Box-Benhken Experimental Design Optimization of the Coagulation Discoloration Process of Waste Water from Dyeing with Acid Dyes

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The efficiency of $Al_2(SO_4)_3$ in discoloration of synthetic dyeing wastewater composed of two acid dye has been investigated. The influence of pH, coagulant concentration and initial dye concentration on the removal efficiency was analyzed in order to obtain optimum results. The optimization study through Box - Benhken experimental design was conducted in jar test to determine the interaction between the three factors and their effect on the discoloration degree. Very good effectiveness was found for the discoloration treatment of Acid Red 97 at optimal pH = 6.54, coagulant concentration 218 mg/L and an initial dye concentration of 181 mg/L, whilst for the second dye, Acid Yellow 42, the process lead to poorer results.

Keywords: discoloration, coagulation, acid dyes, Box - Benhken experimental design

Colloidal particles, which are characterized by kinetic and aggregation stability, have a size ranging from 0.001 to 0.1 micrometers and a complex structure determined by their negative electric charge [1]. They consist of two parts: the nucleus, electrically neutral, which forms the weight of the micelle, and electrical double layer surrounding the particles, an adsorption layer adhered to the core and a diffuse layer consisting of counter ions [2]. Many pollutants in surface waters, but also in wastewater, contain colloidal particles which give stability to the suspension and hence limited capacity to sedimentation caused by the fact that there is no aggregation of these particles.

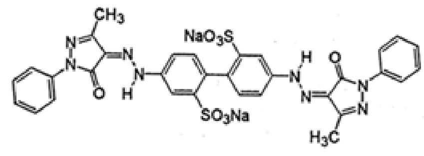
Coagulation, one of the most important physico-chemical operations used in water and wastewater treatment [3], is based on the action of chemical reagents (coagulant agents) that produce ions of opposite sign to the colloidal particles, neutralizing their electric charge, which reduces the repulsive forces between the colloidal particles and leads to their aggregation into larger and heavier particles that settle much quicker. The coagulant agents to be used may be inorganic (salts of weak bases and strong acids), synthetic organic polymers (for example, derivatives of polyacrylamide) or natural (such as microbial cultures) [4, 5]. For the inorganic coagulants their effectiveness increases with the valence of the metal ion (it is considered that the efficiency of a salt of a trivalent metal will be 500 times higher than the salt of a monovalent metal), and this is why the most used are the salts of aluminum or iron [6, 7]. Coagulation can be used to discolorate textile wastewater, and its main advantage is given by the fact that the process eliminates the dyes from the water and not only removes the color by cleavage of the dye molecule into colorless degradation compounds which may have even greater toxic potential than the dye itself [8, 9].

In this study it was analyzed the efficiency of the coagulation in the removal of color from acid dyeing wastewater, knowing that these dyes have a tendency to form colloidal solutions (especially the medium and poor leveling ones). Aluminum sulfate, a coagulant frequently used in the water treatment [10], was used. Aluminum sulfate acts through polihidroxo-complexes of the $[Al_8(OH)_{20}]^{4+}$ type, which are formed in acidic conditions [11, 12], so it is preferable to use it because acid dyeing waste water has a *p*H in this range. Three level Box–Behnken factorial design with three factors and response surface methodology were used to examine and optimize the effects of pH, coagulant concentration and initial dye concentration on the discoloration of Acid Yellow 42 and Acid Red 97 wastewater.

Experimental part

Materials

Two acid dyes have been studied: Acid Yellow 42 and Acid Red 97, both obtained from Dintex Dyechem Ltd.The chemical formulas of the two dyes are presented in figure 1.



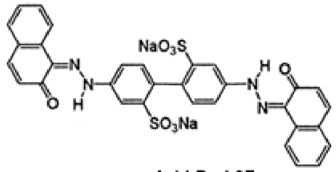


Fig. 1. Chemical structures of the studied dyes

All dyeing solutions were prepared by diluting a basic solution of 1g/L dye, obtained by pasting the dye with some warm water, adding distilled water and boiling to dissolve, and then filling to 1L.The coagulation agent that was used is aluminum sulfate $Al_2(SO_4)_3 \times 18H_2O$, purchased from Sigma-Aldrich. The basic solution used to obtain the coagulant dose required for the experiments was obtained by dissolving 50g of aluminum sulfate to one liter of

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deionized water. A solution 1 M H_2SO_4 has been used to adjuste the initial pH of the dye solution. The *p*H of the samples was determined with a Multi-lab *p*H 315i pH meter.

Tests were conducted using a Flocculator FC 4S 4-position jar tester with stirrer speed control. The tests have been conducted as follows: 3 min rapid stirring (150rpm), 15 min gentle agitation (45rpm) followed by a settling period of 30 min.

Determining the degree of discoloration

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

$$\text{Discoloration degree} = \frac{Abs_o - Abs_f}{Abs_o} \times 100\ ,\ [\%] \qquad (1)$$

where:

Abs_o - absorbance of the untreated sample;

Abs_f - absorbance of the treated sample.

The absorbance was measured at maximum absorption wavelength (453 nm for Acid Yellow 42 and 494nm for Acid Red 97) using a Spectro UV/Vis Dual Beam Labomed UVS-2800 spectrophotometer.

Design of experiments

It was chosen a Box - Behnken experimental program, considered to be the most effective method in the category of response surface experimental design programs [13-20]. Box-Behnken models are a class of models of rotary or nearly rotary order two incomplete factorial models based on three levels, which have the advantage to require a fewer number of runs [21]. The chosen independent variables are the initial *p*H value, the concentration of coagulation agent and initial dye concentration and their codification is presented in table 1.

Table 1

CODIFICATION OF INDEPENDENT VARIABLES

Independent variables	Measurement units	Codified values		
		-1	0	1
pH	pH units	4	6	8
Coagulant concentration	mg/L	50	150	250
Initial dye concentration	mg/L	10	105	200

Table 2

DISCOLORATION DEGREE VALUES FOR ACID YELLOW 42

Nr. experiment	X_1	X_2	X_3	Discoloration degree, %
1	0.00	1.00	-1.00	33.9
2	0.00	-1.00	-1.00	26.5
3	0.00	0.00	0.00	66.4
4	0.00	0.00	0.00	67.3
5	1.00	0.00	-1.00	18.1
6	1.00	0.00	1.00	54.3
7	1.00	1.00	0.00	51.7
8	-1.00	1.00	0.00	38.3
9	0.00	-1.00	1.00	29.4
10	0.00	0.00	0.00	69.8
11	0.00	0.00	0.00	70.2
12	0.00	1.00	1.00	75.8
13	-1.00	0.00	-1.00	33.6
14	1.00	-1.00	0.00	19.1
15	0.00	0.00	0.00	68.3
16	-1.00	-1.00	0.00	21.2
17	-1.00	0.00	1.00	25.5

The experimental field for the first two independent variables was chosen based on data available in the literature [22-24], while initial dye concentration was calculated for dyeing with 1-3% dye at a liquor ratio of 1: 20 - 1:50 and a level of exhaustion of 90%.The results have been processed using Design-Expert 7.1 software (Stat-Ease).

Results and discussions

Discoloration of Acid Yellow 42 through coagulation

The random order of experiments dictated by the statistical analysis program, and the results recorded for the Acid Yellow 42 are presented in table 2.

The coefficients of the response functions have been found by using a Stat-Ease Design Expert 7.1 regression program, and the equation that describes the discoloration of Acid Yellow 42 by coagulation with aluminum sulphate, based on the three selected parameters, is as follows:

$$\text{Discoloration degree} = 68.00+3.13X_1+12.75X_2+9.13X_3+3.75X_1X_2+11.00X1X3+9.75X_2X_3-22.00X_1^2-13.75X_2^2-13.50X_3^2. \qquad (2)$$

Studying the equation, it can be said that the coagulant concentration and the initial concentration of the dye have a great influence on the process, as proven by the high coefficients of terms X_2 (especially) and X_3. It is noticeable the synergistic effect of X_1 and X_3 terms, and X_2 and X_3 respectively (evidenced by the high coefficients of terms X_1X_3 and X_2X_3). The significance of every coefficient was analysed through a P-value test, considering 95% of confidence. A coefficient is considered to be significant for a p-value less than 0.05 and it was found that all the coefficients of the equation are significant.

The analysis of variance tests was also conducted. The obtained value of F-test is very high (109.87), which indicates that the model is significant, with a probability of only 0.01%, that results are adversely affected by noise. The high value of the determination coefficient (R^2 = 0.9081) indicates the accuracy of fitting of the model and the value of the predicted coefficient of determination is consistent with the adjusted coefficient of determination (0.9839). Adequate Precision measures the ratio of signal and noise and it is desirable to have a value greater than 4. The result obtained in this case is 27.957, which indicates an appropriate signal, confirming that the model can be used to browse the chosen experimental space. The diagnosis graphs, such as those that correlate the predicted values with the actual values, and the normal dependence residues respectively (fig. 2) make it possible to characterize the degree of accuracy of the model. One can observe an appropriate agreement between the actual data and data calculated by model, as demonstrated by the fact that points are distributed closely to the diagonal line.

Response surface graphs are shown in figure 3.

It can be observed the symmetry of the three response surfaces and that maximum response values are within the experimental range (contour curves are circular and the maximum is within the experimental area). The intersection of the obtained response surfaces with plans of constant goal function, followed by orthogonal projection of the obtained intersection curves gives the contour curves, whose graphical representation allows viewing the factors that lead to the maximum values of the goal function.

A two-dimensional representation of the discoloration degree of Acid Yellow 42 to the plane of two of the three

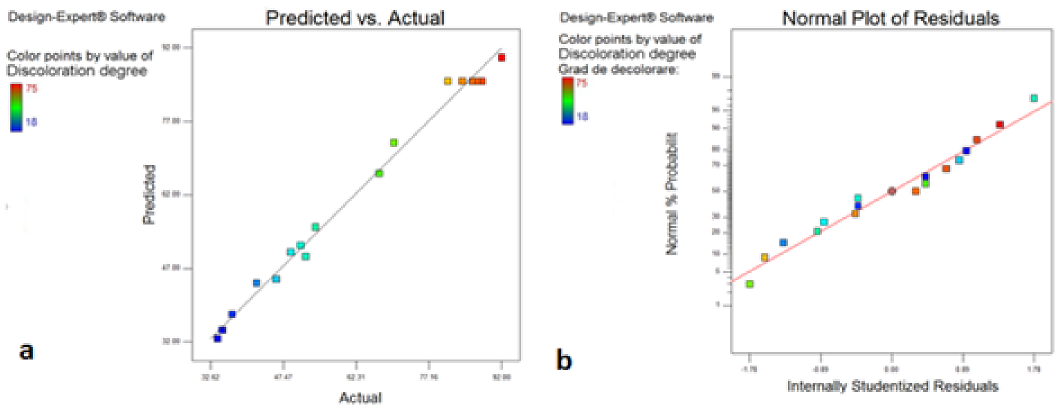

Fig. 2. Diagnostic chart: a - predicted vs. actual for Acid Yellow 42 and b - normal plot of residuals for Acid Yellow 42

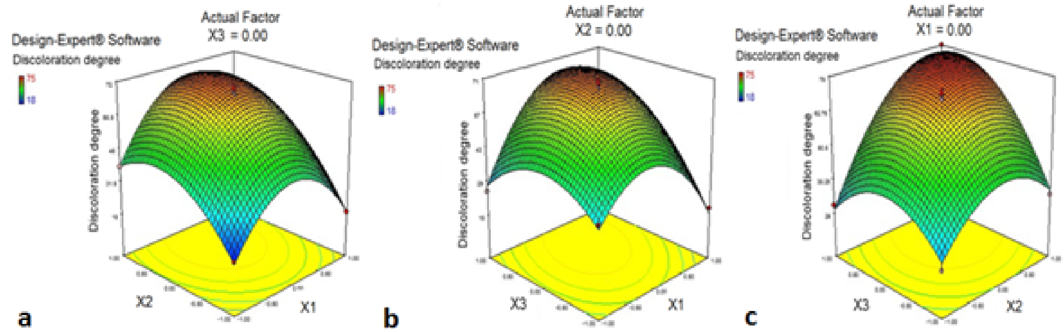

Fig. 3. Three-dimensional plot for discoloration degree of: a - Acid Yellow 42 as a function of X_1 and X_2; b - Acid Yellow 42 as a function of X_1 and X_3; c - Acid Yellow 42 as a function of X_2 and X_3

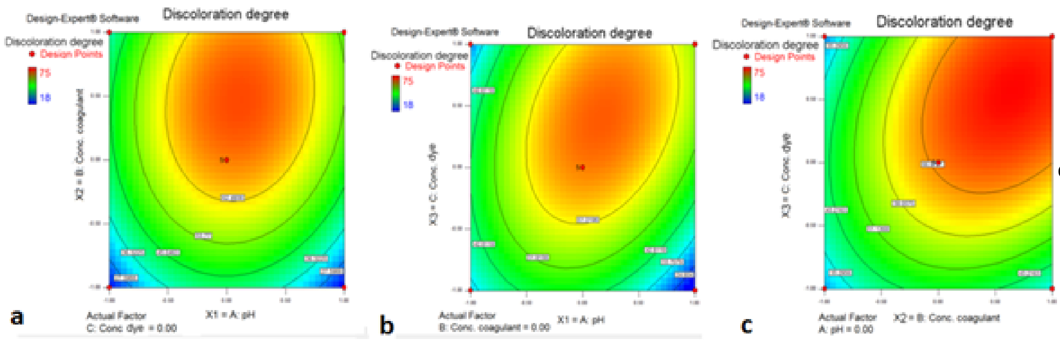

Fig. 4. Contour curves representing discoloration degree: a - $f(X_1, X_2)$; b - $f(X_1, X_3)$; c - $f(X_2, X_3)$

independent variables, while maintaining the third to the central value, is shown in figure 4.

It can be noted that in all three cases, the value indicating the optimum conditions are located in the center of concentric curves contained in the plane of the experiment. By imposing the condition of maximizing the goal function, the values of the three independent variables able to maximise the discoloration effect are found (fig. 5).

These coded values are 0.81 for the *p*H, 0.93 for concentration of coagulant and to 1 for initial dye concentration, and the discoloration degree obtained in these conditions is 72.48%. These values correspond to the actual values: 7.6 for *p*H, 243 mg/L for the concentration of coagulant and 200m g/L for dye concentrations.

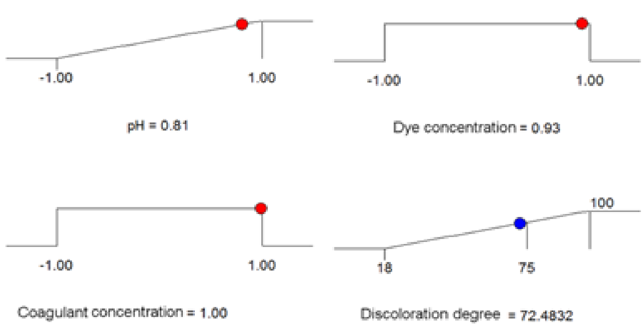

Fig. 5. Values of independent variables leading to maximum discoloration degree of Acid Yellow 42

Discoloration of Acid Red 97 through coagulation

We used the same experimental stages as in the case of the dye Acid Yellow 42. The program Design Expert randomly ordered the 17 experiments, and the results for the Acid Red 97 dye are shown in table 3.

After data processing the estimated values for model coefficients have been obtained. The statistics used to verify the usual assumptions on coefficients indicated that

Table 3

DISCOLORATION DEGREE VALUES FOR ACID RED 97

No. experiment	X_1	X_2	X_3	Discoloration degree, (%)
1	1.00	0.00	1.00	70.9
2	1.00	0.00	-1.00	35.2
3	0.00	0.00	0.00	81.9
4	0.00	-1.00	1.00	46.1
5	1.00	-1.00	0.00	34.8
6	0.00	1.00	1.00	92.4
7	-1.00	0.00	-1.00	52.3
8	0.00	-1.00	-1.00	42.3
9	1.00	1.00	0.00	67.6
10	-1.00	-1.00	0.00	37.1
11	0.00	0.00	0.00	87.9
12	0.00	0.00	0.00	86.2
13	0.00	0.00	0.00	84.8
14	-1.00	0.00	1.00	51.1
15	-1.00	1.00	0.00	54.9
16	0.00	0.00	0.00	88.1
17	0.00	1.00	-1.00	49.9

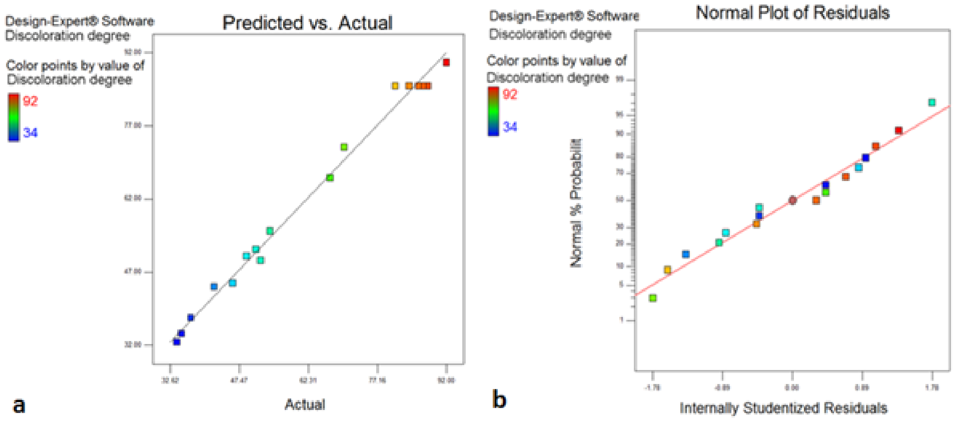

Fig. 6. Diagnostic charts: a - predicted vs. actual for Acid Red 97; b - normal plot of residuals for Acid Red 97

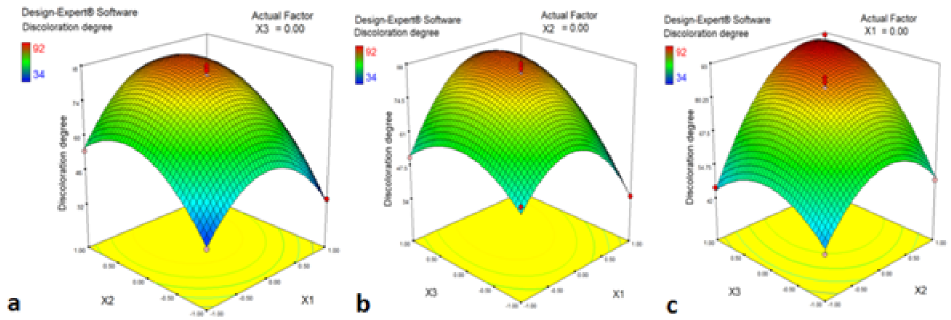

Fig. 7. Three-dimensional plot for discoloration degree of: a - Acid Red 97 as a function of X1 and X2; b - Acid Red 97 as a function of X1 and X3; c - Acid Red 97 as a function of X2 and X3

all the terms are significant, with the exception of X_1. Criterion F value of 87.88 indicates that the model is satisfactory, as there is only a 0.01% probability that the estimated results to be affected by noise factors. The value of 1.31 for *Lack of Fit F-value* indicates the absence of significant lack of adequacy, indicating suitability of the model. The value of the predicted coefficient of determination is high (0.9235) and in accordance with the value adjusted coefficient of determination of 0.9799. The ratio of signal to noise is given by *Adeq Precision*, and a value of over 4 indicates a reduced noise influence. In this case the value of 25.331 indicates the adequacy of the signal. Based on those findings, the equation that describes the process of discoloration of Acid Red 97 in the aluminum sulfate coagulation, according to three chosen parameters, is as follows:

$$\text{Discoloration degree} = 85.20 + 12.88X_2 + 10.13X_3 + 4.00X_1X_2 + 9.00X_1X_3 + 9.75X_2X_3 - 21.23X_1^2 - 15.98X_2^2 - 11.97X_3^2 \quad (3)$$

Studying the equation, it can be seen that for this dye the most influential factors are, in order, the coagulant concentration and the initial dye concentration, as proven by the high coefficients of terms X_2 (especially) and X_3. In addition, the quadratic term corresponding to the coagulant concentration has also a positive coefficient. Using diagnostic charts for evaluating the model (fig. 6) it is found that there is an appropriate agreement between the actual data and data calculated by model.

Response surface graphs for the discoloration of Acid Red 97 are shown in figure 7.

Also in this case, the three response surfaces are symmetrical and the maximum response values are to be found within the experimental field. Contour curves, resulting from the intersection of response surfaces with plans of constant target function, followed by their orthogonal projection, are shown in the figure 8.

It can be noticed that in all three cases the maximum value of the degree of discoloration is positioned in the central concentric curves contained in the experiment area. If the condition of maximizing the goal function is imposed, the values of the independent variables which give the greatest discoloration effect are obtained (fig. 9).

These coded values are 0.27 for *p*H, 0.68 coagulant concentrations and 0.8 for the initial dye concentration, and the degree of discoloration obtained is substantially higher than in the first studied acid dye, namely 93.84%. The actual values are for 6.5 the *p*H, 218 mg/L for the

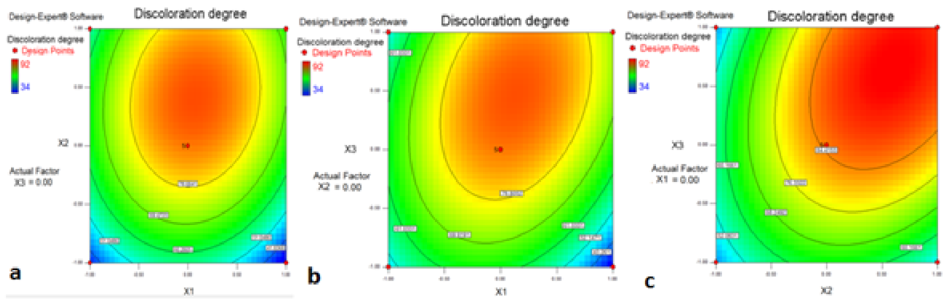

Fig. 8. Contour curves representing discoloration degree: a - f(X1, X2); b - f(X1, X3); c - f(X2, X3)

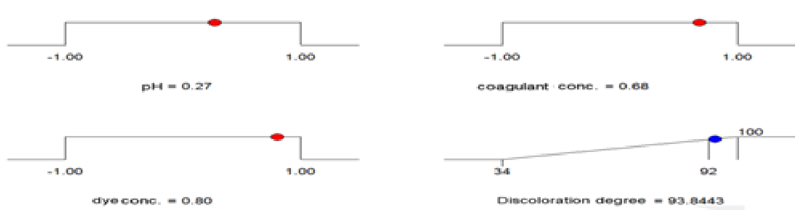

Fig. 9. Values of independent variables leading to maximum discoloration degree of Acid Red 97

coagulant concentration and 181 mg/L for the initial dye concentration.

Conclusions

Using as coagulant aluminum sulfate, a coagulant commonly used in wastewater treatment, it has been studied the possibility of discoloration the residual solutions from dyeing with two acid dyes: Acid Yellow 42 and Acid red 97. The Box–Behnken statistical experimental design and response surface methodology have been used to evaluate the effect of *p*H, coagulant and initial dye concentration on process effectiveness.

The optimum conditions for Acid Yellow 42 discoloration were obtained at a pH value of 7.68 (encoded value 0.81), concentration of the coagulant of 243 mg/L (encoded value 0.93) and an initial dye concentration of 200 mg/L (value coded 1). The results showed good agreement between model predictions and experimental data. Also using the Box - Benhken experimental design to evaluate the effect of the three parameters mentioned above,*p*H, concentration of coagulant and initial concentration of dye on the effectiveness of the process of discoloration by coagulation of Acid Red 97, it was found a good agreement between model predictions and experimental data. It is to note the substantially higher effectiveness of discoloration process compared to the previous dye, obtained at a pH value of 6.54 (0.27 coded value), a coagulant concentration of 218 mg/L (encoded value 0.68) and an initial dye concentration of 181 mg/L (0.8 encoded value). It can be observed that the point of peak discoloration in this case stands in a zone of *p*H near neutral, and the quantity of required coagulant to achieve the highest degree of discoloration is about 25% lower compared to the other studied acid dye.

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