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The use of experimental design for the evaluation of the influence of variables on the H_2O_2/UV treatment of model textile waste water

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Abstract

The evaluation of the influence of variables (NaOH, NaCl, urea, intensity of UV irradiation, concentration of H_2O_2 and decoloration time) on the H_2O_2/UV treatment of textile waste waters by the use of experimental design is described. Experimental design is used to establish which variables influence in the positive or negative sense the efficiency of the decoloration process. A model waste water, polluted with a reactive vinylsulphone dye with C.I. Reactive Black 5 and dye-bath additives was used for the decoloration. Influences were determined by the measurement of absorbance, COD and TOC.

Keywords: Reactive dyes; Decoloration; Hydrogen peroxide; UV irradiation; Ecological parameters; Experimental design

1. Introduction

Experimental design is very important in chemometrics, because chemical experiments have to be performed to get more knowledge about process or system. The science is dependent on chemical experiments and experimental design is used to improve experimental works.

Experimental design methodology is used to decide which experiments are needed to carry out to get information about certain chemical process or product. It is used to decide which factors have an influence on the properties of the chemical process or desirable product. Another question is to define the number of experiments that have to be carried out to obtain more knowledge about the system. It is obvious that optimization of chemical process is essential.

Main methods of experimental design are factorial design including fractional factorial design, orthogonal design (OD), D-optimal design and uniform design (UD). The selection of experiments has an influence on the quality of the system. It is applied to determine the conditions to obtain a product or a process with desirable characteristics. The characteristics of the product or

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process are optimised. The characteristics are also named responses. The factors are independent and the responses are dependent variables. So the experimental design is a set of carefully planned experiments.

The main steps of experimental design are selection of initial factors and responses, selection of experimental domain (extreme values at which factors are studied). With experimental design the response is optimised. After screening design the unimportant factors are discarded and the type of experimental design is chosen. Usually two level factorial design is used for the determination of important factors (variables) and intervals. The optimal response is usually the highest or the lowest value of product or process characteristic. After determining which factors have minimal or no influence on the response (characteristics) the optimum settings of the important factor levels yielding the best characteristics of product or a process, have to be performed [1].

The experimental design was already used in design of dyes of high technical properties for silk [2], in structure optimisation of thiadiazole disperse dyes [3] and also for different decoloration processes [4,5].

Waste waters from textile industries are highly colored and a complex and variable nature. Dyeing and subsequent rising are known to be very important steps in the textile manufacturing process in terms of environmental concern [6].

Reactive dyes have been extremely successful on cotton and wool fibers since a wide amount of bright shades is possible with excellent wash fastness properties. Reactive dyes are poorly substantive to fibers, thus a substantial amount of electrolytes like NaCl, Na_2SO_4 and NaOH must be added in the dyeing process. These electrolytes are additionally polluting the waste water. Dye's substantivity also depends on temperature and pH of the dye-bath [7]. Dyeing of cotton fibers with reactive vinylsulphone dye is carried out by NaCl, NaOH and urea added to the dye-bath [8].

Advanced oxidation methods employing hydrogen peroxide together with UV radiation, ozone or Fenton‘s reagent have been found quite effective in decoloration of waste water with formation of hydroxyl radicals during oxidation [9]. Chemical oxidation using ultraviolet radiation (UV) in the presence of hydrogen peroxide (H_2O_2) is a very promising technique. UV wavelength of 200–280 nm leads to degradation of H_2O_2, with a mercury lamp emitting at 254 nm being the most commonly used. H_2O_2/UV treatment generates hydroxyl radicals which are highly powerful oxidizing species with oxidation potential 1,78 V [10]. The advantages of this process are that no additional disposal problems are involved after treatment because the organics in the water are almost completely destroyed while removing the color [11].

In the present work we are describing the influence of the variables on H_2O_2/UV decoloration of model waste water colored with reactive vinylsulphone dye. The variables are composition of model waste water (dye, NaCl, NaOH, urea) and reaction conditions (the intensity of UV irradiation, concentration of H_2O_2 and decoloration time).

In our case the experimental design is used to find which variables (dye, NaCl, NaOH, urea, intensity of UV irradiation, concentration of H_2O_2 and decoloration time) have the positive or negative influence on diminishing of pollutant parameters (absorbance, COD and TOC) of waste textile waters, treated by advanced decoloration method H_2O_2/UV.

2. Experimental part

Vinylsulphone dye with C.I. Reactive Black 5 (Fig. 1) was used for the experiment of decoloration. C.I. Reactive Black 5 (in continuation Black 5) is one of the most used reactive dyes for textile finishing. It belongs to the group of a diazo dyes, which can be decolorized by H_2O_2/UV treatment. Decolorations were performed on a pilot plant manufactured by Solvay Interlox[12]. The flow of the pilot plant is 180 l/h or 3 l/min. The H_2O_2 solution (35% w/w, with $\rho = 1.13$ g/ml) of analytical grade was obtained from Belinka.

As in our previous work we established that there are seven variables influencing the decoloration process and values of ecological parameters after the treatment by H_2O_2/UV of waste waters,

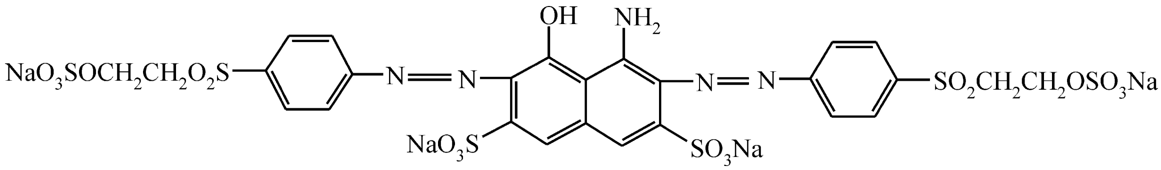

Fig. 1. Chemical structure of reactive vinylsulphone dye with C.I. Reactive Black 5.

polluted with vinylsulphone dye (intensity of UV irradiation, the amount of H_2O_2 added, decoloration time, reactive dye, NaOH, NaCl and urea) [5].

Experiments needed for determination of influences were determined using the same doubled Plackett–Burman experimental design as in our previous work [5]. Table 1 shows the input variables of the experiments that were carried out.

The influences of variables were determined by measuring the values of the ecological parameters: absorbance, chemical oxygen demand (COD) and total organic carbon (TOC). Absorbance was measured on a HP 8452A Diode Array Spectrophotometer, at wavelength of maximum absorbance $\lambda_{max} = 600$ nm and at pH 12. COD was measured using a Thermoreactor CR 2010 and Multilab P5, following DIN 38409-H41-1 standard. Total organic carbon (TOC) was measured on TOC 5000A Shimadzu analyzer. Because of the linear range of activity of the instrument, samples were diluted with distilled water in a 1:10 ratio.

It is desired that the training set consists of such input data so that the individual objects are distributed over the entire measurement space as evenly as possible. This means that all the variables should be represented evenly between the possible maximum and minimum extreme values. The maximum level is the level where the highest concentrations of chemicals were used. The minimum level is the level where the lowest concentrations of the chemicals were used.

Variables influence on the result is significant, if D_i (influence of the variable) is greater than experimental error *EE*. *EE* is the error that occurs because of the imperfection of the measuring method. When the influence of variable on a result is significant, it may be either positive or negative. When the *increase* in variables value causes the

Table 1
The input variables of H_2O_2/UV decoloration

Experiment	Variables						
	UV (W)	H_2O_2 (mmol/l)	Dye (mg/l)	NaCl (g/l)	NaOH (mg/l)	Urea (g/l)	Time (min)
1	1400	52.3	200	3	1.7	10	18
2	1400	52.3	300	3	2.4	15	30
3	1400	96.5	200	3.5	1.7	15	30
4	1400	96.5	300	3.5	2.4	10	18
5	1600	52.3	200	3.5	2.4	10	30
6	1600	52.3	300	3.5	1.7	15	18
7	1600	96.5	200	3	2.4	15	18
8	1600	96.5	300	3	1.7	10	30
9	1400	52.3	100	3	1	5	6
10	1400	8.14	200	2.5	1.7	5	6
11	1400	8.14	100	2.5	1	10	18
12	1200	52.3	200	2.5	1	10	6
13	1200	52.3	100	2.5	1.7	5	18
14	1200	8.14	200	3	1	5	18
15	1200	8.14	100	3	1.7	10	6

ecological parameters to *decrease*, the variable is considered to have a *positive* influence on the result. When the *increase* in variables value causes the ecological parameters to *increase*, the variable is considered to have a *negative* influence on result. When D_i is smaller than the *EE*, the influence of the variable on the ecological parameters is not significant. This means that changing the value of variable within certain limit does not change the result substantially.

3. Results and discussion

Legend for symbols used in Figs. 2–4:

D_i (max) ...influences of variables when variables are at maximum levels;
D_i (min) ...influences of variables when variables are at minimum levels;
EE (max) ...experimental error when variables are at maximum levels;
EE (min) ...experimental error when variables are at minimum levels.

The values of the ecological parameters (results) for dye Black 5, obtained by the H_2O_2/UV process are shown in Table 2. The values of the ecological parameters are higher than values permitted by the law, since the decolorations were not carried out to the end, but were stopped at times, specified by Plackett–Burman experimental design (Table 1). Influences of variables on the decoloration results are shown in Table 3.

As is evident from Fig. 2, all the variables except H_2O_2 at maximum level have a significant influence

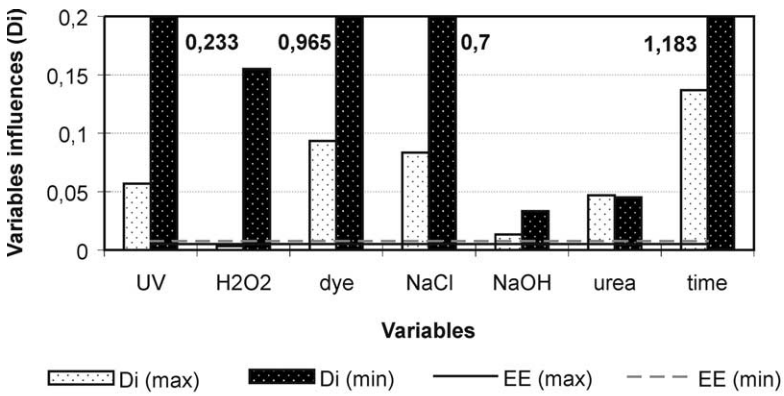

Fig. 2. The influences of the variables on the absorbance.

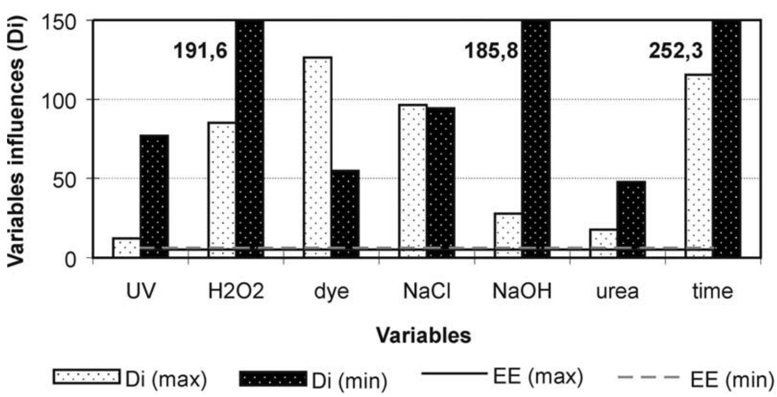

Fig. 3. The influences of the variables on COD values.

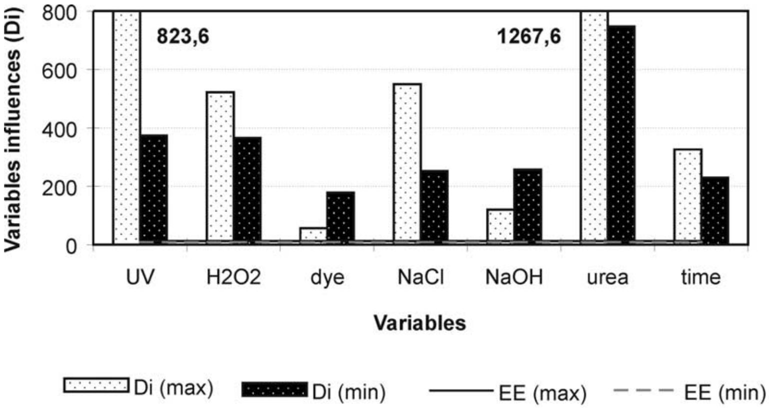

Fig. 4. The influences on TOC values.

Table 2
Values of the ecological parameters, obtained by H_2O_2/UV decoloration of Black 5

Experiment	Result		
	A	COD (mg/l)	TOC (mg/l)
1	0.097	236	2177
2	0.019	257	3054
3	0	285	3091
4	0.293	572	2085
5	0	258	2005
6	0.169	454	3775
7	0.007	344	4669
8	0	345	3252
9	0.303	667	2095
10	2.096	439	1043
11	0.019	270	1995
12	2.248	845	2039
13	0.019	400	984
14	0.477	355	949
15	0.702	319	1846

on absorbance at both, maximum and minimum levels, since their D_i values are bigger than *EE*. Decoloration time and UV irradiation have positive effect on absorbance at both levels. This means that the concentration of the dye in the dyebath decreases with longer decoloration, which is an expected result. Influence of UV irradiation is expected since higher intensity of UV irradiation means, more dye is degraded into smaller products, that no longer absorb light in visible area of the spectrum. H_2O_2 has positive effect only on minimum level, but does not have a significant influence on absorbance at maximum level.

H_2O_2 and NaOH have positive effects on results at minimum, but NaOH has negative effects at maximum level while H_2O_2 has insignificant effect. There is a certain level up to which both chemicals (H_2O_2 and NaOH) accelerate degradation of dye.

Table 3
The influences of the variables on the decoloration results

Dye	Result	Variables influences						
		UV	H_2O_2	dye	NaCl	NaOH	Urea	Time
Black 5	A	po	–/pos	neg	neg/pos	neg/pos	pos/neg	pos
	COD	neg/pos	neg	neg	neg/pos	neg/pos	po	pos
	TOC	neg	neg	neg/pos	pos/neg	pos	neg	pos

pos, positive effect; neg, negative effect; –, effect is insignificant; /, different effect when variables at maximum/minimum level.

But once this limit is exceeded their effect shows in hindering the dye's degradation. We are explaining this by the fact, that part of H_2O_2 is used for the oxidation of an alkali during the decoloration, and as a result, less H_2O_2 is available for degradation of dye [13]. This occurrence is especially noticeable at higher concentrations of peroxide and NaOH. Influence of dye has negative effect at both levels, which was expected, since increasing the concentration of the dye caused higher values of absorbance.

Positive influences on absorbance also has NaCl at minimum level and negative at maximum level. Positive influence of NaCl can be explained by the fact, that salt decreases total absorbance (hypochromic shift) at λ_{max} [8]. Considering that also influences of NaCl and urea are different, when variables at maximum level (NaCl has negative and urea positive effect), we are concluding, that these three variables (dye, salt and urea) have a mutual effect on absorbance, which depends on the commercial product itself. This phenomena can be explained by salt increasing and urea decreasing aggregation of dye molecules and thus in influencing hypochromic and batochromic shift, respectively [8].

Urea have positive effect on absorbance at maximum level, but it has negative influence at minimum level. From this we can conclude, that urea aids in degradation of dye up to a certain limit (absorbance is lowered). Positive effect of urea on absorbance can also be explained by the fact, that with some reactive dyes urea can cause a slight bathochromic shift, thus reducing the absorbance at measured wavelength (λ_{max} of pure dye solution) [8].

From Fig. 3 is evident that all the variables have a significant influence on COD values at maximum and minimum level. Only decoloration time has a positive effect on COD at both levels, which was expected (Table 3). Namely, longer decoloration times mean higher degradation rate of dye into products, that can be completely oxidized with lower oxygen concentrations. Dye and H_2O_2 have negative effect on COD at both levels. Negative effect of dye was expected, since its higher concentrations increase also concentration of compounds, that need to be oxidized in COD test. Reasons for influence of H_2O_2 on COD values are assumed to be the same as on absorbance.

UV irradiation has positive effect on COD at minimum level, which was expected and has negative effect on COD at maximum level. Negative effect was unexpected but it is possible to explain it by assuming that photochemicaly induced new reactions can take place often as a cleveage of the azo functional group and subsequently leading to new uncolored stable molecules. This hypothesis can be explained by positive effect on absorbance and the negative on COD and TOC. We can observe that this does not happen at the minimum level of UV irradiation.

NaCl and NaOH have similar effects on COD. They have negative effect on maximum level and positive effect on minimum level. The influence of

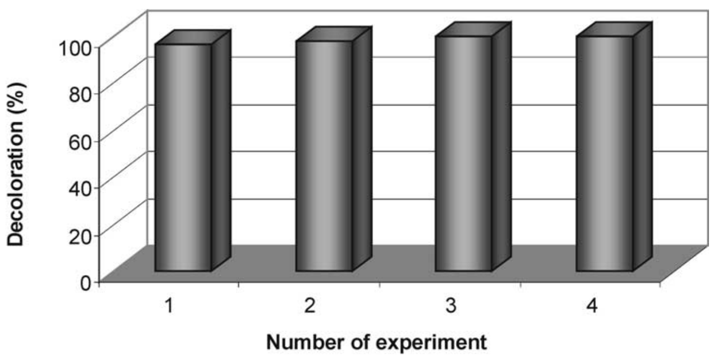

Fig. 5. Removed color in % for the model waste water with dye concentration 300 mg/l regarding to the particular experiment (see Tables 1 and 2).

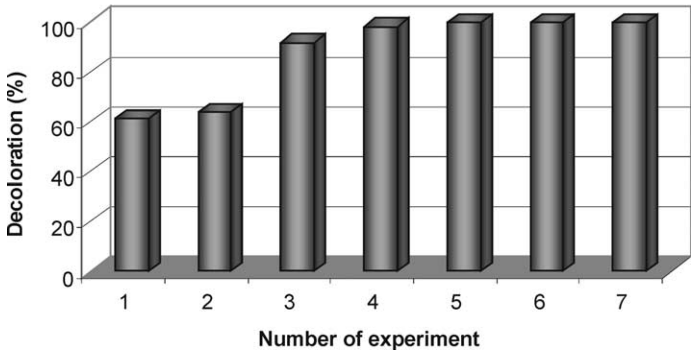

Fig. 6. Removed color in % for the model waste water with dye concentration 200 mg/l regarding to the particular experiment (see Tables 1 and 2).

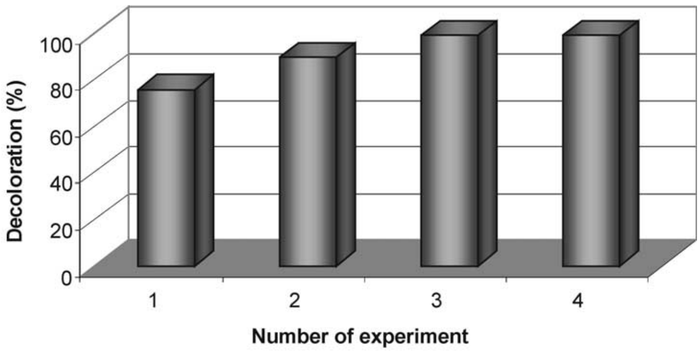

Fig. 7. Removed color in % for the model waste water with dye concentration 100 mg/l regarding to the particular experiment (see Tables 1 and 2).

NaCl and NaOH at high level is surprising, too. Namely, NaCl and NaOH have negative effect at higher level on the absorbance and COD, but positive effect on TOC. Total organic carbon is lower. We can conclude that there is a degradation of the dye but at the same time the formation of new colored molecules.

Urea has a significant influence on COD at maximum and minimum level (D_i value is higher than the EE), it has positive influence at both levels. Positive effect of urea on COD can be explained by the fact, that with some reactive dyes urea can cause a slight bathochromic shift, thus reducing the absorbance at measured wavelength (λ_{max} of pure dye solution) [8].

From Fig. 4 is evident that all the variables have a significant influence on TOC values at maximum and minimum level. Decoloration time and NaOH have both positive effect on TOC at both levels (Table 3). NaCl also has a positive effect on TOC at maximum level. Positive effect of decoloration time was expected. Reasons for influence of decoloration time on TOC values are assumed to be the same as on absorbance and COD. Dye have negative effect on TOC at maximum level and positive at minimum level. Effects of UV irradiation, H_2O_2, dye and urea are all negative on maximum level. Our conclusion is that the concentration of degraded compounds, which contain organically bonded carbon that can be oxidized to CO_2 during the treatment, increases more when variables are at maximum level (lower TOC values in TOC test).

From Figs. 5–7 it is evident that the time of decoloration process has the biggest influence on% removal of color. The intensity of UV irradiation and the concentration of H_2O_2 are the next most important variables.

4. Conclusions

In our previous research [5] we established that among all possible variables the most important one which have influence on the decoloration treatment by H_2O_2/UV are: intensity of UV irradiation, decoloration time, concentration of H_2O_2, the concentration of reactive dye, NaCl, NaOH and urea. In the present work we studied by experimental design how above mentioned selected variables influence in the positive or negative sense the efficiency of the decoloration process of model waste water, colored by C.I. Reactive Black 5. The following conclusions can be done.

The intensity of UV irradiation has mainly significant influence on all ecological parameters at maximum and minimum level. Its effect is positive on absorbance and COD at minimum level. Such results are expected, since higher intensity of UV irradiation means, that more energy is transmitted into a dye-bath, thus leading to higher degree of degradation.

Decoloration time affects positively absorbance, COD and TOC values. From this we can conclude, that longer decoloration times favor degradation of dye into intermediates, that are no longer visible.

H_2O_2 has positive effect on minimum level; this means that we can obtain better results by using lower concentrations of H_2O_2.

The influence of sodium chloride and sodium hydroxide is variable on absorbance, COD and TOC. That means that in some cases we observe positive and in others negative effect. We suppose that NaOH can at higher level reacts with some degradation products and has a negative influence on absorbance (new colored entities) and COD. At the same time both chemicals lower the value of TOC. We suppose that degradation occured to a certain degree.

Urea has positive effect on absorbance at maximum level, but it has negative influence at minimum level. From this we can conclude, that urea aids in degradation of dye up to a certain limit.

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