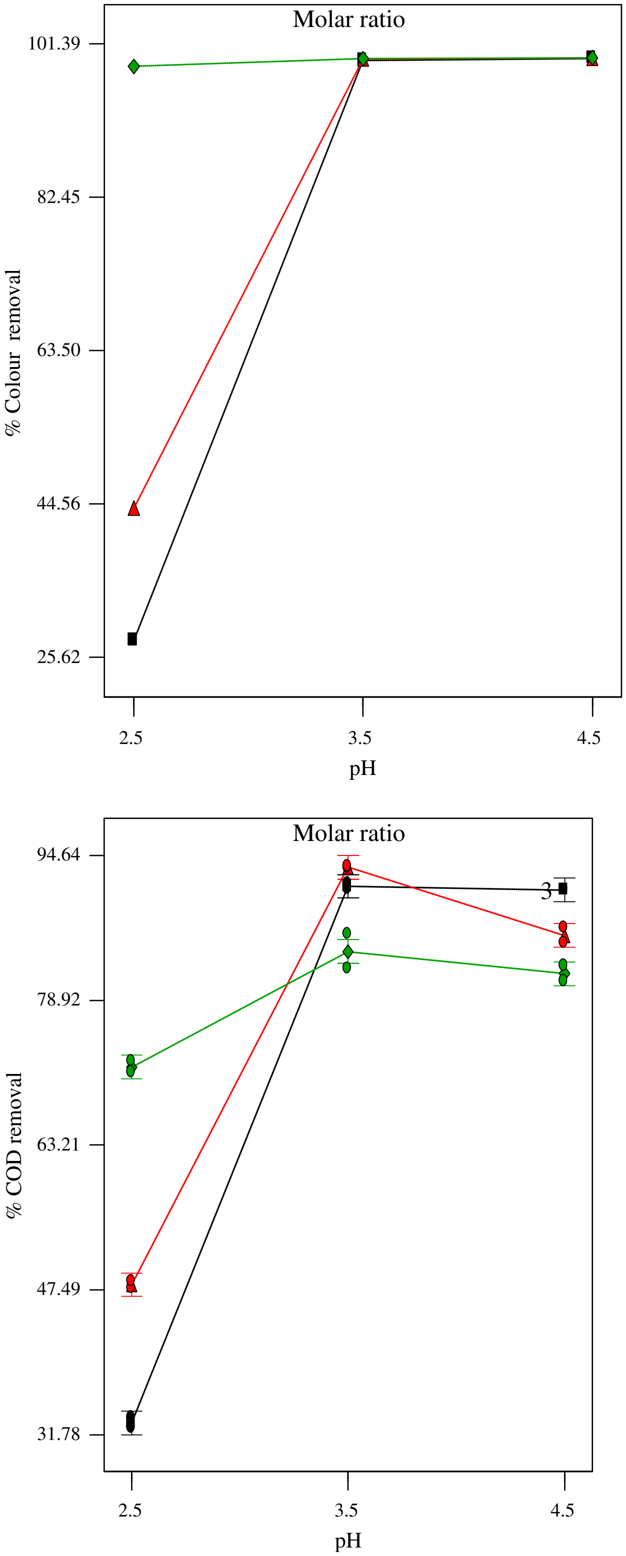

Fig. 6. Interaction plot between pH and molar ratio for COD removal (%) and color removal (%).

The objective of this research is to find maximum COD removal and color removal. Maximum COD removal and color removal was achieved at pH 3.5 and molar ratio 4. The results for COD removal and color removal were 93.28 and 99.53%, respectively. A confirmation experiment was carried out, and the results were found as 91.98% COD removal and 99.32% color removal.

4. Conclusions

The efficiency of dye removal by Fenton oxidation was greatly affected by pH and the dosage of Fenton's reagent. A design of experiment was conducted to optimize the parameters of pH and molar ratio of $H_2O_2/Fe(II)$. The 3^2 factorial designs were employed, since the interaction of pH and molar ratio was significant from the results of ANOVA. Meanwhile, the optimum conditions to achieve the best COD removal and color removal were at pH 3.5 and molar ratio 4 of $H_2O_2/Fe(II)$. The regression model had predicted 93.28% COD removal and 99.53% color removal; experimentally, 90.98% COD removal and 99.32% color removal were obtained.

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