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OPTIMIZATION OF SOME WATER TREATMENT CONTAINING ORGANIC DYES (BROWN VOPSIDER DNRL 101) BY OXIDATION WITH HYDROGEN PEROXIDE ASSOCIATED WITH UV IRRADIATION

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ABSTRACT. It was studied the photooxidation with hydrogen peroxide of some waters containing the organic dye – Brown Vopsider DNRL 101 – in different conditions of operation. It was proposed a mathematical model of the studied process having two independent variables: pH and irradiation time. Also, there were determined the best operational conditions and the optimum value of the decolouring degree. The dye destruction was appreciated through the removal of samples colour expressed through the decolouring degree.

1. INTRODUCTION

From the preliminary studies concerning the decolouring of some aqueous solutions of dyes by oxidation with hydrogen peroxide (H_2O_2) associated with UV irradiation [1], it seems that under the principal factors with high influence on the photooxidation with hydrogen peroxide are the pH and irradiation time. This two factors can be the variables of an wastewater treatment containing the Brown Vopsider DNRL 101.

Into the decolouring processes are difficult to establish the best operational conditions for a satisfactory reduction of colour until a reasonable level for the evacuation into different emissaries.

That is way, it was used a programme of experimental data calculation during the photooxidation with hydrogen peroxide in the presence of a Fe^{2+} cathalyst for some waters containing Brown Vopsider DNRL 101 dye. This programme can be easely applied and adapted for the operational conditions and for other types of waters with different dyes.

To establish the mathematical model of such a decolouring process, it was used the experimental compositive rotative planning of two level (2^2 type) [2].

2. Materials and methods

2.1. Reagents and apparatus

- Brown Vopsider DNRL 101, aqueous solution of 0.1 g/l;
- Hydrogen peroxide, 30 % solution;
- Sulphuric acid, solution 4 N;
- Sodium hydroxide, solution 2 N;
- Iron sulphate, aqueous solution of 10 mg/l Fe^{2+};
- DRELL 2000 Spectrophotometer, HACH company;

- Photooxidation reactor. It was used a tubular reactor [3], with a capacity of ~ 500 cm^3 and 45 cm in height, having a casing for the keeping of a constant temperature. The UV light source of the reactor is a lamp with mercury vapours of medium pressure having 12 cm in length, 20 mm in diameter. It is an alternating curent lamp. The lamp emits UV radiations with a large UV range (180 - 400 nm), representing 30 % of the torch power. The rest represents the contribution of visible radiations (15 %), thermal radiations (35 %) şi the heat losses conduction on the electrodes (20 %).
- PC Computer.

2.2. Analysis methods

The study on the destruction of aqueous dyes solutions by oxidation with hydrogen peroxide associated with UV light was based on the variation vs time of decolouring degree. Under the UV light action, the hydrogen peroxide forms $HO\cdot$ radicals according to reaction [4],[5]:

$$H_2O_2 + h\nu \rightarrow 2HO\cdot$$

and the $HO\cdot$ radicals initiate a chain of radicalic reactions that lead to the destruction of organic matter, respectively to the samples decolouring.

In the presence of iron salts, the formation of $HO\cdot$ radicals:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO\cdot$$

is accelerated and an acidic medium facilitates the decolouring process.

The study of destruction expressed by the variation of decolouring degree was required the determination of samples colour before and during the oxidation process.

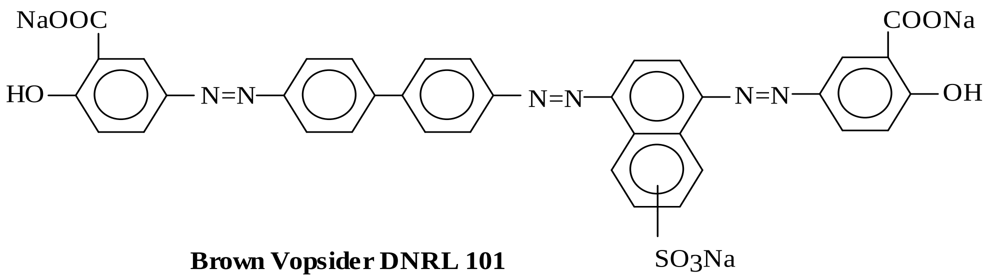
The colour determination was spectrophotometrically done by measurement of absorbance at 456 nm, the blank was the distillated water. The colour was expressed in Hazen units (UH) according to the fact that an absorbance of 0.069 at 456 nm corresponds to 50 UH [5].

The appreciation of decolouring degree (DD) was done according with the relation:

$$DD\% = \frac{C_i - C_t}{C_i} \cdot 100$$

where: C_i - the initial intensity of colour [UH];
C_t - The intensity of colour at *t* time of the photooxidation [UH];

The Brown Vopsider DNRL 101 dye is an unitary compound having the following structure:



Brown Vopsider DNRL 101

Because of the great number of aromatic nucleus, this dye is integrated into the class of nonbiodegradable compounds.

The standard working sample was prepared from 250 ml dye solution with the addition of hydrogen peroxide (2.5 ml), catalyst (5 ml of Fe^{2+} solution) and sulphuric acid or sodium hydroxide according to the followed target. The pH adjustment was done with NaOH 2N or H_2SO_4 4N and directly reading at a HACH pH-meter.

On this standard sample, there were comparatively done kinetic studies concerning the influence of pH and irradiation time on the decolouring process by photooxidation with hydrogen peroxide.

In the case of UV irradiation, the samples was introduced into the photooxidation reactor (Fig.1), and the samples destined for the absorbance measurements were sampling from reactor at intervals of 10 minutes.

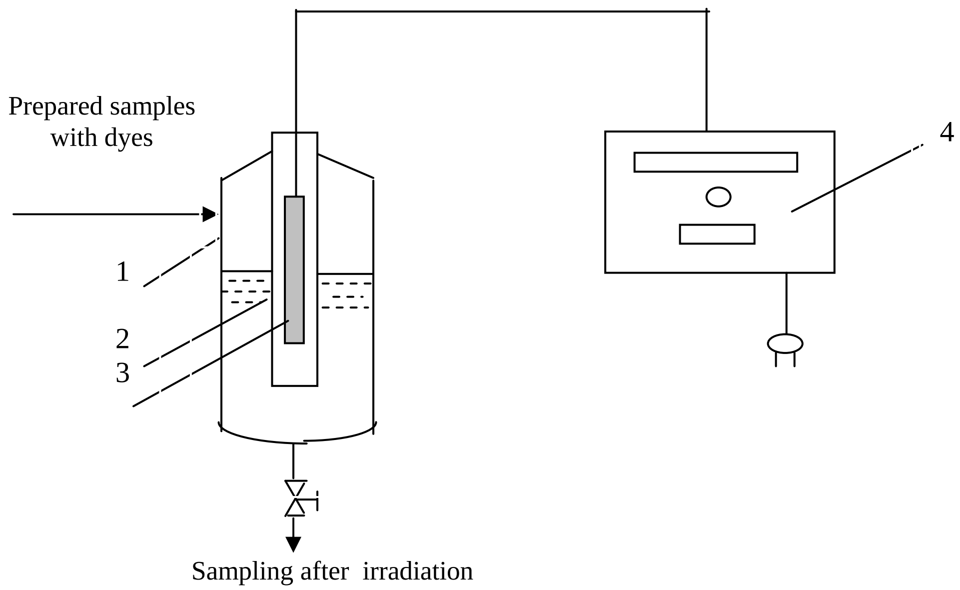


Fig.1. Photooxidation reactor
1 - photooxidation reactor; 2 - quartz tube; 3 - UV lamp; 4 - UV adapter.

The central planning has the advantage of no excessive experiments in comparison with the number of coefficients to be determined.

Into the admisible field of independent variables, for each variable – z_i (pH or irradiation time) – is established a basic value – z_{io} – and a variation step - Δz_{io} of each variables. Adding the variation step at the basic value is obtained the superior and subtraction of the step value leads to the inferior level of variable. The codification value of z_i variable named X_i is determined with the relation [8]: $\mathbf{x_i = \frac{z_i - z_{i0}}{\Delta z_{i0}}}$

So, the superior level is coded *+1*, inferior level *–1* and the basic level *0*. There are possible other values of the variable level (α_ι) [7],[8].

Into this experimental cental compositive planning, the codificated variables will have the next values: -1.414, -1, 0, +1, +1.414 into a specific order.

As an optimization criterion was chosen the decolouring degree. The experimental results during the photooxidation with hydrogen peroxide for the establised values of the two independent variables, are synthetized into the experimental matrix.

After that, it was applied the Fisher test to determine the F value with the relation [9]:

$$F = \frac{(n-1)\cdot\sum_{i=1}^{n}(Y_{ei}-\overline{Y}_e)^2}{(k-1)\cdot\sum_{i=1}^{k}(Y_{eki}-\overline{Y}_{ek})^2}$$

where:

Y_{ei} – the experimental values of the dependent variable (decolouring degree, %);

$\overline{Y}_e$ - the average value of the dependent variable;

Y_{eki} – the experimental values of dependent variable into the centre of the programme;

$\overline{Y}_{ek}$ - the average value of the experimental values into the centre of the programme;

n - the total number of experiments from the experimental matrix;

k - the number of experiments into the centre of the programme.

If F > $F_{tab,}$ (F_{tab} is the value of F test from the statistical tables) [8], it can be said that the deviation of the experimental data from the average value it is not the result of experimental errors, but it is determined by the influence of independent variables (pH and irradiation time) on the decolouring degree.

To establish the relation between the dependent variable (Y - decolouring degree, %) and the two independent variables as a whole, it will be determined the multiple correlation coefficient in accordance with the relation [9].

$$R_{Y_{x1x2}} = \sqrt{1-\frac{\sum_{i=1}^{n}(Y_{ei}-Y_{ci})^2}{\sum_{i=1}^{n}(Y_{ei}-\overline{Y}_e)2}}$$

If the R_{Yx1x2} value is close to one, the independent variables have a significant importance on the dependent variable.

2.3. The central compositive rotative planning of 2^2 type

There were chosen the principal factors that influence the decolouring process of some waters charged with Brown Vopsider DNRL 101 as a result of oxidation with hydrogen peroxide associated with UV irradiation (preliminary experiments). The pH and irradiation time factors were considered as independent variables in this treatment with high influence on the decolouring degree.

The computational programme of the experimental data on the decolouring process by photooxidation with H_2O_2 must be easily applied into good operational conditions.

The experimental central compositive rotative planning of 2^2 type proposes a mathematical model [7]:

$$Y = b_0 + \sum_{i=1}^{2} b_i \cdot X_i + \sum_{i=1}^{2} b_{ii} \cdot X_i^2 + b_{12} \cdot X_1 \cdot X_2$$

The model coefficients are determined using the following relations (Table 1) [7].

Table 1.

Relations for the calculation of the model coefficients.

$b_0 = 0{,}2 \cdot \sum_{i=1}^{13} Y_{ei} - 0{,}1 \cdot (\sum_{i=1}^{13} x_1^2 \cdot Y_{ei} + \sum_{i=1}^{13} x_2^2 \cdot Y_{ei})$
$b_1 = 0{,}125 \cdot \sum_{i=1}^{13} X_1 . Y_{ei}$
$b_2 = 0{,}125 \cdot \sum_{i=1}^{13} x_2 \cdot Y_{ei}$
$b_{11} = 0{,}125 \cdot \sum_{i=1}^{13} x_1^2 \cdot Y_{ei} + 0{,}01875 \cdot (\sum_{i=1}^{13} x_1^2 \cdot Y_{ei} + \sum_{i=1}^{13} x_2^2 \cdot Y_{ei}) - 0{,}1 \cdot \sum_{i=1}^{13} Y_{ei}$
$b_{22} = 0{,}125 \cdot \sum_{i=1}^{13} x_2^2 \cdot Y_{ei} + 0{,}01875 \cdot (\sum_{i=1}^{13} x_1^2 \cdot Y_{ei} + \sum_{i=1}^{13} x_2^2 \cdot Y_{ei}) - 0{,}1 \cdot \sum_{i=1}^{13} Y_{ei}$
$b_{12} = 0{,}25 \cdot \sum_{i=1}^{13} x_1 \cdot x_2 \cdot Y_{ei}$

To verify the significance of the multiple correlation coefficient it is used the Fisher test [9]: $F_c = \frac{n-b-1}{b} \cdot \frac{R^2_{Y_{x_1 x_2 x_3}}}{1 - R^2_{Y_{x_1 x_2 x_3}}}$

where: b – the number of independent variables.

If the Fisher constant for the free degree ν_1= n-k-1=10 and ν_2= k=2 is higher than the value from the statistical table /4/, F_{tab}=4.14, it is considered that the independent variables have a significant importance on the dependent variable.

After that there are tested the model coefficients using the Student test [9].

To verify the model correctness, respectively, its ability to mathematically expressed the decolouring process by photooxidation with hydrogen peroxide, there are compared the experimental data with the values calculated with the proposed model and calculated the deviation *A* using the next relation [2],[7]:

$$A = \frac{Y_{ci} - Y_{ei}}{Y_{ci}} \cdot 100 \cdot$$

3. Results and discussion

The mathematical model is representative for all the similary experiment on some samples of 250 ml synthetic waters initially having a colour coresponding to an absorbance at 456 nm of 2.382 and 1890.476 UH and a COD (carbon organic demand) of 2.6 mg O_2/l (determined using the spectrophotometric method with $K_2Cr_2O_7$ in high acidic medium and COD cathalyst).

The codification of the independent variables for the decolouring process of the synthetic waters containing the Brown Vopsider DNRL 101 dye is presented into the next table (Tabel 2).

Tabel 2.

The Codification of the Independent Variables.

Variable/Value	**Real variable**	**Codificated variable**	**Real basic value, z_{01}**	**Variation step, Δz_i**
pH	Z_1	X_1	8	2
Irradiation time, min	Z_2	X_2	20	10

The experimental matrix of the decolouring process with UV irradiation and hydrogen peroxide is presented into the Table 3 (Y is the decolouring degree, %).

Table 3.

The Experimental Matrix of the Decolouring Process.

Exp.no.	**Z_1**	**Z_2**	**X_1**	**X_2**	**Y [%]**
1	6	10	-1	-1	46.07
2	6	30	-1	+1	78.75
3	10	10	+1	-1	27.2
4	10	30	+1	+1	43.42
5	5.172	20	-1.414	0	72.29
6	13.656	20	1.414	0	49.41
7	8	5.86	0	-1.414	23.12
8	8	34.14	0	1.414	93.34
9	8	20	0	0	69.89
10	8	20	0	0	71.13
11	8	20	0	0	70.64
12	8	20	0	0	70.21
13	8	20	0	0	70.87

The value from the statistical table of the Fisher test is $\mathbf{F_{tab}}(\alpha=99, \nu_1=n-1=12, \nu_2=\kappa-1=1) = 4.75$ and the calculated value is **F** = **155856.35** for the **Y** function.

Because $F > F_{tab,}$ it can be said that the deviation of the experimental values from the average value is not the result of experimental errors, but is determined by the influence of the independent variables. After that, it can be determined the mathematical expression of the dependent variable (Y).

The expression of the mathematical model of Y is:

$$Y = 70.548 - 10.819X_1 + 18.524X_2 - 7.519X_1^2 - 8.829X_2^2 - 4.115X_1 \cdot X_2$$

To establish the relation between the dependent variable and the all independent variables as a whole, it is determined the multiple correlation coefficient.

His value is R_{Yx1x2} =0.939726, value close to unit. This fact demonstrates the important influence of the independent variables on the dependent variable.

The Fisher constant for the free degree ν_1= n-k-1=10 and ν_2= k=2 is F_{tab}=4.14 and F_{calc}= 37.766075, value higher than the value from the statistical table. This fact demonstrates that the independent variables have a significant influence on the dependent variable (Table 4).

Table 4.

The Verifying of the Mathematical Model

No.exp	**X_1**	**X_2**	**Y** [%]	**Y_c [%]**	**Deviation [%]**
1	-1	-1	46.07	42.38	-8.707
2	-1	+1	78.75	86.658	9.125
3	+1	-1	27.2	28.972	6.116
4	+1	+1	43.42	47.79	9.54
5	-1.414	0	72.29	70.812	-2.086
6	1.414	0	49.41	46.216	6.91
7	0	-1.414	23.12	26.702	13.415
8	0	1.414	93.34	89.088	4.77
9	0	0	69.89	70.548	0.933
10	0	0	71.13	70.548	-0.825
11	0	0	70.64	70.548	-0.1304
12	0	0	70.21	70.548	0.479
13	0	0	70.87	70.548	-0.456

The testing of the model coefficient using Student test establishes that all the coefficients are significant.

The application of the classic optimization methods lead to the conclussion that this function – Y - presents a distinct maximum for:

X_1 = -1.07506, X_2 = +1.29957 for a value of dependent variable: Y_{opt} = 88.4 %.

Transposing in real values, these values correspond to a pH of 5.85 and an irradiation time of 32.957 minutes.

To verify the correctness of the mathematical model, there are compared the experimental values with the values calculated with the model and calculated the deviation *A.* The average deviation value is of 3.086 %, each of this individual value being into the interval of $\pm$ 10 %. This fact indicates a good agreement of the experimental values with the values calculated with the mathematical model.

The interpretation of the proposed mathematical model for the decolouring process of the waters containing Brown Vopsider DNRL 101 dye by photooxidation with hydrogen peroxide

Analysing the expression of the Y function. It can be said that the most important influence on the decolouring degree of the waters containing the Brown Vopsider DNRL 101 has the X_2 variable (irradiation time, min), emphasized by the higher value of the X_2 coefficient, as well of the X_2^2 coefficient. Nevertheless, important is also the influence of pH, demonstrated by the relatively higher value of X_1 and X_1^2 coefficients. The pH decreasing leads to an increasing of the decolouring degree, demonstrated by the negative coefficient of X_1X_2. The influence of X_2 variable is almost of 1.7 degree higher than of X_1 variable and their effect is opposite.

Into the next figures are presented the dependences of the decolouring degree (%) of the two independent variables, pH and irradiation time (Fig.2), as well as the dependence of the decolouring degree of each variable, in the conditions of a constant keeping of the other variable at the codificated value of 0 (Fig.3).

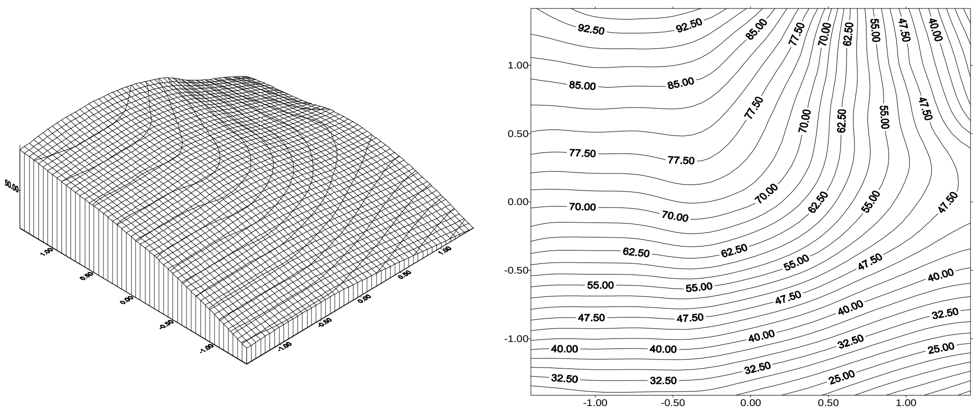
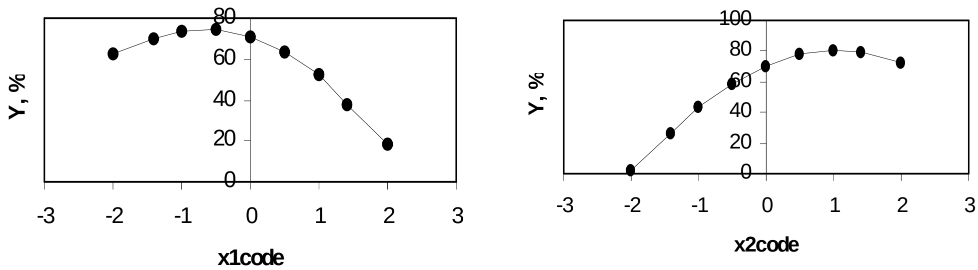


Fig.2. The dependence of Y vs the two variables



a: $Y=Y(x_1,0)$

b: $Y=Y(0,X_2)$

Fig.3. The dependence of Y vs each variable.

In figure 3a is represented the dependence of decolouring degree versus the X_1 (pH); it seems that exists a maximum (x_1= -0.7194) that corresponds to a pH of 6.5612, for a constant value of the irradiation time (20 minute, the basic value).

In figure 3b, it seems that exists into the experimental field a maximum of the decolouring degree vs the X_2 variable (irradiation time) for a value of +1.049 for X_2 which corresponds to an irradiation time of 30.49 minutes, in the conditions of a constant value of pH (pH=8).

CONCLUSSIONS

1. The photooxidation with hydrogen peroxide in the presence of Fe^{2+} catalyst leads to high decolouring degree for relatively low irradiation time and acidic value of pH.

2. It was established a mathematical expression of the decolouring process by oxidation of some waters containing Brown Vopsider DNRL 101 dye by oxidation with hydrogen peroxide associated with UV irradiation and Fe^{2+} cathalyst. The mathematical model is elaborated considering as optimization criterion – the dependent variable - the decolouring degree and as independent variables - the pH and irradiation time.

3. There were determined the optimum values of the independent variables that correspond to a pH of 5.85 and an irradiation time of 32.957 minutes.

4. It seems that there are obtained high values of the decolouring degree (88.4 %) at the specific optimum values of pH and irradiation time.

5. It was verified the mathematical model and it seems that this model is adequate, the average deviation having the value of 3.086 % being into the admisible limits of deviation (± 10 %).

6. There were represented the dependences of the decolouring degree vs the variation of the independent variables, as well as individually of each independent variable in the conditions of a constant value of the other (the basic value). It seems that exists a maximum for the considered values of independent variables corresponding to a pH of 6.512 and, respectively, to an irradiation time of 30.49 minutes.

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