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Optimization of Acid Orange 7 Degradation in Heterogeneous Fenton-like Reaction Using Fe_3-xCoxO_4 Catalyst

M Z Ibrahim[1], R Alrozi[1], N A Zubir[1], N A Bashah[1], S A Md Ali[1] and N Ibrahim[2]

[1]Faculty of Chemical Engineering, Universiti Teknologi MARA, Cawangan Pulau Pinang, Kampus Permatang Pauh, 13500 Permatang Pauh, Pulau Pinang, Malaysia
[2]Faculty of Chemical Engineering, Universiti Teknologi MARA, Shah Alam, 40450 Shah Alam, Selangor, Malaysia

rasyidah.alrozi@ppinang.uitm.edu.my

Abstract. The oxidation process such as heterogeneous Fenton and/or Fenton-like reactions is considered as an effective and efficient method for treatment of dye degradation. In this study, the degradation of Acid Orange 7 (AO7) was investigated by using Fe_3-xCoxO_4 as a heterogeneous Fenton-like catalyst. Response surface methodology (RSM) was used to optimize the operational parameters condition and the interaction of two or more parameters. The parameter studies were catalyst dosage (X_1), pH (X_2) and H_2O_2 concentration (X_3) towards AO7 degradation. Based on analysis of variance (ANOVA), the derived quadratic polynomial model was significant whereby the predicted values matched the experimental values with regression coefficient of R^2 = 0.9399. The optimum condition for AO7 degradation was obtained at catalyst dosage of 0.84 g/L, pH of 3 and H_2O_2 concentration of 46.70 mM which resulted in 86.30% removal of AO7 dye. These findings present new insights into the influence of operational parameters in the heterogeneous Fenton-like oxidation of AO7 using Fe_3-xCoxO_4 catalyst.

1. Introduction

Water is important for human daily lives. The main sources of water came from groundwater, river and reservoir. There are many uses of water in industries that give benefit to human lives. Wastewater is any water that has been adversely affected in quality by anthropogenic influence [1]. It needs to be treated to minimize the effect on human's health and environment. The causes of pollution in the water are virtually endless. The major of water pollution is originally from textile industries. Textile manufacturing sector has been considered an important and dynamic component in the economic growth in recent years. Like any other industries, this industry also generates industrial wastes namely liquids, solids and gases. Due contaminated wastewater, dyes are difficult to be decolorized and decomposed biologically due to their complex structure [2]. The discharge of this wastewater into receiving streams causes damage not only to aquatic life but also to human beings. In facts, the dye contaminated wastewater is also considered as toxic or carcinogenic to human being. They stimulate mutagenic effects which causes the errors in DNA replications [3].

According to Su et al. [4], the oxidation process such as heterogeneous Fenton and / or Fenton-like reactions were previously found as an effective and efficient method for treatment of dye degradation. This process used iron oxide (magnetite) as the catalyst and hydrogen peroxide (H_2O_2) being used as an oxidant. One of the major drawbacks of this treatment however is due to its inability to recycle magnetite since this catalyst's activity continuously diminishes after numerous reaction cycles, which leads to unnecessary fresh catalyst required. Therefore, isomorphic substitutions by using a few transition metal cations have been added to the magnetite structure in order to prolong its catalytic activity for longer periods besides making it more stable [5].

The optimization of analytical procedures has been carried out by using multivariate statistic techniques. Among the most relevant multivariate techniques used in analytical optimization is response surface methodology (RSM). RSM is a collection of mathematical and statistical techniques based on the fit of a polynomial equation to the experimental data, which describe the behaviour of a data set with the objective of making statistical previsions. It can be well applied when a set of interest responses are influenced by several variables. Hence, the objective of this work is to optimize the operational parameters (i.e catalyst dosage, pH and concentration of H_2O_2) on the oxidative degradation of AO7 using Fe_3-xCoxO_4 catalyst.

2. Materials and Method

2.1. Acid Orange 7

An anionic dye, Acid Orange 7 (AO7) with molecular weight of 350.33 g/mol, was selected as model pollutant in order to evaluate the degradation efficiency of the Fe_3-xCoxO_4 catalyst in heterogeneous Fenton-like reaction. The molecular structure of AO7 is shown in Figure 1. All chemical reagents used in this study were of analytical grade.

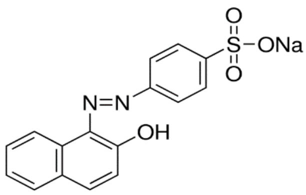

Figure 1. Structure of Acid Orange 7

2.2. Catalyst Synthesis

$Fe_{3-x}Co_xO_4$ catalyst has been synthesized according to the previous works by Yang et al. [6] with some modification. 5 mL of 2 mol L−1 $CoCl_2$•6H_2O in HCl 7.4% solution and 40 mL of 0.5 mol L−1 $FeCl_3$•6H_2O in double distilled water were pre-heat to 50 ºC. The solutions then were mixed and decanted into a boiling solution of 200 mL of 1 mol L−1 NaOH under vigorous stirring for 30 min. After was cooled to room temperature, the dark brown precipitate was separated from the dispersion medium by using a permanent magnet. The resulting suspension was dried in oven at 100 ºC for 5 h.

2.3. Catalytic Test

Batching process was applied to AO7 solution that has been prepared in the series of Erlenmeyer flask. A total of 20 Erlenmeyer flasks of AO7 solution with different catalyst dosage, pH and H_2O_2 concentration were batched by using top orbital shaker (Model SK-300, Malaysia). This process was carried out in room temperature (27-30 ºC) with agitating speed of 150 rpm until it reached the desired contact time. The percentage dye degradation at equilibrium was calculated based on common equilibrium equation.

2.4. Design of Experiment

RSM was employed in this work because it is capable for modelling vast numbers of numerical experiments. RSM can evaluate the relationship of the controlled experimental factors and measured responses. CCD was applied to study the variables for AO7 degradation involve in three categories of runs which are 2n factorial runs, 2(n) axial runs and 6 center runs where n is the number of the process variables. Independent process parameters in qualitative form were calculated as follows:

$$Y = f(X_1, X_2, X_3, \ldots X_n) \pm \varepsilon \qquad (1)$$

where Y is the response, f is the response functions, ε is the experimental error and $X_1, X_2, X_3, \ldots, X_n$ are the independent parameter that involved in the experiment [7]. Experimental error and the reproducibility of the data can be obtained by using the center point [8]. The axial point is located at ± α for each of variables where ± α is the distance of the axial point from the center point. Hence, the response with linear function model can be written as:

$$Y = C_o + C_1X_1 + C_2X_2 + \cdots + C_nX_n \pm \varepsilon \quad (2)$$

where Y is the response, C is the coefficient, X is the coded values of the process variables and ε is the experimental error. However, when the curvature occurs, the higher order polynomial such as quadratic model may be used. The quadratic equation is written by equation:

$$Y = C_o + \sum C_iX_i + \sum C_{ii}X_i^2 + \sum C_{ij}X_iX_j \quad (3)$$

where Y is predicted response, C_o is the constant coefficient, C_i is the linear effect, C_{ii} is the squared effect, and C_{ij} is the interaction effect [9]. In this experiment, the process variables that were investigated were catalyst dosage (g/L, X_1), pH (pH, X_2) and H_2O_2 concentration (mM, X_3). The parameters were coded at three levels of -1, 0, 1, where the center point of the experiment was at 0.55 g/L catalyst dosage, pH 5.75 and 26.25 mM of H_2O_2 concentration. Table 1 shows the complete design matrix that has been developed with their responses values.

Table 1. Experimental design matrix for AO7 degradation

Run	Catalyst dosage, X_1 (g/L)	pH, X_2	H_2O_2 concentration, X_3 (mM)	AO7 degradation (%)
1	-1.00	-1.00	-1.00	42.41
2	1.00	-1.00	-1.00	99.75
3	-1.00	1.00	-1.00	9.03
4	1.00	1.00	-1.00	32.43
5	-1.00	-1.00	1.00	57.80
6	1.00	-1.00	1.00	99.59
7	-1.00	1.00	1.00	14.98
8	1.00	1.00	1.00	42.46
9	-1.00	0.00	0.00	39.80
10	1.00	0.00	0.00	48.10
11	0.00	-1.00	0.00	98.98
12	0.00	1.00	0.00	35.31
13	0.00	0.00	-1.00	42.91
14	0.00	0.00	1.00	45.68
15	0.00	0.00	0.00	42.20
16	0.00	0.00	0.00	40.78
17	0.00	0.00	0.00	43.16
18	0.00	0.00	0.00	41.38
19	0.00	0.00	0.00	42.28
20	0.00	0.00	0.00	43.11

2.5. Model Fitting and Statistical Analysis
The experimental data was analyzed by using Design Expert 7.0.0 software (Stat-Ease, Inc.) for regression analysis and statistical significance of the equation derived.

3. Result and Discussions

3.1. Development of Regression Model Equation
CCD was used as a polynomial regression in order to determine the interaction between the parameters variables and responses. The quadratic models of AO7 degradation was suggested by the

software. The selection of the quadratic model is based on the higher order polynomial. Eq. 4 is the final empirical formula model for AO7 degradation:

$$Y = 45.25 + 15.83X_1 - 26.43X_2 + 3.4X_3 - 6.03X_1X_2 - 1.43X_1X_3 + 0.095X_2X_3 - 0.594X_1^2 + 17.26X_2^2 - 5.6X_3^2 \quad (4)$$

In this study, the R^2 values for Eq. 4 was 0.9399 (as shown in Figure 2) indicated that 93.99% of total variation in the AO7 discoloration was much closer to the actual value. In other words, the models developed were successful in capturing the correlation between the operational parameters variables to the response of AO7 degradation.

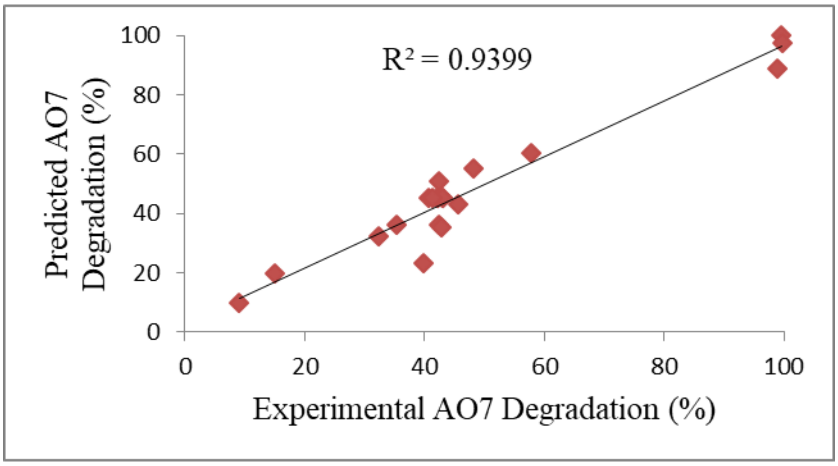

Figure 2. Predicted versus experimental AO7 degradation

3.2. *Statistical Analysis*

In this study, analysis of variance (ANOVA) was used to analyze and justify the significance and adequacy of the models. The results of the surface quadratic model of ANOVA are given in Table 2. The model terms are considered as significant if the F-value is relative high and the value Prob.>F is less than 0.05. The F-value was 17.69 and the prob.>F was less than 0.0001 indicated that the model was relevant and significant. Meanwhile, the significant model terms obtained were X_1, X_2 and X_2^2. In contrast, X_3, X_1X_2, X_1X_3, X_2X_3, X_1^2 and X_3^2 were insignificant model terms to the model. The model developed was successful because the predicted values obtained were closer to the actual experimental data.

3.3. *AO7 Degradation*

From Table 2, the catalyst dosage and solution pH were observed as the most significant factors that contributed to AO7 degradation. Meanwhile, the quadratic effect of solution pH was considered least significant. Figure 3 shows the effect of solution pH and catalyst dosage on the AO7 degradation when H_2O_2 concentration was fixed. From Figure 3, when the catalyst dosage and solution pH were decreased, the AO7 degradation increased. The results obtained was supported by previous study that was conducted by Xu et al. [10] which reported that at high catalyst dosage, more active sites were presence on the catalyst surface in accelerating the decomposition of H_2O_2. On the other hand, when the solution pH decrease, the number of negatively charged sites decrease. This can attributed to reducing of the degradation of the dye due to electrostatic repulsion. Similar observation was obtained by Xu et al. [11] where RhB decoloration was increased with increasing catalyst dosage and decreasing pH solution. In addition, Sun et al. [12] found that increasing the catalyst dosage gave significant effect on degradation of Orange G (OG) by fenton oxidation but increasing of H_2O_2 resulted to negative impact on the degaration of OG.

Table 2. Analysis of variance (ANOVA) for AO7 discoloration

Source	Sum of squares	Degree of freedom	Mean square	F value	*p*-value (Prob > *F*)	
Model	10742.96	9	1193.66	17.69	< 0.0001	Significant
X_1	2506.09	1	2506.09	37.15	0.0001	
X_2	6986.91	1	6986.91	103.57	< 0.001	
X_3	115.50	1	115.50	1.71	0.2200	
X_1X_2	291.13	1	291.13	4.32	0.0645	
X_1X_3	16.42	1	16.42	0.24	0.6324	
X_2X_3	0.072	1	0.072	0.001061	0.9747	
X_1^2	97.09	1	97.09	1.44	0.2579	
X_2^2	818.83	1	818.83	12.14	0.0059	
X_3^2	86.12	1	86.12	1.28	0.2849	
Residual	674.58	10	67.46	-	-	

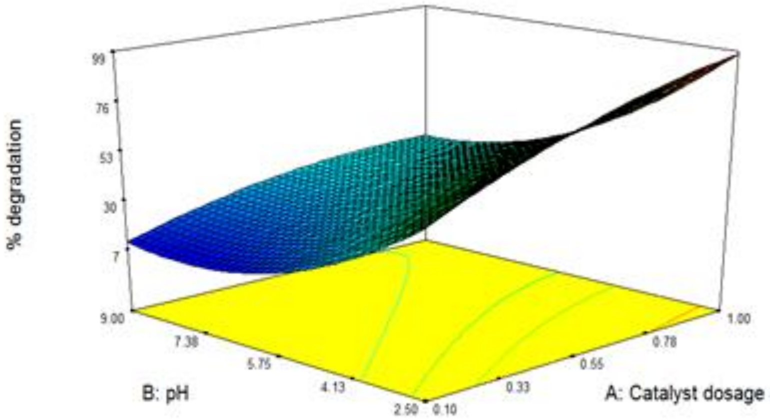

Figure 3. Three-dimensional response surface plot of AO7 discoloration (effect of pH and catalyst dosage, H_2O_2 concentration = 46.70 mM)

3.4. Process Optimization

RSM was used to determine the optimum parameters condition for the maximum AO7 degradation. During analysis process, the response was set as maximum value whereas all the parameters were fixed in the range. Table 3 shows the experimental results and predicted results of AO7 degradation at the optimum condition. The optimum condition for AO7 degradation was selected based on the highest value of model desirability. The optimum condition was obtained at catalyst dosage of 0.84 g/L, pH solution of pH 3.14 and H_2O_2 concentration of 46.70 mM which resulted in 86.30% of AO7 degradation.

Table 3. Model validation for AO7 degradation

Model of desirability	Catalyst dosage, X_1 (g/L)	pH, X_2	H_2O_2 concentration, X_3 (mM)	AO7 degradation (%)		
				Predicted	Experimental	Error (%)
1.00	0.84	3.14	46.70	86.30	85.43	0.87

4. Conclusion

In conclusion, AO7 can be efficiently removed by heterogeneous Fenton-like reaction using $Fe_{3-x}Co_xO_4$ catalyst. RSM was successfully used to investigate the parameters that influenced the AO7 discoloration. Based on the parameters studied, catalyst dosage and solution pH were found as

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significant factors that contribute to the AO7 discoloration. By using RSM, the optimum condition for AO7 degradation was obtained at catalyst dosage of 0.84 g/L, pH solution of pH 3 and H_2O_2 concentration of 46.70 mM which resulted in 86.30% of AO7 degradation.

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