Application of the Taguchi Method in the Optimization of the Photo-Fenton Discoloration of Wastewater from Reactive Blue 19 Dyeing

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The objective is to achieve higher degrees of discoloration, the larger the better criterion has been used to maximize the degree of discoloration. An orthogonal array L16 and four levels with four parameters were used to obtain the set of values of the parameters that lead to best results and the experimental results were processed using the software Minitab 17. In the paper it is examined the possibility of using the Taguchi method to optimize the process of Photo Fenton discoloration of wastewater from dyeing with Reactive Blue 19, a reactive dye widely used for both printing and dyeing cotton fabrics. Four input parameters were investigated: pH, treatment time, dye concentration and UV power.

Keywords: reactive dyeing wastewater, photo-Fenton discoloration, Taguchi optimization

Photo Fenton wastewater discoloration is part of the advanced oxidation processes, which involve the use of an oxidant associated with a suitable catalyst and/or UV radiation [1-5]. The photo-Fenton process associates UV radiation to the action of hydrogen peroxide / ferrous salt. In the reaction of the ferrous salt with hydrogen peroxide ferric ion is form, which further forms complexes with hydrogen peroxide [6-9]:

$$H_2O_2 + Fe^{3+} \rightarrow Fe(O_2H)^{2+} + H^+ \qquad (1)$$

$$H_2O_2 + Fe(OH)^{2+} \rightarrow Fe(OH)(O_2H)^+ + H^+ \qquad (2)$$

These compounds slowly thermally decompose after one of the reactions below:

$$Fe(O_2H)^{2+} \rightarrow Fe^{2+} + \cdot O_2H \qquad (3)$$

$$Fe(OH)(O_2H)^+ \rightarrow Fe^{2+} + \cdot O_2H + HO^- \qquad (4)$$

The formed $HO\cdot_2^-$ ion reduces ferric ion to the ferrous form, restarting the Fenton type reaction.

$$\cdot O_2H + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^+ \qquad (5)$$

The presence of UV radiation accelerates HO_2^- ions formation and contributes to the reformation of the ferrous catalyst by reducing the ferric ion. In this way the concentration of Fe^{2+} increases and the overall reaction is accelerated [1, 10-15].

$$Fe(O_2H)^{2+} + h\nu \rightarrow Fe^{2+} + \cdot O_2H \qquad (6)$$

The Taguchi method was used to analyze the photo Fenton discoloration of waste waters from Reactive Blue 19 dyeing in order to find optimal conditions to maximize the efficiency of the process with the minimum number of experiments. The Taguchi method, which was widely used in recent years, but still very little applied in the field of the chemical finishing of textiles, has the advantage that the results of the designed experiment can be analyzed using both analysis of variance (ANOVA) and signal to noise ratio (S/N) [10, 16-19].

Experimental part

Materials, reagents and equipment

Reactive Blue 19 dye, whose formula is shown in figure 1, was obtained from Sigma-Aldrich.

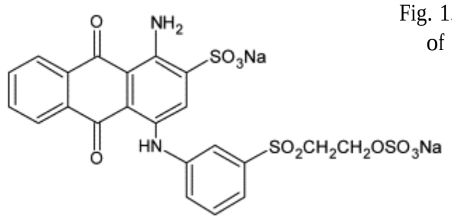

Fig. 1. Chemical formula of reactive Blue 19

All solutions which were used in the experiment were obtained from a solution of 1g/L obtained by adding to the pasted-up dye 100mL of distilled water and boiling for dissolution, and then filling to 1 L. Acidification to the *p*H requested in the experiment was achieved using H_2SO_4 and *p*H control was made with a 315i Multi-lab pH meter. The usual catalyst for the Fenton reagent, $FeSO_4 \cdot 7H_2O$, was obtained from Merck Chemical Corp. A catalyst solution of 100mM was used in all measurements. The hydrogen peroxide (purity 30%) was obtained from Merck Chemical Corp. All the other reagents were provided also by Merck Chemical Corp. The solution used in the study was prepared with distilled water.

To determine the discoloration degree, solutions of appropriate dye concentration (provided by the experimental program) have been maintained at constant temperature. After the addition of the Fenton reagent the solution was stirred for 15 to 60 min, while being subjected to UV radiation produced by a quartz lamp with medium pressure mercury vapor. The discolored wastewater was filtered through crucibles, after which the absorbance has been measured at maximum absorbance wavelength (583nm) using a Spectro UV / Vis Dual Beam Labomed UVS-2800 spectrophotometer [20-23].

Determination of discoloration degree

The discoloration degree was calculated as the ratio between the percentage relative decrease in the absorbance and the absorbance of the untreated sample:

$$\text{Discoloration degree} = \frac{Abs_o - Abs_f}{Abs_0} \times 100, [\%], \qquad (7)$$

where:

Abs_o - absorbance of the untreated sample;

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Abs_f - absorbance of the treated sample;

Experimental program

The stages in Taguchi method are as follows [24-27]:

- selection of the optimized variable. In this case, the target function is the discoloration degree;
- identification of the factors (independent variables) and their levels; based on previous experimental studies [28-31] four factors were chosen. Each of these factors has been studied at four levels[32-34]. Taguchi orthogonal matrix factors and levels are shown in table 1;
- choice of the orthogonal matrix; based on the number of factors and the number of levels the corresponding orthogonal matrix was determined, i.e. L16 Taguchi design. Taguchi L16 design matrix is shown in table 2;
- analysis of the results using the signal/noise (S/N) and analysis of variance (ANOVA);
- identification of the optimum parameters; the experimental data were processed using the Minitab 17software.

Table 1

EXPERIMENTAL MATRIX ELEMENTS

Levels	Factors			
	A pH	B Time (min)	C Dye concentration, (mg/L)	D UV power, (KW/L)
1	2	15	2	3
2	3	30	7	6
3	4	45	10	9
4	5	60	15	15

Table 2

EXPERIMENTAL VARIABLES AND THEIR LEVELS ACCORDING TO L16 EXPERIMENTAL PLAN

	Levels					Levels			
Parameters	A	B	C	D	Parameters	A	B	C	D
1	1	1	1	1	9	3	1	3	4
2	1	2	2	2	10	3	2	4	3
3	1	3	3	3	11	3	3	1	2
4	1	4	4	4	12	3	4	2	1
5	2	1	2	3	13	4	1	4	2
6	2	2	1	4	14	4	2	3	1
7	2	3	4	1	15	4	3	2	4
8	2	4	3	2	16	4	4	1	3

Results and discussions

The experimental results obtained corresponding to the experimental design are shown in table 3.

The experimental results were converted into reports S/N (signal/noise), which are shown in table 4.

The graphs in figure 2 and figure 3 show separately the variation in individual responses for the four parameters that have been analyzed, namely *p*H, duration, dye concentration of radiation power.

In these graphs the horizontal axis indicates the value of each process parameter at the 4 levels, and the ordinate represents the S/N ration and the response value, respectively. The horizontal line indicates the mean values of the ordinate. From these graphs, it can be seen that a decrease in factors A and C leads to an increase of the desired effect, while for the other two factors the relationship is of direct proportionality. The dependency is similar in the case of S/N ratio.

Table 3

EXPERIMENTAL RESULTS

Number of experiment	Discoloration degree, (%)	Number of experiment	Discoloration degree, (%)
1	75.30	9	73.10
2	83.90	10	76.50
3	89.30	11	89.40
4	96.50	12	77.60
5	76.20	13	55.30
6	99.30	14	60.90
7	71.60	15	87.60
8	81.40	16	95.80

Table 4

S/N VALUES

Parameters	A	B	C	D	S/N
1	1	1	1	1	37.5359
2	1	2	2	2	38.4752
3	1	3	3	3	39.0170
4	1	4	4	4	39.6905
5	2	1	2	3	37.6391
6	2	2	1	4	39.9390
7	2	3	4	1	37.0983
8	2	4	3	2	38.2125
9	3	1	3	4	37.2783
10	3	2	4	3	37.6732
11	3	3	1	2	39.0268
12	3	4	2	1	37.7972
13	4	1	4	2	34.8545
14	4	2	3	1	35.6923
15	4	3	2	4	38.8501
16	4	4	1	3	39.6273

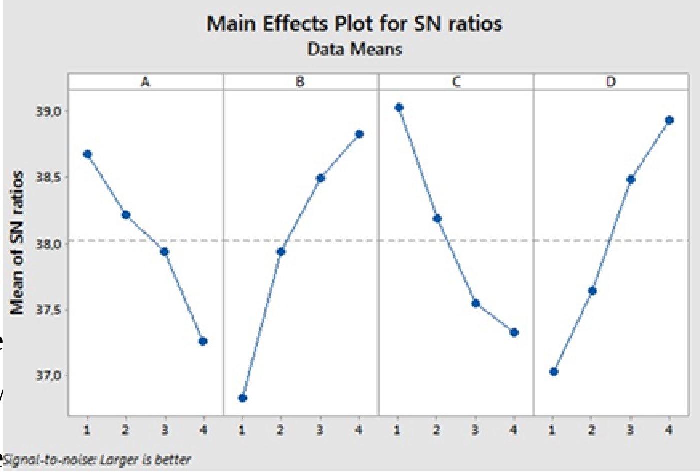

Fig. 2. Variation of S/N ratio for each parameter

Taguchi design replaces the full factorial experimental design with a partial factorial experiment, less expensive and faster. Since the partial experiment is only a selected set of complete factorial combinations, the analysis of the partial experiment must include a confidence analysis to qualify the results, represented by the analysis of variance (ANOVA), which is frequently used to provide the measure

Fig. 3. Variation of target function with the four parameters

Table 5
ANALYSIS OF VARIANCE (AFTER TAGUCHI)

Source	DF	Adj SS	Adj MS	F	P
A	3	275.36	91.787	142.54	0.001
B	3	721.24	240.412	373.34	0.002
C	3	556.68	185.559	288.15	0.001
D	3	730.68	243.561	378.22	0.001
Error	3	1.93	0.644		
Total	15	2285.89			

of confidence of the results. The technique does not directly analyze the data but determines their variability, and the degree of trust is measured by the variance. By understanding the source and magnitude of the variance optimal operating conditions can be predicted [35-38].

The analysis of each model provides the coefficients for each factor, the values of p and an analysis of variance, which allows determining whether the factors are significantly related to the response data and the relative importance of each factor of the model. ANOVA results are presented in table 5.

The value of R is 99.92%, indicating a very good agreement of the model, meaning that 99.92% of the variability of the response could be explained by the model. The adjusted coefficient of determination R-sq adjusted is 99.58%, indicating a high capacity of the model to reproduce the process. The mathematical relation of the model is:

$$Y = 80.606 + 5.644\,A1 + 1.519\,A2 - 1.456\,A3 - 5.706\,A4 - 10.631\,B1 - 0.456\,B2 + 3.869\,B3 + 7.219\,B4 + 9.344\,C1 + 0.719\,C2 - 4.431\,C3 - 5.631\,C4 - 9.256\,D1 - 3.106\,D2 + 3.844\,D3 + 8.519\,D4 \quad (8)$$

The order of coefficients in absolute value indicates the relative importance of each factor in relation to the answer; the factor with the highest coefficient has the greatest impact. The sequential and adjusted sums of squares also indicate the relative importance of the factor; the factor with the largest sum of squares has the greatest influence on the result.

The tables generated by the program include Delta parameter, which compares the relative magnitude of the effects. Delta statistics is given by the difference between the highest and lowest average for each factor. Minitab assigned ranks based on Delta values; first place to the highest value Delta, 2nd place to the second highest, and so on. From the Delta values calculated for the four factors it can be seen that the greatest importance has the duration of treatment, followed in order by the degree of irradiation, the dye concentration and *p*H. Delta values for the four studied factors are show in table 6.

The existence or the absence of interactions between factors can be seen from the graphs of the interaction matrix. The parallel lines indicating the absence of interactions, whereas the intersection show the presence of interactions between factors [39-41].

Such interactions are shown in figure 4. It can be seen that the factor 2 interacts with all the other three factors, and one can observe a limited interaction between factors 1 and 4 (the *p*H value and irradiation power).

The graph that displays the dependence of the residues and the adjusted values is shown in figure 5.

It can be concluded from figure 5 that the hypothesis of constant variance of the error term for all levels of the independent process parameters is not violated because there is not a significant pattern. Figure 6 shows the normal probability chart, which is useful for evaluating the fit of a distribution data.

This graph is obtained by creating an estimated cumulative distribution function based on experimental results by plotting the value of each observation to estimated cumulative probability. Graphs are processed so that the distribution forms a straight line. A good fit of the distribution is present if the observations are in the vicinity of the line. It can be seen from figure 6 that there is a linear trend on normal probability graph, which indicates

Larger is better

Level	A	B	C	D
1	38,68	36,83	39,03	37,03
2	38,22	37,94	38,19	37,64
3	37,94	38,50	37,55	38,49
4	37,26	38,83	37,33	38,94
Delta	1,42	2,00	1,70	1,91
Rank	4	1	3	2

Response Table for Means

Level	A	B	C	D
1	86,25	69,97	89,95	71,35
2	82,13	80,15	81,33	77,50
3	79,15	84,47	76,17	84,45
4	74,90	87,83	74,97	89,13
Delta	11,35	17,85	14,98	17,78
Rank	4	1	3	2

Table 6
DELTA VALUES FOR THE FOUR STUDIED FACTORS

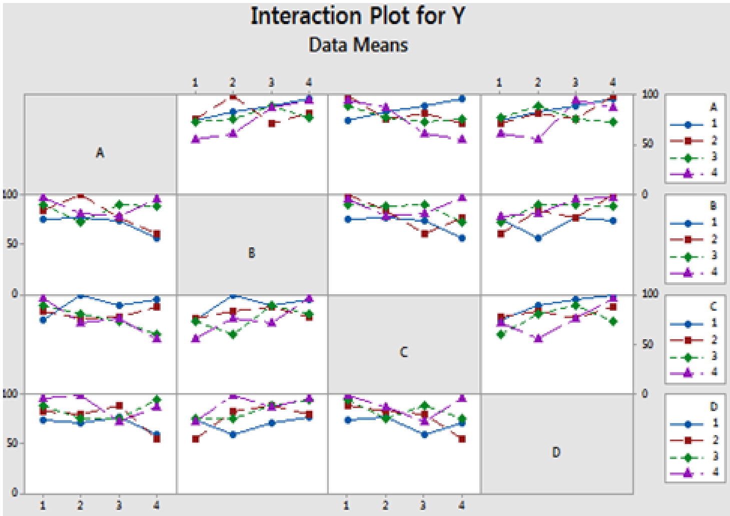

Fig. 4. Interactions between factors

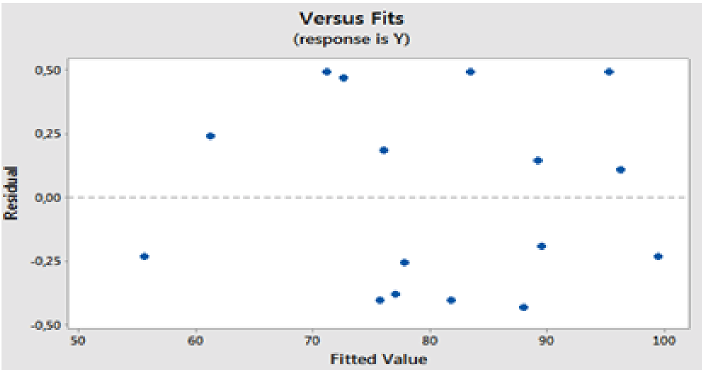

Fig. 5. Interactions between factors

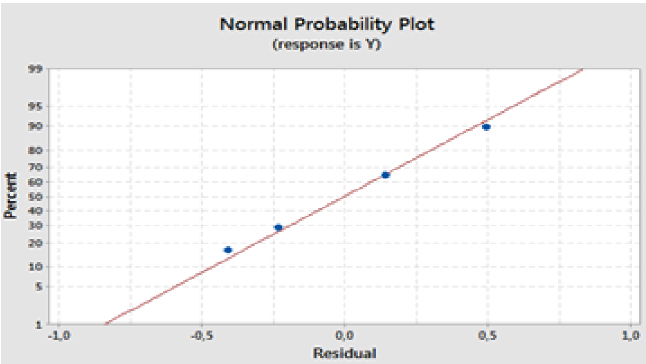

Fig. 6. Dependence between the residues and the adjusted values

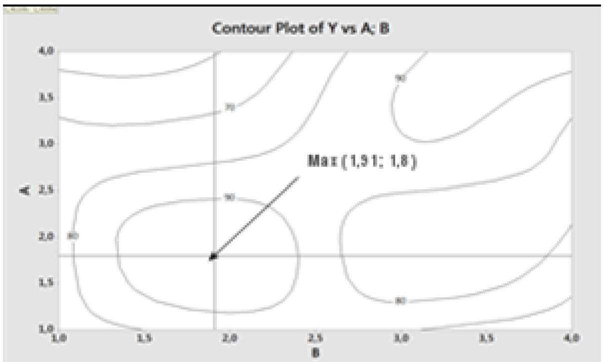

Fig. 7. Normal probability curve

that the assumption that the error term has a normal probability distribution is achieved. The effects of combination of two factors on the degree of discoloration are shown in figure 7 and figure 8.

From figure 7 and 8 it can be observed that the maximum values of the degree of discoloration is achieved for A = 1.91 and B = 1.8, and A = 1.12 and C = 3.75 respectively,

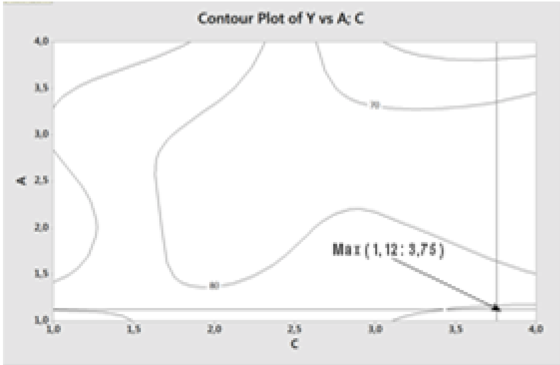

Fig. 8. Effect of factors A and B on the discoloration degree

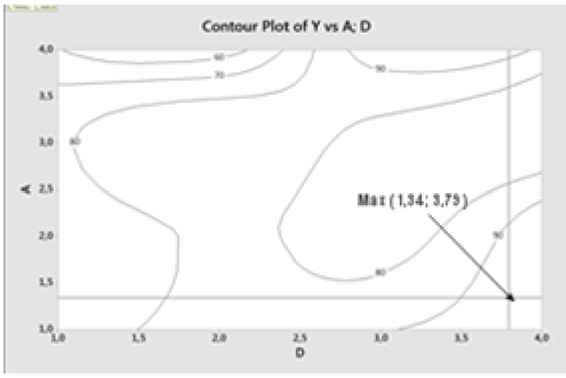

Fig. 9. Effect of factors A and C on the discoloration degree

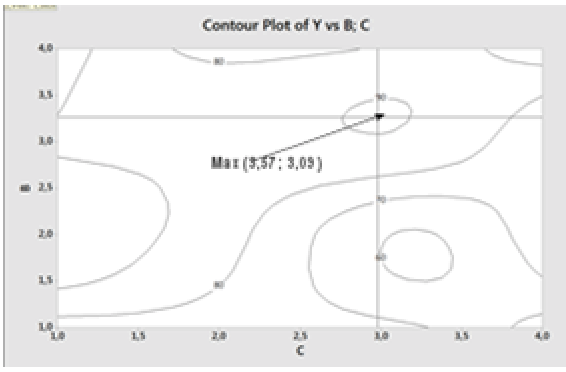

Fig. 10. Effect of factors A and D on the discoloration degree

which confirms the importance of both treatment duration of dye concentration.

The graphic illustration of the dependence degree of discoloration degree with factors A and D (*p*H and irradiation power); figure 9 shows that the maximum discoloration values are obtained for A = 1.34 and 3.79, hence at strong acidic *p*H and high irradiation power. In figure 10 is can be seen that the dependent on the degree of discoloration with factors B and C has a maximum for B = 3.57 and C = 3.09.

Figure 11 shows the change in the discoloration degree with factors B and D, and the optimum is recorded for B = 3.57 and D = 3.09. For the dependence of the degree of discoloration with the factors C and D, (fig. 12), the optimum is obtained for C = 1.73 and D = 3.95, which indicates that increasing the power of irradiation leads to substantially reduced processing time.

Based on these data, the Minitab program calculates the global maximum that is obtained for A2, B4, C1 and D4.

Conclusions

Taguchi method of experimental design was used to optimize photo-Fenton discoloration process of wastewaters from Reactive Blue 19 dyeing. Four input parameters were analyzed. Since the objective is to achieve

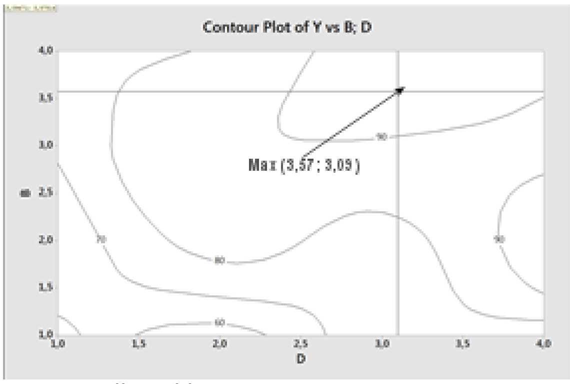

Fig. 11. Effect of factors B and C on the discoloration degree

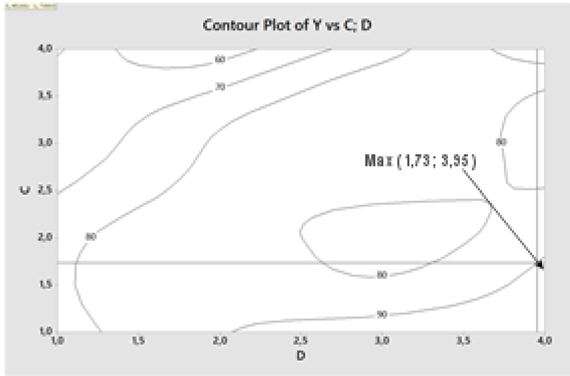

Fig. 12. Effect of factors C and D on the discoloration degree

higher degrees of discoloration, the criterion larger the better has been used to maximize the degree of discoloration. An orthogonal array L16 and four levels with four parameters have been used to obtain the set of values of parameters that lead to best results. The experimental values were processed using the software Minitab 17, receiving as an optimum value of 2 for *p*H, duration of treatment of 60 minutes, the concentration of dye 2mg/L and the power of radiation of 15kW/L, conditions that give a 99.45% degree of discoloration.

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