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The use of full factorial design for modeling the effects of process parameters on decolorization of Reactive Yellow 15 by using Fe/ZrO_2 catalyst

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ABSTRACT

This study is an application of full factorial design to determine the effects of operational parameters on heterogeneous Fenton oxidation of Reactive Yellow 15 (RY15). Fenton oxidation was conducted using a Fe/ZrO_2 catalyst in the presence of hydrogen peroxide (H_2O_2) in a batch process. The effects of pH of the reaction, catalyst concentration and reaction time were examined under the following conditions: 28°C of temperature, 50 ppm initial dye concentration, 6% Fe and 50 mM H_2O_2 concentration. The factors and levels used during experiments were as follows: initial pH (2.0 and 6.0), catalyst concentration (0.1 and 0.3 g/25 mL), contact time (60, 120 min). The significance of the effects was investigated by the analysis of variance (ANOVA) with a confidence level of 95%. After the statistical procedure, analysis of variance, studentized *t*-test, and residual analysis, the regression model equation was obtained for RY15 decolorization. The ANOVA results showed that the catalyst concentration (B) had the greatest positive effect on RY15 removal, followed by pH (A) with a negative effect and contact time (C) with a positive effect. When the initial pH was 2, catalyst concentration was 0.3 g/25 mL, and the contact time was 120 min, the maximum RY15 removal efficiency was obtained as 94.89%.

Keywords: Dye; Reactive Yellow 15; Fenton oxidation; Catalyst; Fe/ZrO_2; Full factorial design

1. Introduction

The azo dyes have such wide types as acidic, reactive, disperse, vat, metal complex, mordant, direct, basic and sulphur. Among these, the reactive azo dyes are the most used and are the most problematic pollutants of textile wastewaters [1]. The decolorization of this kind of wastewater is very important in public water treatment plants due to aesthetic reasons. Besides, many dyes and their breakdown products are not also toxic to aquatic life but also mutagenic to humans [2]. Due to the variability of organic dyes and the resultant waste solution, it is difficult to treat this kind of wastewater using traditional treatment processes [3]. The traditional treatment techniques applied in textile wastewaters, such as coagulation/flocculation, membrane separation (ultrafiltration, reverse osmosis) or elimination by activated carbon adsorption, and biological treatment [1]. Biological treatment is not a complete solution to the problem due to biological resistance of some dyes. Other methods are usually non-destructive, inefficient, costly and usually results in the production of secondary waste products. Therefore, purification of azo dye wastewater is becoming a matter of great concern and it is necessary to develop novel and cost-effective technologies to treat azo dye wastewater [4].

Advanced oxidation processes (AOP) using ozone, titanium dioxide (TiO_2), ultra violet (UV), and Fenton's reagent (H_2O_2 and ferrous ion) have received considerable attention

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as effective pretreatment processes of less biodegradable wastewater [5,6]. Among AOP, one of the most well-known method is the oxidation with Fenton's reagent, where hydrogen peroxide reacts with iron in acidic medium, leading to the production of powerful radicals (HO·), which are able to attack the organic compounds [7]. Additionally, the Fenton process is the complete destruction of pollutants to harmless compounds, such as carbon dioxide and water [8]. Besides, Fenton oxidation is relatively cheap, easily operated and maintained compared with other treatment methods, since iron is abundant and nontoxic [9]. However, the use of Fe(II)/Fe(III) as a homogeneous catalyst has several disadvantages [10] such as i) the requirement to remove Fe ions from water after wastewater treatment and catalyst loss due to formation of sludge as a result of the precipitation of iron hydroxide, and ii) the necessity to work in the tight range of pH (2–3) for a good catalytic performance [11–13]. These disadvantages could be overcome by using heterogeneous catalysts in the Fenton system, which often incorporates the iron ions or iron oxides into the catalyst support. Unlike the homogeneous Fenton reaction, immobilized Fenton catalytic systems provide the possibility of working in a wider pH range and to recover and reuse solid iron catalyst [12,14].

Several authors have studied different types of iron catalysts immobilized on an inert support surface [11,13,15–21]. The criteria for the choice of catalyst support are mainly based on availability, cost and the composition of the support to be applied for the decomposition of H_2O_2 and for the pollutants to be degraded [12]. Among these inert supports, ZrO_2 is a well-known active metal oxide catalyst utilized in many chemical reactions [22]. It is increasingly used as a support in catalyst. It has low thermal conductivity, and high corrosion resistance [23]. Therefore, in this study, we have selected the Fe/ZrO_2 as metal oxide catalyst.

The Heterogeneous Fenton techniques depend on various parameters such as the catalyst concentration, H_2O_2 concentration, pH, reaction time, stirring speed and temperature. In conventional methods used to determine the influence of each of these factors, experiments are carried out by systematically changing the studied factors and keeping the others as constant [24]. Experimental design is a powerful technique that reveals the possible interactions with a minimum number of experiments and reduces the time and overall research cost [25,26]. Additionally, the most important advantage of experimental design is the evaluation opportunity of not only the effects of individual parameters but also their relative importance in a given process. The interaction of two or more variables can also be derived in contrast to classical experiment of one factor at a time [24].

Factorial designs are widely used in experiments involving several factors where it is necessary to study the joint effect of the factors on a response [27]. This study is an application of the full factorial design of experiment to determine the effects of operational parameters on the heterogeneous Fenton-type oxidation of the RY15.

In this study, heterogeneous catalyst (Fe/ZrO_2) was synthesized and used in the decolorization of RY15. In order to find out the optimum Fenton oxidation conditions, a two-level factorial design (2^3) was used. To the best of our knowledge, a statistical design of color removal of RY15 using Fe/ZrO_2 as a catalyst has not been reported previously.

2. Materials and Methods

2.1. Materials

Reactive Yellow 15 (RY15) dye ($C_{20}H_{20}N_4Na_2O_{11}S_3$, MW= 634.57 g/mol, λ_{max} = 413 nm) was obtained from Burboya (Bursa, Turkey). The chemical structure of RY15 is shown in Fig. 1. Hydrogen peroxide (30% wt/wt) and $Fe(NO_3)_3{\cdot}9H_2O$ as a source for Fe^{3+} ions were purchased from Sigma-Aldrich. $ZrO(NO_3)_2{\cdot}6H_2O$ was supplied from Acros. All chemicals were used without any subsequent purification. Moreover, all of the solutions were prepared using distilled water.

2.2. Methods

2.2.1. Preparation of the catalyst

Co-precipitation procedure was used to synthesize the catalyst. For this purpose, solutions containing the metal salt and salt of a compound that would be converted into the support were contacted by stirring with a base solution in order to precipitate as hydroxide form. After washing, it is converted into oxides by being heated.

According to general procedure given above, Fe/ZrO_2 (6% w/w) catalyst was synthesized. First of all, $Fe(NO_3)_3{\cdot}9H_2O$ and $ZrO(NO_3)_2{\cdot}6H_2O$ salts were dissolved in 100 mL of distilled water. Then, the solution was heated up to 65°C by stirring. The pH of this solution was increased from 8 to 9 by adding NH_4OH with 10 mL/min. The next step on the process was aging of the solution for 2 h at 65°C and stirring at 300 rpm. After the aging process, the precipitate was washed with ethanol and dried for 24 h in an oven at 110°C. Finally, grounded precipitate was calcined at 600°C for an hour in dry air atmosphere [28,29].

2.2.2. Decolorization of azo dye from dye solution

Experiments were carried out at 28°C temperature in 100 mL flasks kept in thermostatic water-bath with 25 mL of reaction mixture of dye, Fe/ZrO_2 catalyst and H_2O_2. The required amounts of catalyst and H_2O_2 were added simultaneously into the dye solution. Thereafter, samples were withdrawn periodically and centrifuged to remove suspended particles for 5 min and analyzed using a UV–vis spectrophotometer (Shimadzu, model UV-120-01) at maximum wavelength. Finally, the color removal was determined using Eq. (1).

$$\%\ \text{Color removal} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \tag{1}$$

where C_0 is the initial dye concentration in mg/L and C_t is dye concentration at any time t.

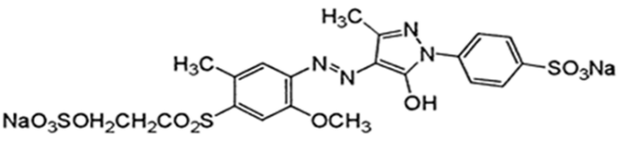


Fig. 1. Structure of RY15.

3. Results and Discussion

3.1. Preliminary experiments

Fe/ZrO_2 (6% w/w) catalyst was characterized by XRD (X-ray Diffraction). XRD pattern of the catalyst is shown in Fig. 2. As seen in Fig. 2, molecular structure of Fe/ZrO_2 catalyst is highly crystalline of tetragonal symmetry.

Initially, preliminary experiments were conducted to decide the most influential operating parameters such as pH, catalyst concentration, contact time and their levels. Some results of preliminary experiments were shown in Fig. 3. The effect of pH was investigated in the range of 2–6 under the following conditions: 28°C of temperature, 50 ppm initial dye concentration and 50 mM H_2O_2 concentration. High temperature more than 28°C was not preferred because of its high cost in macro scale. According to the Fig. 3(a), when the contact time is 120 min and catalyst concentration is 0.3 g/25 mL, the low level of pH = 2 significantly increases color removal. On the other hand, when the pH = 2, and the contact time = 120 min, maximum color removal (94.89%) was reached at catalyst concentration of 0.3 g/25 mL as seen in Fig 3(b). Fig 3(c) shows that low initial dye concentration has a positive impact on color removal when all the parameters are constant. Finally, according to the Fig 3(d) the optimum color removal was reached at 150 min contact time with the value of 95.44. However, when the contact time is held at 120 min, there is a slight difference for the percentage color removal (94.89), so the contact time can be held at 120 min by considering economic conditions in macro scale.

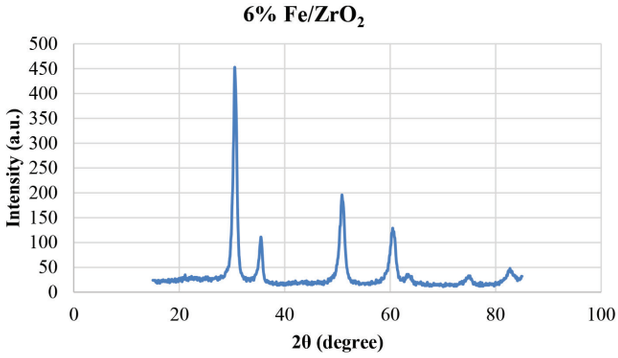
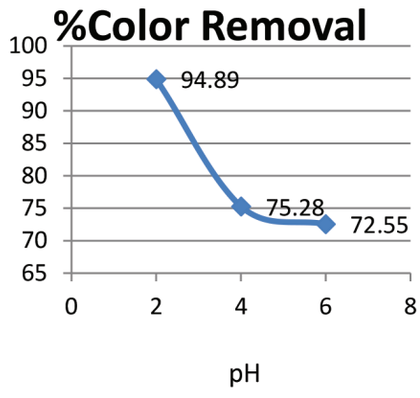
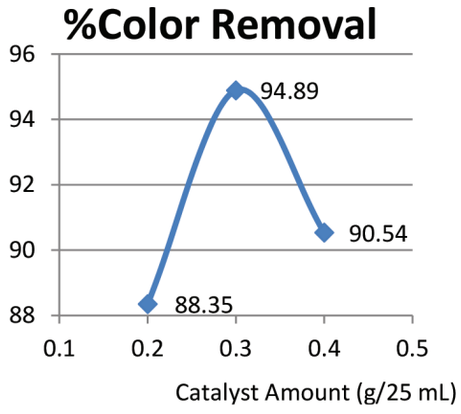


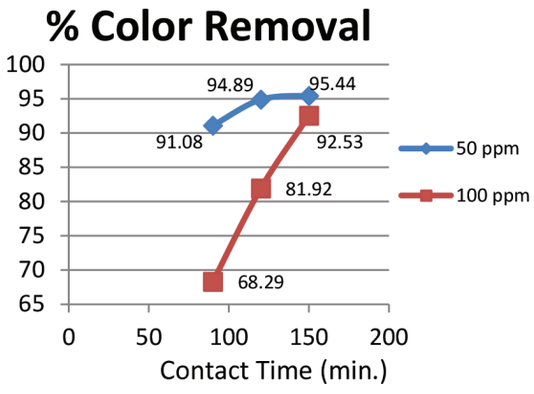
Fig. 2. XRD pattern of Fe/ZrO_2 catalyst.



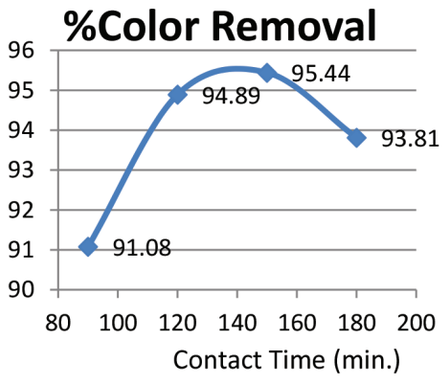
(a) C. time=120 min. C. amount=0.3 g/25 mL H_2O_2 = 50mM



(b) pH=2, C. time=120 min. H_2O_2 = 50mM



(c) pH=2, C. amount=0.3 g/25 mL H_2O_2 = 50mM



(d) C. time=120 min., C. amount=0.3 g/25 mL H_2O_2 = 50mM

Fig. 3. Preliminary experiment results for color removal.

3.2. Experimental design and modeling

After the preliminary experiments, three different factors were chosen for analysis: initial pH of the reaction (*A*), contact time (*B*) and catalyst concentration (*C*) under the following conditions: 28°C of temperature, 50 ppm initial dye concentration, 6% Fe and 50 mM H_2O_2 concentration. The factors and levels used in the experiments were shown in Table 1.

A 2^3 full factorial design (with two repetitions) was employed for the optimization of RY15 decolorization. Base level experiments were carried out to determine critical factors and respected levels (Table 2). Experimental data were analyzed using Minitab Software.

The significance of the effects was checked by the ANOVA (Table 3) with a confidence level of 95%. According to the ANOVA results, all the main effects (A, B, C) are statistically significant ($p < 0.05$) and the remaining effects are statistically not significant at 95% confidence level. Additionally, normal plot and Pareto chart of the standardized effects in Fig. 4 verify these results. The main effect plots in Fig. 5 shows that catalyst concentration (C) had the greatest positive effect on RY15 removal, followed by pH (A) with a negative effect and the contact time (B) with a positive effect.

After the statistical procedure, coefficients of the empirical model for percentage of color removal were calculated through regression analysis and tested for significance by Student's *t*-test at 95% confidence level. For omitting the coefficients not significant at 95% confidence level, the estimated coefficients are obtained as seen in Table 4 in terms of coded variables.

Similarly, Y_1 was given in terms of coded variables and represents % color removal in Eq. (2):

Table 1
Variable levels of the factors

Factors	–1	+1
pH of the reaction *(A)*	2	6
Contact time *(B)* min	60	120
Catalyst concentration *(C)* g/25 mL	0.1	0.3

Table 2
Full factorial experiments for color removal

				Color Removal %	
Run	A	B	C	Actual	Predicted
1	+1	–1	+1	75.28	68.85
2	+1	+1	+1	80.19	81.14
3	–1	+1	–1	78.00	78.55
4	+1	+1	–1	64.38	65.99
5	–1	+1	+1	91.08	93.70
6	–1	–1	+1	77.46	81.41
7	+1	–1	–1	58.38	53.69
8	+1	+1	+1	76.92	81.14
9	+1	+1	–1	66.56	65.99
10	–1	–1	–1	67.65	66.26
11	–1	+1	–1	87.27	78.55
12	+1	–1	–1	50.51	53.69
13	–1	–1	–1	56.21	66.26
14	–1	+1	+1	94.35	93.70
15	+1	–1	+1	67.10	68.85
16	–1	–1	+1	87.81	81.41

Table 3
ANOVA results for color removal

Analysis of variance for % removal (coded units)						
Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	2154.48	2154.48	718.160	23.99	0.000
*pH	1	631.39	631.39	631.391	21.09	0.002
*Time	1	604.55	604.55	604.545	20.20	0.002
*Catalyst	1	918.54	918.54	918.545	30.69	0.001
2-Way Interactions	3	89.65	89.65	29.884	1.00	0.442
pH*Time	1	38.41	38.41	38.409	1.28	0.290
pH*Catalyst	1	0.23	0.23	0.228	0.01	0.933
Time*Catalyst	1	51.02	51.02	51.015	1.70	0.228
3-Way Interactions	1	12.13	12.13	12 .128	0.41	0.542
pH*Time*Catalyst	1	12.13	12.13	12.128	0.41	0.542
Residual Error	8	239.46	239.46	29.932		
Pure Error	8	239.46	239.46	29.932		
Total	15	2495.72				

*Significant effects at 95% confidence level ($p < 0.05$)

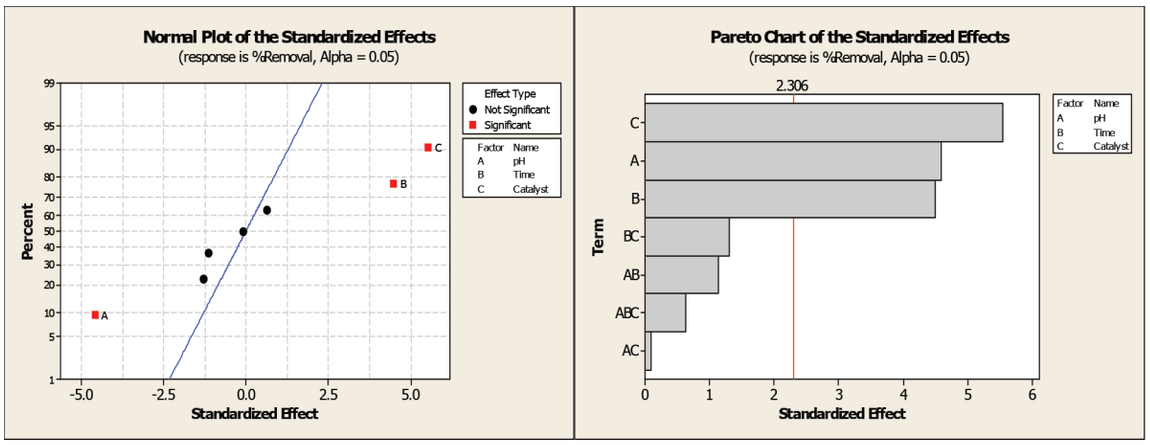


Fig. 4. Normal plot and pareto chart of the standardized effects.

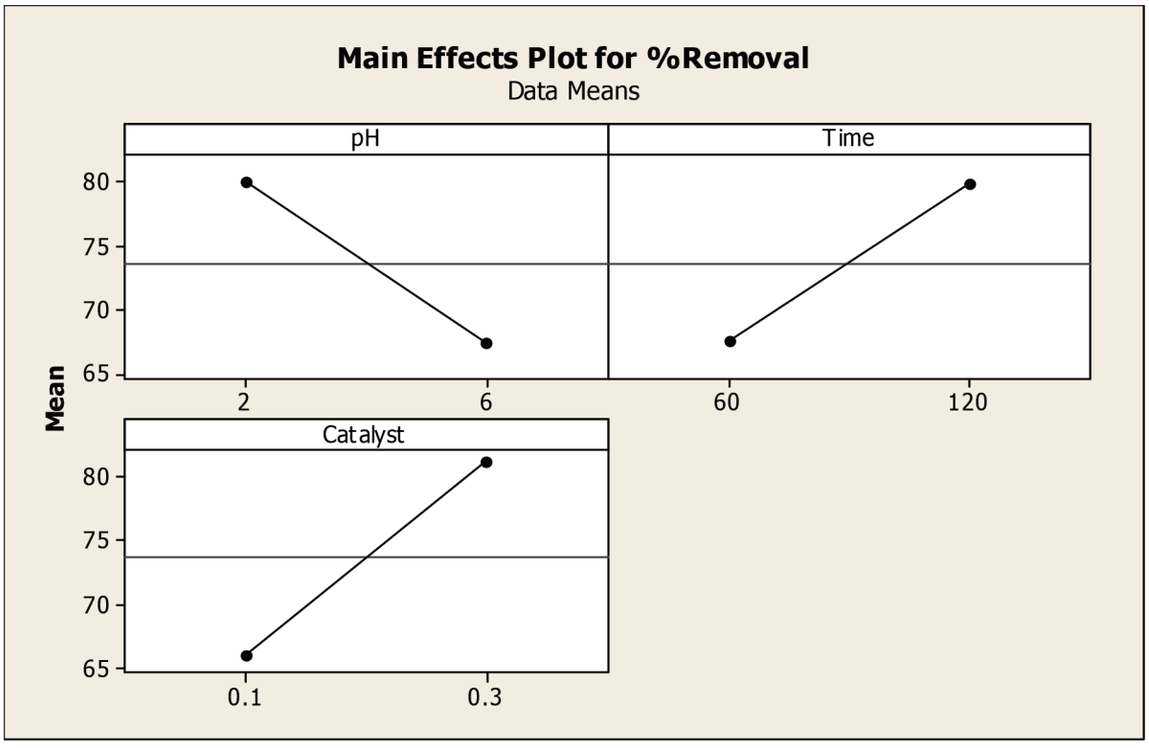


Fig. 5. The main effect plots for color removal.

Table 4
Estimated effects and coefficients for color removal

Estimated effects and coefficients for % removal (coded units)					
Term	Effect	Coef	SE Coef	T	P
Constant		73.697	1.333	55.28	0.000
pH	–12.564	–6.282	1.333	–4.71	0.001
Time	12.294	6.147	1.333	4.61	0.001
Catalyst	15.154	7.577	1.333	5.68	0.000
S = 5.33259		PRESS = 606.646			
R-Sq = 86.33%		R-Sq (pred) = 75.69%		R-Sq (adj) = 82.91%	

$$Y_1 = 73.697 - 6{,}282A + 6.147B + 7.577C \quad (2)$$

The regression model provide higher R^2 (86.33), adjusted R^2 (82.91) and predicted R^2 (75.69) as shown in Table 4. Predicted R^2 value is in a good agreement with adjusted R^2. Thus, it can be concluded that the reduced model may be used for precisely estimating the percentage of color removal. By using the regression model presented in Eq. (2), predicted values of percentage color removal were obtained and shown in the last column of Table 2. The maximum value of predicted percentage color removal is 93.70%. The following results are concluded from the regression model: low level of initial pH, high levels of contact time and catalyst concentration provide higher

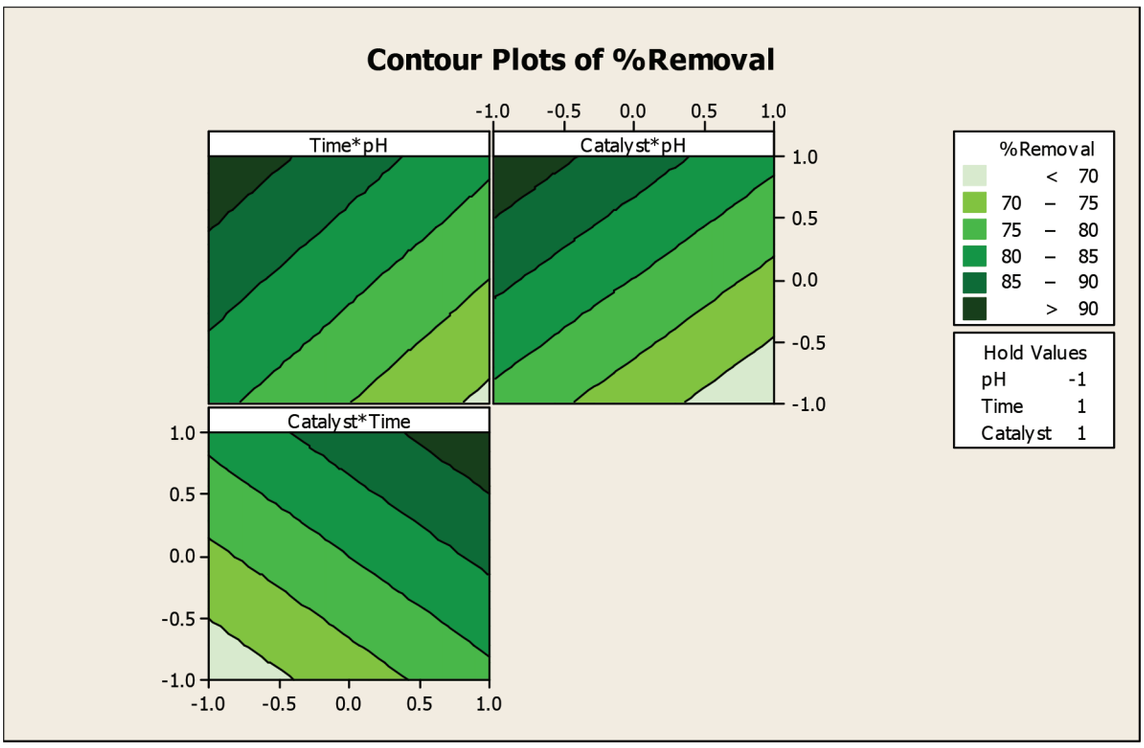


Fig. 6. Contour plots of color removal.

percentage of color removal. In addition, catalyst concentration is considered as the most important factor among the others. Contour plots in Fig. 6 show percentage color removal regions for low and high levels of pH, contact time and catalyst concentration.

4. Conclusion

The aim of the study was to investigate the color removal by the heterogeneous Fenton-type oxidation of the RY15 using Fe/ZrO_2 catalyst in the presence of hydrogen peroxide (H_2O_2) in a batch process. In order to determine the effects of various operational parameters, a full factorial design was performed. According to the statistical procedure, although the influential factors such as pH of the reaction, contact time and catalyst concentration are highly significant, the interaction effects are not significant for 5% significance level. The model is fitted very well to the experimental data as confirmed by the high R^2, adjusted R^2 and predicted R^2 values. Under the optimum conditions (the initial pH = 2, catalyst concentration = 0.3 g/25 mL, and contact time = 120 min), color removal is predicted as 93.70% and the corresponding confirmatory trial value is 94.89. This value fits well to the dataset of predicted values by considering 95% prediction interval.

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