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APLICATION OF 2^k FACTORIAL DESIGN IN WASTEWATER DECOLORIZATION RESEARCH

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Abstract − This research deals with the decolorization of synthetic wastewater prepared with 1:2 metal complex textile dye C.I. Acid Blue 193 by AOP ozonation (O_3) and H_2O_2/O_3 process. In order to minimize the number of experiments, experiments were performed using the 2^5 factorial design. Five influential parameters were examined: initial dye concentration, ozone flow rate, initial pH value, decolorization time and H_2O_2 addition. According to the variance test analysis, only the first four parameters and their first and higher order interactions are significant, while the fifth factor, i.e. H_2O_2 addition, proved insignificant within the range examined in our tests. With the help of the significant factors, a regression model was constructed and model adequacy checked. The obtained regression polynomial was used to model the relation between absorbance and influential process parameters by fitting the response surface. Response surface may be used to predict absorbance resulted from a set of influential parameters, or it can be rearranged in such a way to predict the set of process decolorization parameters, necessary to reduce the absorbance of wastewater with the given initial dye concentration below the prescribed limit. It is also shown that 2^k factorial design can be suitable to predict ozonation operating expenses.

Keywords: wastewater decolorization, 2^k factorial design

1. INTRODUCTION

Wastewater from textile industries is intensively colored and has a complex and variable nature. All structural types of dyes can be decolorized under the optimized conditions [1]. The use of advanced oxidation processes (AOP) has shown the greatest efficiency in treating textile wastewater. The extensive literature of several AOP's use for textile wastewater treatment has been reviewed by Al-Kdasi *et.al.* [2]. Nowadays, ozonation is one of the most commonly used advanced oxidation technologies. Ozone is known as an effective oxidizing agent for the decolorization of dyes in a wide pH range of at least 2 to 12 and has the advantage of being applied either to a concentrated stream or as an end-of-pipe treatment [1]. The addition of H_2O_2 and O_3 to water accelerates the decomposition of O_3 and enhances production of hydroxyl radicals ($OH^•$) [2] which eventually degrades the chromophores. In consequence to this procedure, dyes lose their colour by oxidative cleavage of chromophores [3], without the production of and by-products or waste.

Since studies of decolorization processes by classical experimental methods are very expensive, time consuming and difficult to manage with a high number of experiments, contemporary research designs rely on statistical experiments [4]. Several experimental design methods have already been published for the modeling of a decolorization process, determination of optimum conditions and process variables and their effect on the removal of dyes from textile wastewater by O_3 and H_2O_2 process [3], [5] [6].

For the purpose of this research (our knowledge), we present for the first time decolorization of C.I. Acid blue 193 dye by O_3 and H_2O_2/O_3 process and process modeling, so our experiments were carried out according to the 2^k factorial design method [4]. The effects of 5 factors (initial dye concentration, O_3 flow rate, initial pH value, treatment time and H_2O_2 addition) were statistically examined to obtain more information about the influential variables for the future optimization of the decolorization system process. The parameters were set at two levels to observe the main and joint effects. Afterwards, the experimental results of absorbance measurements were used to model the relation between absorbance and influential parameters by fitting the response surface. The response surface may be used to predict absorbance, resulting from a set of influential parameters, or it can be rearranged in such a way to predict the set of process decolorization parameters, necessary to reduce the absorbance of wastewater with the given initial dye concentration below the prescribed limit. It can also be suitable for the prediction of ozonation operating expenses.

2. METHODS

2.1. Materials and chemicals

C.I. Acid Blue 193, water-soluble, 1:2 metal complex dye, was used without further purification (50-60% purity approx.). Its chemical structure is generally a complex of two monoazo dye residues around a complex bonded Cr^{2+} ion and was selected as a complex model pollutant of textile effluents due to its potentially carcinogenic structure.

Prior to decolorization, the synthetic wastewaters were prepared by diluting the stock solution of the dye C.I. Acid

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Blue 193 and dissolved in 1 L of distilled water at room temperature in order to reach the closest possible similarity to real wastewater solutions after dyeing with acid dyes. According to the minimum (5%) and maximum (20%) % of dye lost in effluent [7], the initial dye concentration, minimum (0.1 g/L) and maximum (0.4 g/L), was calculated presuming that 100 g of fabric was colored in a 2% colour shade at bath ratio 1:10. For the experiments carried out with the initial pH of the colored wastewater was not modified, while the initial pH 4 and 12 was adjusted during the steering using 0.1 M HC1 solution purchased by Riedel-de Hoën and/or 0.1 M NaOH purchased by Merck, prepared with distilled water.

Common knowledge is, that the early stage of oxidation reactions destroy key chromophores in dye molecules, causing loss of most of the colour with relatively small doses of oxidant [1]. In addition, the conjugate base H_2O_2 at milimolar concentrations can initiate the decomposition of ozone into hydroxyl radicals ($OH^\bullet$) much more rapidly than with the hydroxide ion. Therefore, as stated by Oguz and Keskinler [8], 7 ml/L of mM H_2O_2 solution was added to the wastewater in the reactor before ozone input to obtain rapid activation of H_2O_2. Therefore, the H_2O_2 obtained from Belinka Perkemija was prepared as a solution (w = 0.2%) in distilled water.

2.2. Apparatus

Decolorization with O_3 and H_2O_2/O_3 process of synthetic wastewater was performed on a lab scale ozonator Ozomatic LAB 802 manufactured by Wedeco GmbH, Germany. Ozone gas was generated from oxygen using generator LAB 802, with the maximum ozone flow rate 4 g/h. The oxidation processes (O_3 and H_2O_2/O_3) of synthetic wastewater took place in a 1 L batch reactor with the ozone gas supplied at the bottom of the reactor. Excess ozone gas was trapped into a 2% potassium iodide solution (KI).

Samples were collected prior and during the decolorization process in 10 minute intervals. Absorbance was measured by a Varian Cray 50 spectrophotometer according to the standard SIST EN ISO 7887. The decolorization effect was determined at three wavelengths in visible range according to Slovenian environmental regulations (Ur.L. RS 7/2007: λ_1 = 436 nm, λ_2 = 525 nm in λ_3 = 620 nm), where the wavelength λ_2 = 525 nm corresponds to the maximum of acid dye absorbance λ_{max} = 578 nm and the desired spectral absorbance coefficient (SAC) after decolorization process must reach 5 m^{-1}. pH value was determined according to SIST ISO 10523 standards, whereas conductivity according ISO 7888 standards.

2.3. Statistical method

2^k factorial designs are widely used in experiments involving several factors, where it is necessary to study the joint effect of the factors on a response. The most important is that of the *k* factors, each at only two levels (minimum and maximum). A complete replicate of such a design requires 2^k observations and is called 2^k factorial design. 2^k factorial design allows the performance of an analysis of variance and the fitting of a response surface. It provides the smallest number of runs with which *k* factors can be studied in a complete factorial design. Because there are only two levels for each factor, it is assumed that the response is approximately linear over the range of the factor levels chosen.

The experimental results (behavior of the system) of 2^k factorial design can be easily expressed in terms of a regression model response explained by the following first-degree polynomial Eq. (1):

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i} \sum_{< j} \beta_{ij} x_i x_j + \in \quad (1)$$

where: y = response, β_i = regression model coefficients, x_i = coded variables, and $\in$ = random error [4].

According to practical experiences with the O_3 and H_2O_2/O_3 processes [3], [8], the following five process parameters initial dye concentration – factor A, ozone flow rate – factor B, initial pH value – factor C, ozonation time – factor D, and H_2O_2 addition – factor E were foreseen as affecting the decolorization. Minimum and maximum levels of each influential factor are seen in Table 1.

Table 1. Influential factors and their min. and max. level.

Parameter	Factor	Level	
		min	max
Initial dye conc. (g/L)	A	0.1	0.4
O_3 flow rate (g/h)	B	1	2
Initial pH value	C	4	12
Treatment time (min)	D	10	40
H_2O_2 addition (ml)	E	0	7

3 RESULTS AND DISCUSSION

Fig. 1 shows a typical variation of absorbance at wavelengths 436 nm, 535 nm, and 620 nm with time in decolourization process. As presented, the rate of dye removal is high at the beginning of the process. Afterwards, the decolorization is less pronounced; therefore, we chose the simple factorial design 2^5 and limited our modeling research on a linear response within the 10 minutes to 40 minutes interval.

The wavelength 525 nm corresponds to the maximum of acid dye absorbance (λ_{max} = 578 nm) and, therefore, the decolorization process efficiency was analysed at this wavelength.

3.1. Application of unreplicated factorial 2^5

For an even moderate number of factors, the total number of treatment combinations in a 2^k factorial design is large. Our specific study examines 5 factors. Our factorial design therefore, has 32 treatment combinations. In order to reduce the total number of experiments, we have decided to apply only single replicate of the 2^5 design in the first step, which should serve as a screening experiment for the effect significance test of factors.

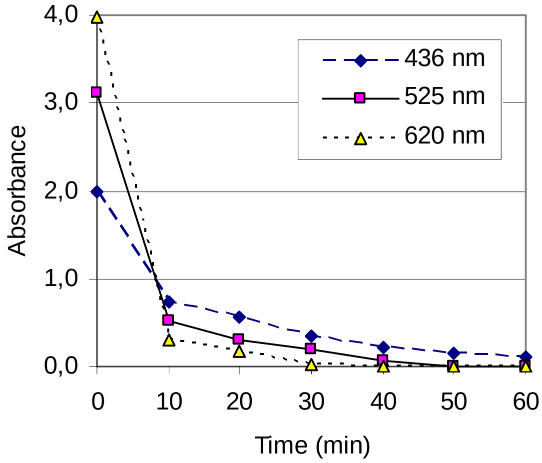

Fig. 1. Reduction of absorbance with time (all influential factors at their max level).

With only one replicate, there is no internal estimate of error. In order to overcome this problem, it is usually estimated that certain high-order interactions are negligible, and their mean squares are combined to estimate the error. However, when high order interaction is present then the use of an error mean square obtained by pooling high-order interactions is inappropriate. Montgomery [4] suggested examining a normal probability plot of the estimates of the effects in such cases. The effects that are negligible are normally distributed with mean zero and variance σ^2 and will tend to fall along a straight line, whereas significant effects will have non-zero means and will not lie along a straight line. Thus the preliminary model can be specified so as to contain those effects that are apparently non-zero, based on a normal probability plot.

The lack of space does not allow us to present the results of the single replicate of the 2^5 design. However, the procedure was quite straightforward. Using the Yates algorithm [4], the contrasts were calculated and used as an estimate of 31 factorial effects. These were then classified from their minimal to maximal values and used to obtain a normal probability plot.

Fig. 2 shows a normal probability plot. Instead of using a normal probability y scale, an ordinary y scale is used and the standardized normal scores Z_j are plotted against the effects (e_j), where the standardized normal scores satisfy

$$\frac{j-0.5}{n} = P(Z \le Z_j) = \Phi(Z_j) \qquad (2)$$

with $\Phi(Z_j)$ = cumulative standard normal distribution.

According to Montgomery [4], all of the effects that lie along the line (Fig. 2) are negligible, whereas the large effects are far from the line. The important effects that emerge from this analysis are the main effects of A, B, C, and D, the first-order interactions AB, AD, and CE and the second-order interaction ABC. Interestingly, the main effect of E, i.e. H_2O_2 addition, is not significant. It affects only the initial pH value, thus this interaction (interaction CE) proves to be significant. However, by setting the initial pH value after the H_2O_2 addition, their interaction effect on the decolorization process vanishes.

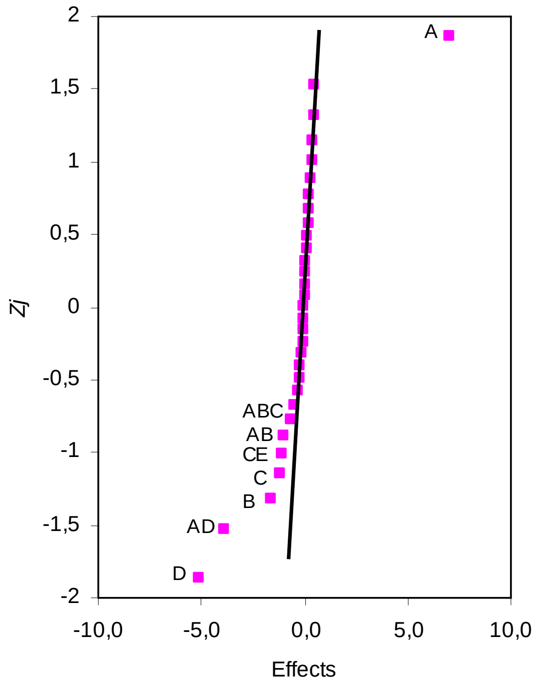

Fig. 2. Normal probability plot of the effects.

Because E (H_2O_2 addition) is not significant and all interactions involving E, except the already discussed CE interaction, are negligible, we may discard E from the experiment, so that the design becomes a 2^4 factorial in A, B, C and D. Since it was not possible to neglect the CE interaction and simply use the experimental results obtained at max. E level as a second replicate, a new set of experiments was performed with no H_2O_2 addition and applied as a second replicate. Results are presented in Table 2. Standard procedure of the Yates' algorithm [4] was applied to process the experimental data.

After calculating the contrasts of the main and joint effects, these were used to perform the significance test with an analysis of variance. This time, the test proved all effect significant, except the first-order CD interaction, which turned to be insignificant.

The significant effects were used to write a regression model in the coded variables. After the adequacy of the model was checked, decoding was performed and the regression polynomial

$$\begin{aligned} a = &-5.32\cdot10^{-2} + 3.02A - 6.14\cdot10^{-2}B - 1.02\cdot10^{-2}C + \\ &+ 7{,}92\cdot10^{-4}D - 0.14AB + 6.72\cdot10^{-2}AC + 4.09\cdot10^{-3}BC - \\ &- 5.6\cdot10^{-2}AD + 1.4\cdot10^{-3}BD - 3.81\cdot10^{-2}ABC \end{aligned} \qquad (3)$$

was obtained. The polynomial enables the prediction of absorbance a as a function of initial dye concentration, initial pH, O_3 flow rate, and ozonation duration. Not only the main effects, but also their interactions are modeled, which is the main advantage of 2^k factorial design against the traditional approach. It has to be pointed out, that the application of the regression model should be applied within the limits (min. and max. level – Table 1) of any influential factor.

Table 2. Treatment combination in 2^4 design and resulted absorbance at λ = 525 nm.

	Influential parameters				Absorbance at λ = 525 nm replicate	
	A Initial dye conc. (g/L)	B O_3 flow rate (g/h)	C Initial pH value	D Treatment time (min)	1	2
1	0.1	1	4	10	0.14300	0.13700
2	0.4	1	4	10	0.83500	0.82300
3	0.1	2	4	10	0.07062	0.07320
4	0.4	2	4	10	0.71600	0.72800
5	0.1	1	12	10	0.10611	0.09500
6	0.4	1	12	10	0.92000	0.93000
7	0.1	2	12	10	0.02100	0.03300
8	0.4	2	12	40	0.66200	0.68300
9	0.1	1	4	40	0.14100	0.20000
10	0.4	1	4	40	0.99400	0.98800
11	0.1	2	4	40	0.08100	0.09500
12	0.4	2	4	40	0.79600	0.78100
13	0.1	1	12	40	0.03800	0.02523
14	0.4	1	12	40	0.71600	0.70040
15	0.1	2	12	40	0.02200	0.03000
16	0.4	2	12	40	0.51700	0.50200

The regression polynomial (Equation (3)) may simply be rearranged to predict any influential factor, if the final absorbance is set as a constant (for example equal to maximum allowed limit). An example is shown in Fig. 3. The process duration, necessary to reduce the absorbance of wastewater with the initial dye concentration 0.15 g/L below the desired limit (SAC = 5 m^{-1}), is plotted against O_3 flow rate and pH value. This figure clearly shows that wastewater decolorization increase significantly with the O_3 flow rate. By neutralizing wastewater to alkaline or highly alkaline pH, there is also an increase in decolorization. Lower ozone flow rates and acidic pH are, therefore, not appropriate, since such conditions can double the decolorization time.

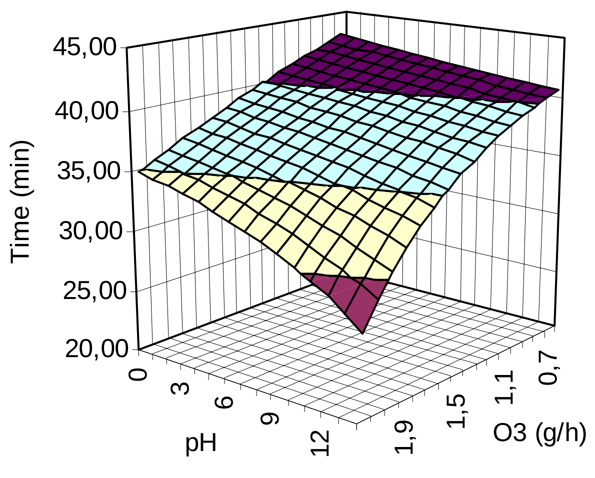

Fig. 3. *Ozonation time for attaining SAC = 5 m^{-1} C.I. Acid Blue 193; initial dye concentration 0.15 g/L.*

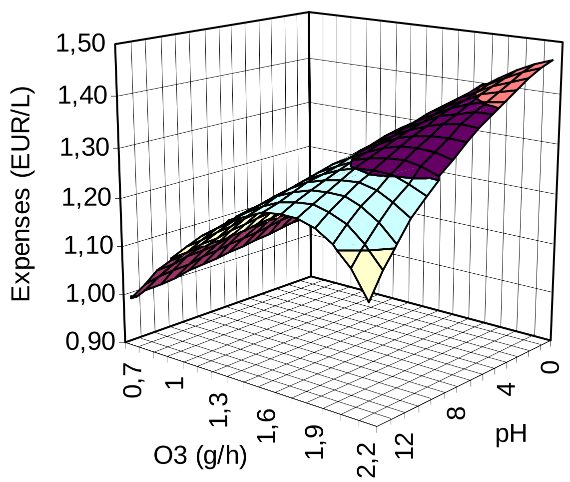

Fig. 4. *Decolorization expences for attaining SAC = 5 m^{-1} C.I. Acid Blue 193; initial dye concentration 0.15 g/L.*

If the expenses of all three process parameters (O_3 flow rate, initial pH value and process duration) are evaluated and coupled with the response surface from Fig. 3, an additional diagram can be obtained, which shows the possible costs of different decolorization strategies (Fig. 4). As can be seen, expenses are the lowest at low O_3 flow rates, since the costs for oxygen exceed electrical energy costs at low to moderate O_3 flow rates. However, in the region of high pH values and high O_3 flow rates, the expenses drop significantly, since the reduced duration of the process, reduces electricity costs below the costs of oxygen. This is very promising, since it allowes, the reduction of processing time without special penalty on expenses.

4. CONCLUSIONS

Decolorization results of synthetic wastewater containing C.I. Acid Blue 193 dye by O_3 and H_2O_2/O_3 process show that both processes enable the decolorization of the majority of the initial dye, after only 10 minutes, depending on the process parameters. However, the application of 2^5 factorial design, showed no significant difference between the two processes, moreover, it proved that H_2O_2 addition and its interaction with other process parameters is insignificant. The research was, therefore, focused on the remaining four process parameters: initial dye concentration, O_3 flow rate, initial pH value, and the decolorization time. Applied 2^4 factorial design resulted in the regression polynomial which was rearranged in such a way to predict the time of decolorization necessary to reduce wastewater absorbance bellow the desired limit (SAC = 5 m^{-1}). It shows that 20 to 40 minutes are enough to decolorize synthetic wastewater and that the decolorization rate increases with O_3 flow rate especially under highly alkaline conditions. An examination of the decolorization expenses showed increased decolorization costs in acid conditions, which can be reduced by an increase in the O_3 flow rate or, to simplify, by presetting the initial pH value to attain alkaline conditions.

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