Optimization of Orange Acid 10 Degradation by Fenton process. Application of Box-Behnken

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Abstract

The present study concerns the modeling and optimization of the degradation of Orange acid 10 by Fenton process. The objective was to use a minimum of experiments by applying a modeling design of the Box-Behnken type. The effects of the different parameters and their interactions on the response were analyzed statistically by studying the variance with respect to the various experimental tests. Thereafter the mathematical model was determined by analyzing the polynomial regression of the response according to the different considered factors and effects. Finally, the optimal conditions were determined by means of the mathematical model and were confirmed experimentally. The best yield value was 99.03% and was obtained after 120 min of contact. This value was close to that given by the mathematical model which was of the order of 99.99%.

Keywords: *Fenton process; Orange acid 10; Box-Behnken; optimization*

I. Introduction

Currently, the most recent advances in wastewater treatment have been made in advanced oxidation processes (AOP) which appear to be more efficient techniques for the destruction or the degradation of pollutants. The Fe^{2+} / H_2O_2 system has been the subject of numerous studies both in terms of the reaction mechanism [1-2] and in terms of its applications in the field of the oxidation of organic pollutants in aqueous solutions [3-4]. Some studies have shown that the Fenton reaction uses only Fe (II) as an electron donor to H_2O_2 and such would be a transfer reaction of the electron from the external sphere without interaction of the bond directly, between the donor and the acceptor of the electron. (Mechanism I, Figure 1) [5].

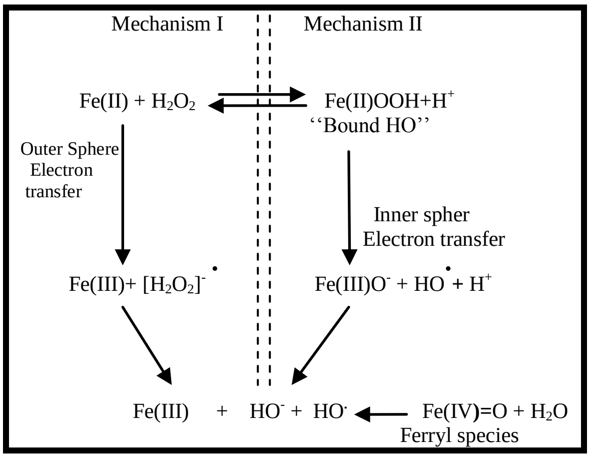

Figure 1: Basic and intermediates reaction involved in the Fenton reaction [6].

On the other hand, recent studies have shown and favored the mechanisms of electron transfer from the inner sphere which involves the direct bond between Fe^{2+} and H_2O_2. This interaction could produce (Fe(II) OOH) which can react and produce $HO^\bullet$ radicals (Mechanism II, Figure1).

II. Materials And Methods

A. Materials

Orange acid 10 (Sigma-Aldrich) was used as a pollutant and its molecular structure is shown in Figure 2. Hydrogen peroxide H_2O_2 (30%) was supplied by Merck, Ferrous sulphate $FeSO_4$, $7H_2O$ (99%) by Sigma-Aldrich, HNO_3 (60%) by Shanghai Chemical Reagents and NaCl (M=58.44g) by Acros Organics.

Figure.2: Molecular structure of Orange acid 10

B. Methods

The aqueous solutions of orange acid 10 were prepared by dissolving the required amount in distilled water. The pH of the solution was adjusted by adding HNO_3. The experimental device consisting of a perfectly stirred reactor (capacity of 600 ml) in which a volume of 500 ml of solution has been treated. The temperature was controlled by a thermostatic bath (Tectron Bio, Selecta) and the stirring was carried out using a mechanical stirrer (Janke & Kunkel RW 20).

The discoloration of the dye was carried out by a Fenton reagent which is composed of a mixture of $FeSO_4$ and H_2O_2. The necessary amounts of Fe^{2+} and H_2O_2 were added simultaneously to the colored solution; the oxidation reaction began upon the introduction of H_2O_2. The concentration of the dye in the reaction mixture at different reaction times was determined by measuring the absorption intensity at 484 nm using a visible spectrophotometer (Secomam Anthelie light). The yield of AO10 discoloration was calculated using the following equation:

$$R(\%) = \frac{(C_0 - C_t) \times 100}{C_0} \qquad (1)$$

C_0: Initial concentration of AO10,
Ct: Concentration of AO10 at each instant (t),
R: Degradation Percentage (yield)

The Box-Behnken design was applied with initial AO10 concentrations of 30 ppm, a temperature of 25 ° C, a stirring speed equal to 250 rpm and NaCl salt concentration of 0.1 ppm. The sampling was carried out for a period of 120 min by varying the three considered factors or parameters, according to the design.

III. Statistical analysis

A. Considered factors and ranges

The considered coded and non coded factors as well as the respective ranges are shown in the following table 1:

Table 1 : Considered factors and ranges

Factor	**Unit**	**Level**		
		Low (-1)	**Medium (0)**	**High (+1)**
$[H_2O_2]$	ppm	15	22.5	30
pH	/	2.5	3.5	4.5
$[Fe^{2+}]$	ppm	2	3	4

B. Box Behnken design

Fifteen runs were evaluated according to the Box-Behnken design with three factors (the concentration of H_2O_2, the concentration of Fe^{2+} and the pH of the solution at the three considered levels. Twelve different formulations were generated and the center was evaluated three times. The results are shown below.

IV. Results and discussion

A. Experimental data fitting and comparison

The experimental yield values were fitted to a second-order response surface model expressed by the following polynomial equation:

$$R = a_0 + \sum_{i=1}^{3} a_i X_i + \sum_{i=1}^{3} a_{ii} X_i^3 + \sum_{i=1}^{3} \sum_{j=i+1}^{3} a_{ij} X_i X_j \qquad (2)$$

Where *Y* represents the response variable (yield, Y %), a_0, a_i, a_{ii} and a_{ij} are constant coefficients of intercept, linear, quadratic and interactive terms, respectively. X_i and X_j are the coded independent variables ($[H_2O_2]$, pH and $[Fe^{2+}]$). The coefficients of the response surface equation were determined using MINITAB software [7] and the results are shown in the following table 2.

Table 2: Analysis of variance for Yield

Term	**Coef**	**SE Coef**	**P**
Constant	-626.98	49.058	0.000
$[H_2O_2]$	3.97	1.976	0.101
pH	306.57	16.084	0.000
$[Fe^{2+}]$	66.89	14.818	0.006
$[H_2O_2]$* $[H_2O_2]$	-0.073	0.035	0.094
pH*pH	-39.54	1.989	0.000
$[Fe^{2+}]$* $[Fe^{2+}]$	-5.71	1.979	0.034
$[H_2O_2]$*pH	0.29	0.254	0.299
$[H_2O_2]$*pH	0.29	0.254	0.299
$[H_2O_2]$* $[Fe^{2+}]$]	-0.39	0.254	0.185
pH*$[Fe^{2+}]$	-5.89	1.901	0.027

Therefore the polynomial giving the response Y in terms of the three factors denoted as X_1, X_2 and X_3 for ($[H_2O_2]$, pH and [**Fe**$^{2+}$], respectively is expressed as follows:

$$R = -626.980 + 3.968 * X_1 + 306.572 * X_2 + 66.894 * X_3 - 0.073 * X_1^2 - 39.542 * X_2^2 - 5.712 * X_3^2 + 0.294 * X_1 * X_2 - 0.390 * X_{1*} X_3 - 5.893 * X_2 * X_3 \qquad (3)$$

Once the polynomial model was determined, an analysis of variance was carried out to assess how closely it represented the data. This analysis was also performed to compare the relative significance of each parameter. The results of the analysis of variance or ANOVA [8, 9] given by the MINITAB software are shown in Table 3 corresponding to the use of the encoded data. MINITAB is an interface to statistical software and guides the user through the phases of data analysis and interpretation of results. The comparison of the calculated results by means of the response polynomial, to the experimental values is shown in the following table 3:

Table 3: Experimental and calculated yields

Run	[H_2O_2]	pH	[Fer]	R% (exp.)	R %(calc)
1	22.5	3.5	3	98.33	98.36
2	22.5	4.5	4	66.57	69.14
3	15.0	2.5	3	35.48	34.04
4	22.5	2.5	2	27.85	25.27
5	22.5	3.5	3	98.19	98.36
6	15.0	3.5	2	74.21	78.23
7	22.5	2.5	4	40.70	43.52
8	30.0	3.5	2	91.05	92.43
9	15.0	3.5	4	91.91	90.53
10	22.5	4.5	2	77.29	74.47
11	30.0	2.5	3	36.80	38.00
12	30.0	4.5	3	78.38	79.82
13	22.5	3.5	3	98.55	98.36
14	15.0	4.5	3	68.25	67.05
15	30.0	3.5	4	97.06	93.05

Also the plot of Figure 3 showing the calculated responses versus the experimental ones confirmed the quite good agreement between the two sets of values, with a correlation factor of 0.992.

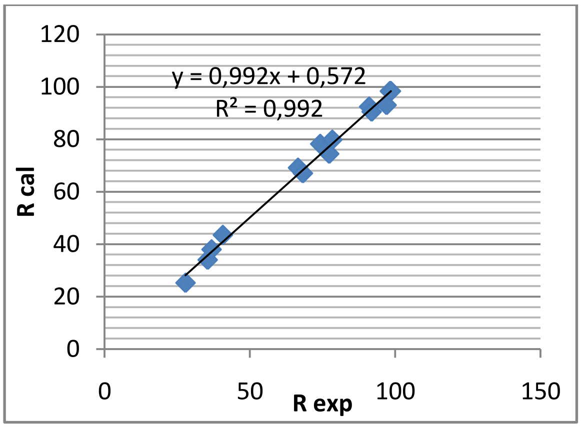

Figure .3: Comparison of the calculated and experimental yields

The significant terms on the degradation yield of the orange acid 10 are Iron with a p-value of 0.006, the initial pH of the solution (p = 0.000), the term Iron squared where p is 0.035, the pH squared with p of zero and the interaction pH-[Fe * Iron where p is equal to 0.027. All other terms are not significant of degradation of the dye.

B. Data reliability assessment

In order to assess the data reliability the histogram for the residual yield values was plotted and shown in Figure 4. It can be seen that it follows a bell curve, indicating that the residual values were distributed almost normally and the experimental results were reproducible and described the phenomenon reasonably well.

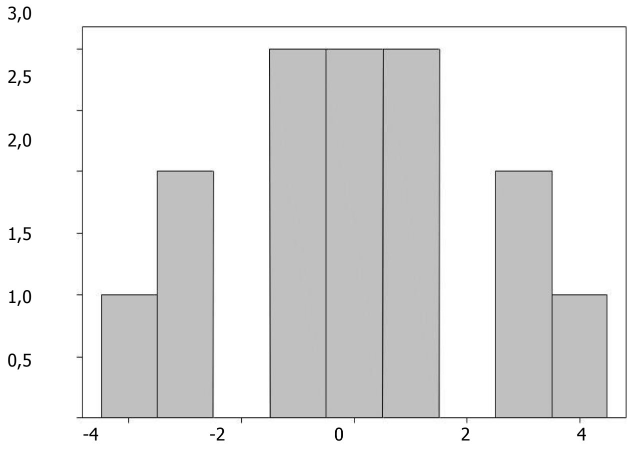

Figure 4 : Histogram of residual yield values

Henry's lines are a useful tool for evaluating the normality of a data file, even for cases where the number of observations is quite low. Therefore in the present work the Henry's line for residual yield values had also been plotted and is shown in

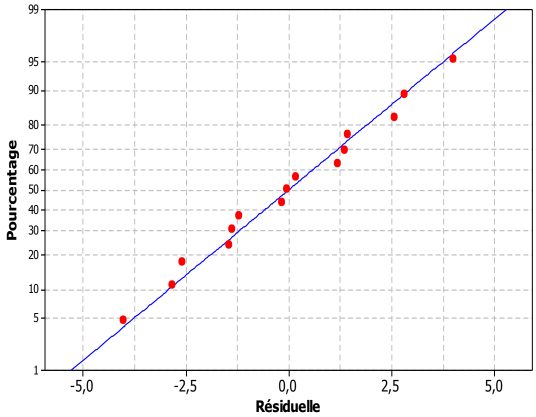

Figure 5: Henry's line of residual values for yield

Figure 5 where it can be seen that the points tend to form a straight line, indicating that the residual values are distributed and scattered normally around this line. However it can be observed that near the ends the distribution deviated slightly from normality.

C. Operating parameters main effects

In order to compare the influence of each factor on the process performance, the effects of the three considered factors had been plotted as shown by graphs of Figure 6:

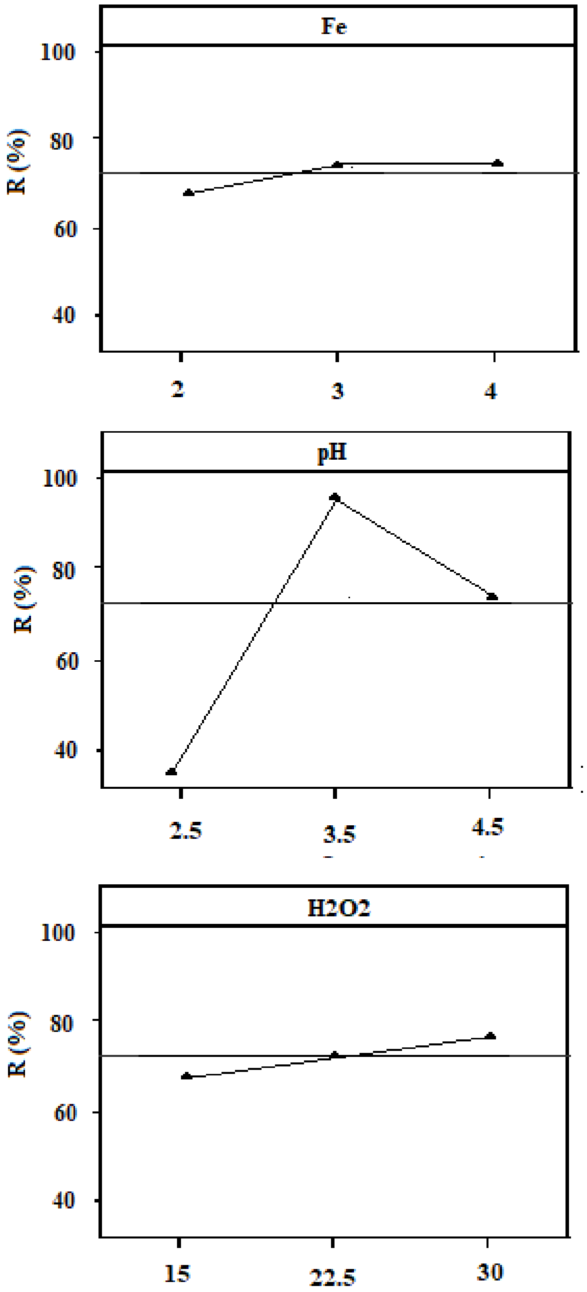

Figure 6: Diagrams of main effects

Figure 6 shows that the degradation of AO10 increased with an increase in [Fe^{2+}] while the highest degradation efficiency was recorded at [Fe^{2+}] = 4ppm after 60 min of time of reaction. This is explained by the production of OH radicals, but increased further in the amount of Fe^{+2} did not lead to an increase in the rate of degradation [10, 11].

- Hydrogen peroxide played the role of an oxidizing agent in the Fenton oxidation process and the selection of its optimal concentration for the degradation of the pollutant by Fenton oxidation was important from a practical point of view because of its cost. The increase in [H_2O_2] from 15 to 30 ppm was positive;

- For pH, several studies confirmed that the optimal pH value giving better discoloration was located in a range between 2 and 4 in which the formation of Fe(OH)$^+$ ions was very favored and the production of $HO^{\bullet}$ radicals was maximum. The maximum bleaching efficiency of dyes was obtained at pH = 3, in agreement with several reported studies [12-15].

D. Response and contour surfaces

Minitab's response surface methodology was used plotting features to help visualize the factors effects. Two types of response surface graphs could be generated: the contour graph and the surface diagram. These graphs show the relationships between a response variable and two factors from an equation model, keeping the possible additional factors constant. They also made it possible to obtain the desired response values and conditions of use. It is also noted from this representation that the orientation of the response surface changed as a function of the levels of the values of the operating parameters pH, H_2O_2 and [Fe^{2+}]. Moreover the greatest yield was located at average pH = 3.5 (Figures. 7,8). Also the best yield was reached when setting the initial concentration of [Fe^{2+}] at 3 ppm (Figures. 9,10).

E. Optimization

To find an optimal interval or zone of the experimental domain for the response with a desirability (D) equal to 0.999, the yield may be obtained with a value of 99.99% where the overall solution of the factors is 22.42 ppm for the concentration of H_2O_2, 3.19 ppm for the [Iron]0 and 3.59 for the pH (Figure 11).

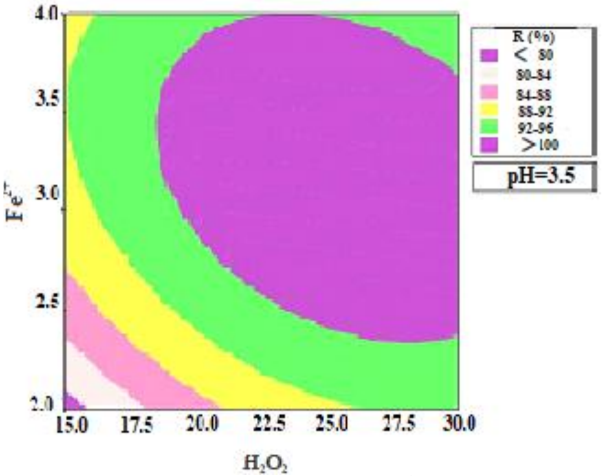

Figure 7: Contour surface of R(%) *vs* [Fe^{2+}]-H_2O_2 at pH=3.5

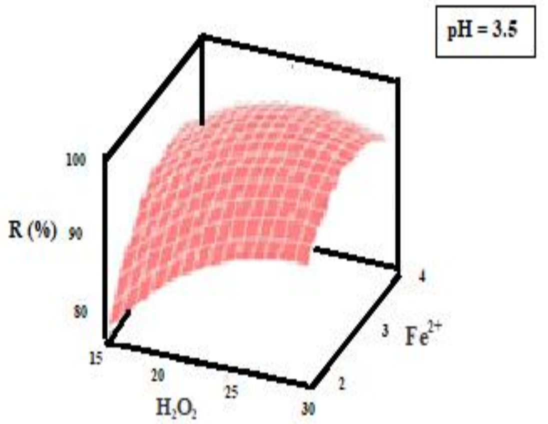

Figure 8: Surface response of R(%) in terms of [Fe^{2+}]-H_2O_2 at pH = 3.5

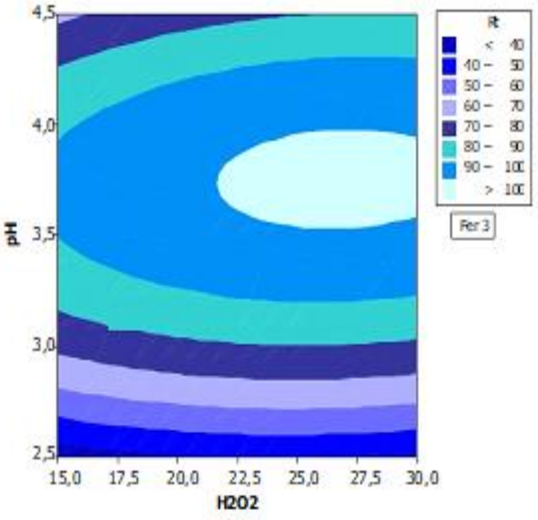

Figure 9: Contour surface of R (%) in terms of pH- [Fe^{2+}] at average [Fe^{2+}]

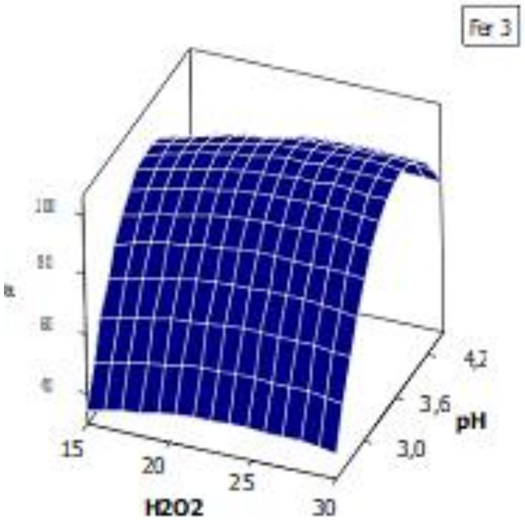

Figure 10 Response surface of R(%) as a function of pH-H_2O_2 at average [Fe^{2+}]

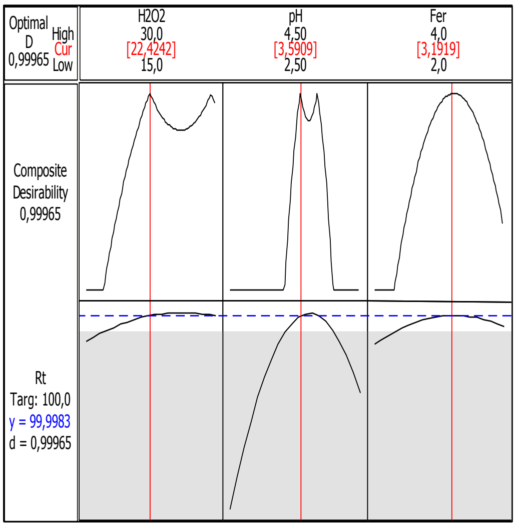

Figure 11: Optimization of the yield R

F. Exclusion of terms

We exclude all non-significant terms one by one until the simplest possible model is obtained. The result of this exclusion is represented by the equation 4.

Optimal equation for uncoded units

$$R = - 626.980 + 306.572 * pH + 66.894 * Fer - 0.073 * (H_2O_2)2 - 39.542 * (pH)^2 - 5.712 \times (Fe)^2 - 5.893 \times (pH * Fe). \quad (4)$$

G. Checking

In order to assess the obtained optimal conditions, the same experimental setup was considered and the temperature was fixed at 25 °C, the speed at 250 rpm, the concentrations of AO10, NaCl, H_2O_2 and [Fe^{2+}] at 30, 0.1, 22.42 and 3.19, respectively and an initial PH at 3.59. The discoloration of AO10 gave a yield of 99.03% after a time of 120 minutes, a value close to the calculated one equal to 99.9983%.

V. Conclusion

The search for optimal conditions was carried out using the response surface methodology to find the optimal conditions for a maximum of the degradation. The mathematical model represented well the phenomenon and could be used for any operating condition. Indeed, the maximum yield had been determined by the model and the results were compared to experimentally determined values with a quite good agreement. Finally, the optimal conditions of the degradation of Orange acid 10 by Fenton process, were determined by means of the mathematical model and were confirmed experimentally. The best yield value was 99.03% and was obtained after 120 min of contact. This value was close to that given by the mathematical model which was of the order of 99.99%.

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