

The study of the effects of the variables on H_2O_2 /UV decoloration of vinylsulphone dye: part II

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Abstract

As a continuation of part I [Dyes and Pigments 42 (1999), 123] where modeling of H_2O_2 /UV decoloration of monochlorotriazine azo dye C.I. Reactive Red 120 was discussed, this part deals with the study of the effects of the variables on H_2O_2 /UV decoloration of reactive vinylsulphone dye C.I. Reactive Blue 19. Influence of chemicals (NaOH, NaCl, urea), added to the dye-bath for dyeing with stated colorant, as well as the influence of reaction conditions (intensity of UV irradiation, concentration of hydrogen peroxide and decoloration time) is described. Influences were determined by the measurement of ecological parameters: absorbance, COD, TOC and TIC. © 2002 Elsevier Science Ltd. All rights reserved.

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

1. Introduction

Due to their extremely heterogeneous composition, waste waters from the textile industry are difficult to treat efficiently. Effluents from textile mills are composed of individual partial drains from different plants and therefore loaded with various toxic compounds which are present in different concentrations. In order to achieve an effective waste water treatment it is therefore necessary to determine qualitative and quantitative composition of toxic compounds in the waste waters as accurately as possible.

In the quantity sense, unfixed, washed out and unused dyes and optical bleachers represent only

1% of the total pollution of the waste waters from the finishing processes. Hence the loading of waste water with dyes is minimal, but different from loading with other hazardous compounds. Namely, dyes are more visible and are therefore primarily an aesthetic problem. This aesthetic problem becomes even more global if we take into consideration the fact, that dyeing may cause pollution with heavy metals which are structural elements in certain dyes [1].

2. Theory

2.1. Classification of dyes [2,3]

Generally, dyes can be classified with regard to their chemical structure, with regard to the

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method and domain of usage, and with regard to chromogen (Table 1).

2.2. Characteristics of reactive dyes

Reactive dyes are widely used because of their good stability during washing, and because of the relatively simple dyeing procedures [4]. They are used for dyeing of cellulosic, woolen and polyamide (PA) fibers. Dyes are water-soluble, and bond with covalent bonds to OH groups of the cellulosic and NH_2 groups of the woolen and PA fibers. They can also react with OH groups of a water molecule, resulting in hydrolysis of the dye. The result of the hydrolysis is a dye that cannot bond onto fibers anymore. From the ecological point of view this causes pollution of the waste water. Reactive dyes are poorly substantive to fibers, thus a substantial amount of electrolytes

(primarily NaCl and Na_2SO_4) 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. Increase in temperature and pH decreases substantivity of a dye [2].

2.3. Waste water treatment methods

The color of water, polluted with organic colorants reduces, when the cleavage of the $-\text{C}=\text{C}-$ bonds, the $-\text{N}=\text{N}-$ bonds or heterocyclic and aromatic rings occurs. The absorption of light by the associated molecules shifts from the visible to the UV or IR region of the electromagnetic spectrum [5]. To reduce the color of waste waters, physical, chemical and biological methods of treatment are known. One of the most important factors for evaluation of treatment efficiency is the

Table 1
Classification of the dyes

Classification		
	Subclass	Characteristics
<i>With regard to chemical structure (C.I.)</i>		
	E.g. azo, anthraquinone, triphenylmethane, indigo,...	The classification of a dye by chemical structure into a specific group is determined by the chromophore group.
<i>With regard to method and domain of usage (C.I.)</i>		
	E.g. direct, acid, basic, reactive, reductive, sulphuric, cromatic, metal-complex, disperse, pigments,...	Dyes used in the same technological process of dyeing and with similar fastnesses are classified into the same group.
<i>With regard to chromogen</i>		
$n \rightarrow \pi^*$	E.g. absorptive, fluorescent and dyes with energy transfer,...	This classification is based on the type of the excitation of electrons, which takes place during light absorption.
Donor – acceptor	E.g. 1-aminoanthraquinone, <i>p</i> -nitroaniline,...	These chromogens contain a donor electron (unbound electron couple), which directly bonds to the system of conjugated p electrons.
Acyclic and cyclic Polyene	E.g. polyolefin, annulenes, carotenoids, rhodopsin,...	Chromogen polyene contains sp^2 (or sp) hybridised atoms. The molecules enclose single and double bonds that form open chains, circles, or combination of both.
Cyanine	E.g. cyanines, amino substituted di- and tri- arylmethane, oxonols, hydroxyarylmethanes,...	Cyanine chromogens have a system of conjugated p electrons, in which the number of electrons matches the number of p orbitals.

ability to reduce concentrations of chemical substances in waste waters.

2.3.1. Physical methods of treatment

Physical methods of treatment include:

- precipitation methods (coagulation, flocculation, sedimentation);
- adsorption (on activated carbon, biological sludge, silicagel);
- reverse osmosis, filtration;
- combustion, incineration;
- other special methods that are used only exceptionally (distillation, extraction).

The disadvantage of precipitation methods is sludge formation. The disadvantage of adsorption methods is, that the dye is only transferred to the adsorbent, which therefore needs to be regenerated regularly. This is associated with additional costs, and sometimes with very time-consuming procedures.

2.3.2. Chemical methods of treatment

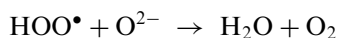
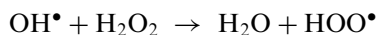
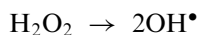
Chemical methods of waste water treatment are primarily used for decoloration purposes:

- oxidation (air oxygen; ozone; oxidants such as NaOCl, H₂O₂);
- reduction (Na₂S₂O₄);
- compleximetric methods;
- ion exchange.

There are also known chemical methods, that are not designated directly for decoloration purposes, e.g. neutralization, catalysis, electrolysis, etc [1].

The basic chemical waste water treatment method is oxidation with air oxygen. This process, which is spontaneously occurring also in nature, is no longer sufficient due to heavy pollution. For this reason the largest part of water pollution must be taken care of by industrial processes. Due to efficiency and easy handling, one of more popular methods is oxidation of waste waters with hydrogen peroxide, which, due to its stability in pure

form, needs to be activated. Hydrogen peroxide activated with UV light decomposes into oxygen, which is not problematic [6]:



2.3.3. Biological methods of treatment

There are two different basic biological methods of waste water treatment:

- aerobic treatment (revival of biological sludge in aeration basins);
- anaerobic treatment (decay and rot in stabilizing lagoons).

Another means of biological treatment is also known, i.e. degradation by means of special fungi [7].

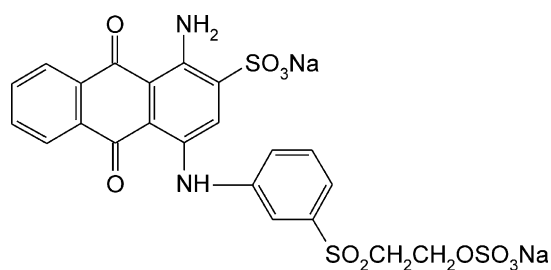


Fig. 1. Chemical structure of the reactive vinylsulphone dye with C.I. Reactive Blue 19.

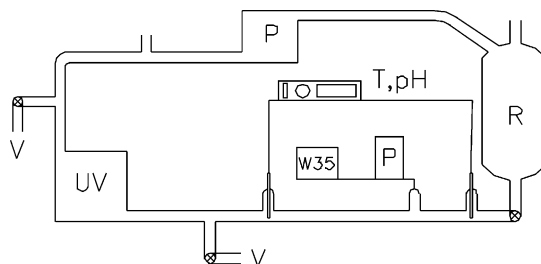


Fig. 2. Scheme of the pilot plant used for the decoloration with H₂O₂/UV. P, pump; UV, reactor with high pressure radiation; R, reservoir; W35, hydrogen peroxide; V, draw sample.

3. Experimental

For the decoloration two reactive vinylsulphone dyes with C.I. Reactive Blue 19 were used: Durable Brilliant Blue VR (Blue VR in continuation) and Goldenzol Brilliant Blue Special R (Blue R in continuation). These dyes have the same chemical structure (Fig. 1), but originate from two different manufacturers. Decolorations were performed on a pilot plant manufactured by Solvay Interlox (Fig. 2).

In our previous work it was determined, there are 7 variables influencing the decoloration process and values of ecological parameters after the treatment [8]:

- reaction conditions:
 1. intensity of UV irradiation,
 2. the amount of H₂O₂ added,
 3. decoloration time,
- concentration of compounds present in the exhausted dye-bath:
 4. reactive dye,
 5. NaOH,
 6. NaCl and
 7. urea.

Namely, when these input parameters had different values, the results, i.e. values of ecological

Table 2
The input variables of H₂O₂/UV decoloration

Experiment	Variables						
	UV (W)	H ₂ O ₂ (ml/l)	Dye (mg/l)	NaCl (g/l)	NaOH (ml/l)	Urea (g/l)	Time (min)
1	1400	4.5	200	3	1.7	10	18
2	1400	4.5	300	3	2.4	15	30
3	1400	8.3	200	3.5	1.7	15	30
4	1400	8.3	300	3.5	2.4	10	18
5	1600	4.5	200	3.5	2.4	10	30
6	1600	4.5	300	3.5	1.7	15	18
7	1600	8.3	200	3	2.4	15	18
8	1600	8.3	300	3	1.7	10	30
9	1400	4.5	100	3	1	5	6
10	1400	0.7	200	2.5	1.7	5	6
11	1400	0.7	100	2.5	1	10	18
12	1200	4.5	200	2.5	1	10	6
13	1200	4.5	100	2.5	1.7	5	18
14	1200	0.7	200	3	1	5	18
15	1200	0.7	100	3	1.7	10	6

parameters measured after the treatment differed quite a great deal. Experiments, needed for determination of influences were determined using the same doubled Plackett–Burman experimental design as in our previous work [8]. Table 2 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), total organic carbon (TOC) and total inorganic carbon (TIC). Absorbance was measured on a HP 8452A Diode array spectrophotometer, at wavelength of maximum absorbance $\lambda_{\max} = 592$ nm. COD was measured using a Thermoreactor CR 2010 and Multilab P5, following DIN 38409-H41–1 standard. Total organic (TOC) and inorganic (TIC) carbon were measured on a 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.

Influences were calculated with the EF¹ computer program. The variables influence on the result is significant, if D_i (1) is bigger than experimental error EE . EE is the error that occurs because of the imperfection of the measuring method [9].

$$D_i = \sum_{j=1}^p \frac{y_{ij}^{(at+i)}}{p} - \sum_{j=1}^p \frac{y_{ij}^{(at-i)}}{p} \quad (1)$$

When the influence of the variable on a result is significant, it may be either positive or negative. When the *increase* in the variable's value causes the ecological parameters to *decrease*, the variable is considered to have a *positive* influence on the result. When the *increase* in the variable's value causes the ecological parameters to *increase*, the variable is considered to have a *negative* influence on the 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 the variable within certain limits does not change the result substantially [10].

¹ Program written by Simona Bohanec, MSc, Lek Inc., Ljubljana, Slovenia.

4. Results and discussion

The values of the ecological parameters (results) for both dyes, obtained by the H₂O₂/UV process are shown in Table 3. It is evident from the table that the results are almost identical for both dyes. Such results were expected since the dyes have the same chemical structure (only originate from different manufacturers). Slight deviations in the

results are probably the consequence of different purity levels of either dye, or different stabilizers used for storage and the use of the dye, present in the commercial product.

Also influences of variables on the decoloration results are similar for both dyes, as shown in Table 4. There are some differences though, which are discussed in the continuation, for each dye separately.

Table 3

Values of the ecological parameters, obtained by H₂O₂/UV decoloration of Blue VR and Blue R^a

Experiment	Blue VR				Blue R			
	A (–)	COD (mg/l)	TOC (mg/l)	TIC (mg/l)	A (–)	COD (mg/l)	TOC (mg/l)	TIC (mg/l)
1	0.0473	390	285	20	0.0573	325	195	15
2	0.0414	475	340	25	0.0453	395	260	15
3	0.0219	405	390	20	0.0063	340	345	15
4	0.3904	540	245	25	0.3959	415	210	20
5	0.0097	350	230	25	0.0049	380	205	20
6	0.2848	505	345	15	0.1150	410	310	15
7	0.0743	440	310	25	0.0403	335	305	20
8	0.0182	465	215	15	0.0061	330	205	15
9	0.2456	355	110	10	0.1918	295	115	10
10	1.0022	440	110	15	1.0606	345	120	15
11	0.0368	350	210	10	0.0521	275	225	10
12	0.7688	465	190	10	0.7448	380	225	10
13	0.0214	305	110	15	0.0223	285	130	15
14	0.4937	450	110	10	0.6310	350	135	10
15	0.3928	360	210	15	0.3536	345	210	20

^a 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 2).

Table 4

The effects of the variables on the decoloration results

Dye	Result	Variables influences						
		UV	H ₂ O ₂	Dye	NaCl	NaOH	Urea	Time
Blue VR	A	po	neg/po	po/neg	po	neg/po	–/po	po
	COD	–/po	neg/po	neg	–/–	–/po	neg/–	po
	TOC	po/neg	po/neg	po/neg	neg	po/neg	neg	–/neg
	TAC	po/–	–/neg	po/–	–/–	neg	–/neg	–/–
Blue R	A	po	neg/po	neg	neg/po	neg/po	po	po
	COD	po	–/–	neg	neg/–	–/–	neg	–/po
	TOC	po	neg/–	po/–	neg/po	po	neg	neg
	TAC	–/po	–/po	–/po	–/–	neg	–/neg	–/–

po: positive effect; neg: negative effect; –: effect is not significant; /: different effect when variables at maximum/minimum level.

4.1. Dye Blue VR

Legend for symbols used in Figs. 3–10:

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

Absorbance indicates the quantity of the incoming radiation that is being absorbed by the molecules of the substance. As it is evident from Fig. 3, all the variables except urea have a significant influence on absorbance at both, maximum and minimum levels, since their D_i values are bigger than the EE .

The most notable influence is that of the decoloration time, at both, maximum and minimum level. Table 4 shows that the decoloration time has a positive effect on the absorbance. This means that the concentration of the dye in the dye-bath decreases with longer decoloration, which is an expected result. Positive influences on absorbance at both levels also have UV irradiation and NaCl. 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 the visible area of the spectrum. Positive influence of NaCl can be explained by the fact, that salt decreases total absorbance (hypochromic shift) at λ_{\max} [11].

Urea does not have a significant influence on absorbance at maximum level (D_i value is smaller than the EE), but it has a positive influence at minimum level. From this we can conclude, that urea aids in degradation of dye up to a certain

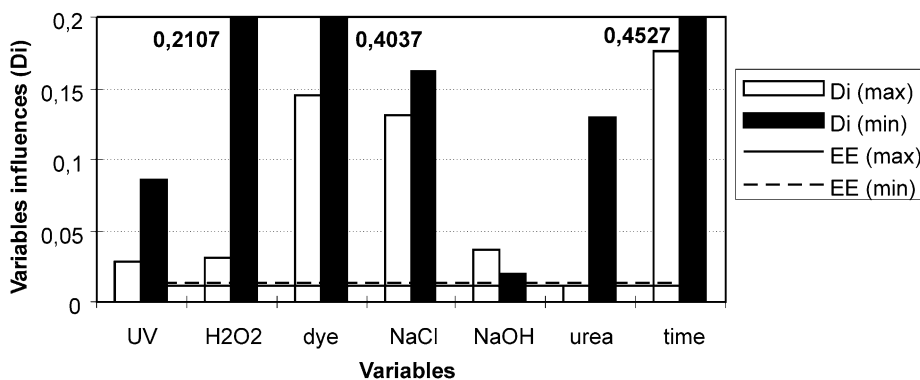


Fig. 3. The influences of the variables on the absorbance.

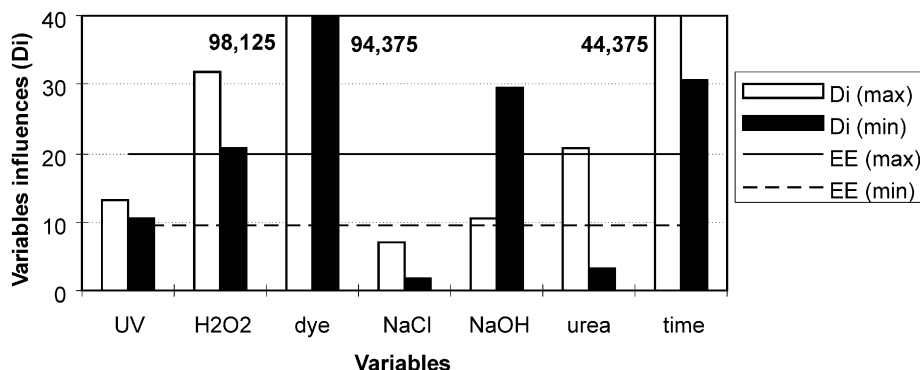


Fig. 4. The influences of the variables on COD values.

limit (absorbance will be smaller), above which urea does not change the value of absorbance significantly anymore. 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) [11].

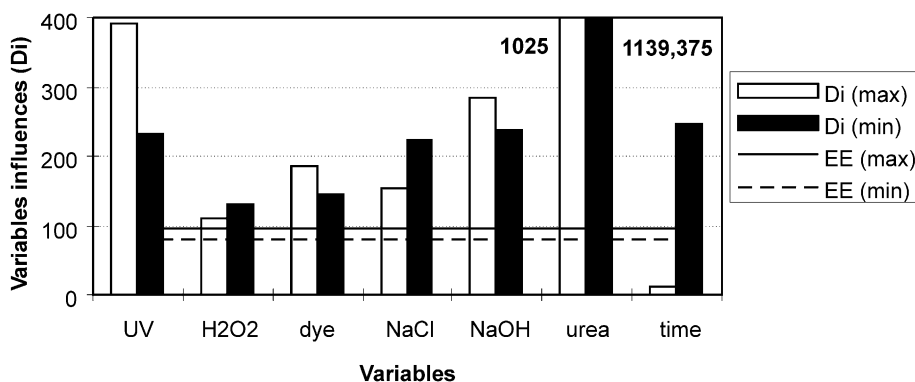


Fig. 5. The influences of the variables on TOC values.

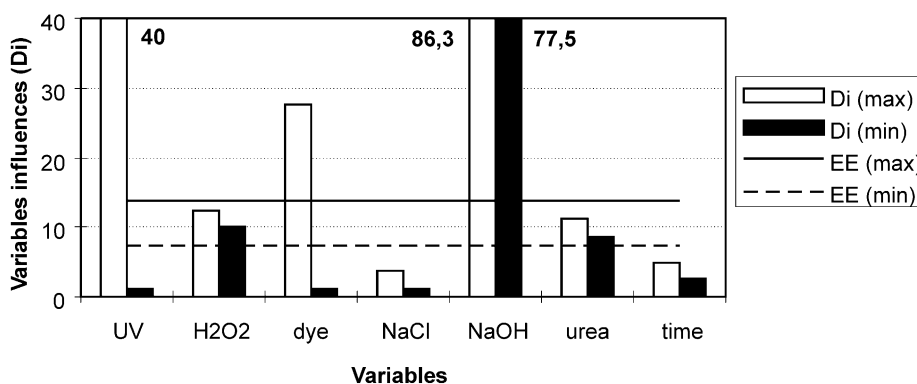


Fig. 6. The influences of the variables on TIC values.

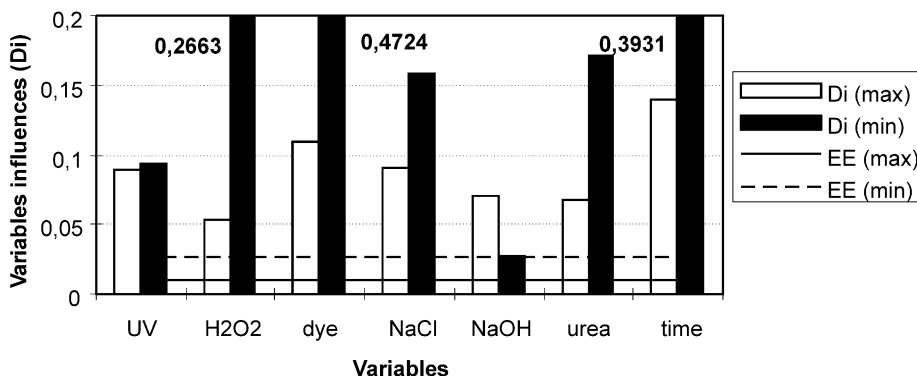


Fig. 7. The influences of the variables on absorbance.

H_2O_2 and NaOH have positive effects on results at minimum, but negative effects at maximum level. As in the case of urea, also for these two variables there is a certain level up to which both chemicals accelerate degradation of dye. But once

this limit is exceeded their effect shows in hindering the dye's degradation. We explain this by the fact, that part of H_2O_2 is used for the oxidation of an alkali during the decoloration (2), and as a result, less H_2O_2 is available for degradation of

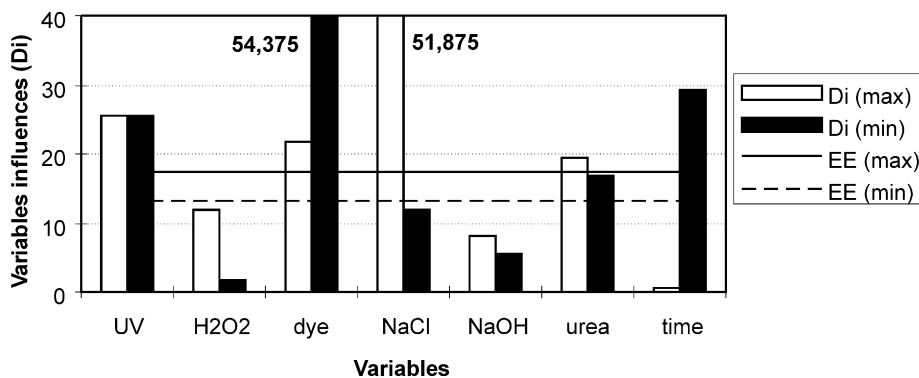


Fig. 8. The influences of the variables on COD values.

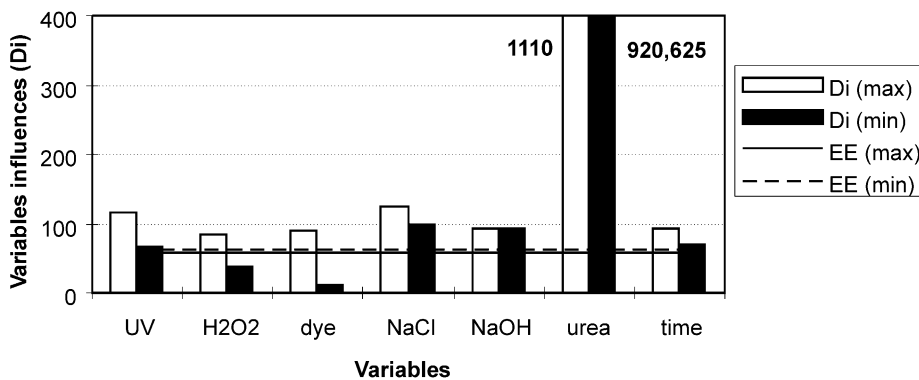


Fig. 9. The influence of the variables on TOC values.

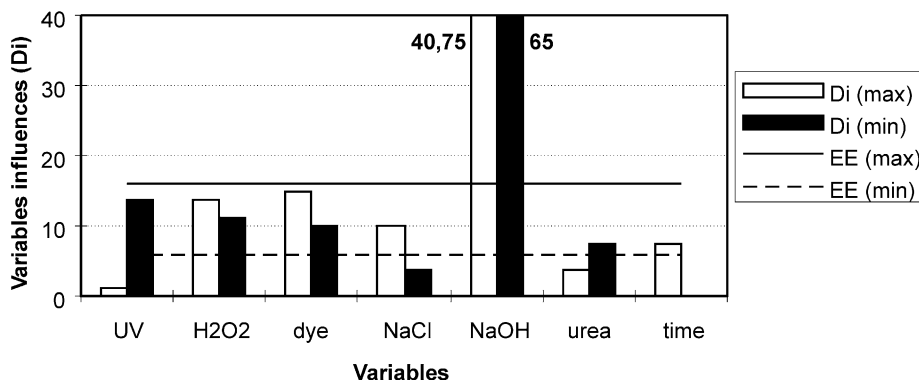
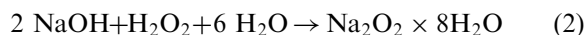


Fig. 10. The influences of the variables on TIC values.

dye [12]. This occurrence is especially noticeable at higher concentrations of peroxide and NaOH.



Influence of the dye at the minimum level is expected (negative effect), since increasing the concentration of the dye caused higher values of absorbance. The fact that the dye's influence at the maximum level becomes positive can be explained by a larger number of dye molecules being present in the dye-bath, meaning interactions between H_2O_2 and dye molecules are more frequent, which results in increased degradation of dye.

COD indicates how much oxygen is needed for a complete chemical oxidation of the substance in a specific volume of a water sample. It is evident from Fig. 4 that at maximum levels the significant influences on COD values only have H_2O_2 , dye, urea, and the decoloration time. As shown in Table 4, out of these variables, only decoloration time has a positive effect (also at minimum levels), which was expected. Namely, longer decoloration times mean higher degradation rate of dye into products, that can be completely oxidized with lower oxygen concentrations. Also negative effects at maximum levels of dye and urea are expected, since their higher concentrations increase also the concentration of the compounds, that need to be oxidized in COD test. Furthermore, urea does not have a significant influence on COD values at the minimum level. From this we can conclude that, there is a limit in urea concentration, beneath which slight variations in urea concentrations do not change COD values substantially. Reasons for the influence of H_2O_2 on COD values are assumed to be the same as on absorbance.

At the minimum level all variables except NaCl and urea have significant influences on COD values. Considering UV irradiation and NaOH do not have a significant influence at the maximum level and influence this ecological parameter positively at minimum level we can conclude, that up to a certain limit higher intensity of UV irradiation and higher concentration of NaOH aid in degradation of the dye into products that can be more easily oxidized in the COD test. Above this

limit neither of them changes COD values significantly anymore.

NaCl does not have a significant influence on COD values at either level, meaning that toleration of NaCl addition in the dye-bath is quite wide.

TOC is the measure for the quantity of organically bonded carbon that oxidizes to CO_2 . As shown in Fig. 5, all the variables at both levels have a significant influence on the TOC values. Exception is decoloration time at maximum level, where its influence is insignificant. Since its influence at minimum level is significant and negative (Table 4) we are concluding, that up to a certain time there are not enough intermediates with organically bonded carbon formed during decoloration, which could oxidize to CO_2 already during the treatment (thus higher TOC values in the TOC test).

Influences of urea and NaCl at both levels are negative. Such effect of urea is expected since it contains organically bonded carbon, thus the higher concentration of urea results in higher TOC values. Negative effect of NaCl implies, that the salt inhibits degradation of dye during decoloration into smaller compounds, which can oxidize to CO_2 already during the treatment. Keeping in mind, that salt increase aggregation of dye molecules [11], such a result is expected.

Effects of UV irradiation, H_2O_2 , dye and NaOH are all positive on maximum and negative on minimum level. From this we can conclude, 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 the maximum level (lower TOC values in TOC test), in comparison with their concentration when variables are at the minimum level (higher TOC values in TOC test).

The values of the TIC are affected by various carbonates and bicarbonates, that can oxidize to CO_2 and are present in the sample. From Fig. 6 it is seen, that only UV irradiation, dye, and NaOH have a significant influence on the TIC values at maximum levels. Influence of NaOH is significant also at the minimum level, in both cases the effect is negative. This probably means, that also in this case too much H_2O_2 is used for oxidation of

NaOH [Eq. (2)] instead of dye, which apart from urea is the only substance in the bath that may produce (bi)carbonates. Effects of UV irradiation and dye at the maximum level are positive and influences not significant at minimum level. This means that for these two variables there is a limit beneath which slight changes in their values do not influence TIC values substantially. Positive effect of dye at the maximum level is unexpected, but it is possible to explain it by stabilizers present in commercial dye, that might accelerate degradation of dye into carbonate products easier to oxidize to CO_2 during TIC analysis.

Influences of H_2O_2 and urea are significant only at minimum level, in both cases the effect is negative. Such results for urea indicate, that part of organically bonded carbon oxidizes to carbonates, which influence TIC values more, when urea at minimum level. At maximum level the concentration of urea is so big already, that slight variations in its concentration do not change TIC values considerably. Negative effect of H_2O_2 at the minimum level probably means, that the rate of carbonate intermediates formation from organically bonded carbon is bigger than in the case of H_2O_2 at maximum level. In another words, above certain concentration limit, addition of H_2O_2 does not improve TIC values.

Similar as on COD values, NaCl does not have a significant influence also on TIC values at either level. The same is valid for decoloration time, its influence on TIC values at both levels is insignificant.

4.2. Dye Blue R

By comparing effects of variables on absorbance for both dyes (Table 4) we can see, that influences of UV irradiation, H_2O_2 , NaOH and decoloration time for this dye are the same as those for Blue VR. In comparison with Blue VR, it can be seen from Table 4, that the concentration of Blue R dye has a negative effect also at the maximum level. Considering also that influences of NaCl and urea are different in the case of Blue R, 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 phenomenon again can be explained by salt increasing and urea decreasing aggregation of dye molecules and thus in influencing hypochromic and bathochromic shift, respectively [11].

By comparing effects of variables on COD values for both dyes (Table 4) it is evident, that only concentration of dye has the same effect on COD values as in the case of Blue VR. The biggest difference in influences is exhibiting H_2O_2 . In the case of Blue VR peroxide's effects at maximum and minimum levels were negative and positive, respectively. In the case of Blue R peroxide's influence is insignificant at both levels.

UV irradiation, urea and decoloration time have similar effects on COD values as in the case on Blue VR. The difference in the case of Blue R is, that the influence is significant also at maximum level for UV irradiation, at minimum level for urea and is not significant at maximum level for decoloration time.

In the case of Blue R, NaCl has very important influence on COD values at maximum level. Since salt had no significant effect on COD values in the case of Blue VR (which has the same chemical structure) we are concluding, that such results are a consequence of differences in commercial product (different purity level or different stabilizers used).

NaOH does not have any significant influence at either level in the case of this dye, which is in compliance with its influence on COD values in the case of Blue VR at maximum level. The fact that NaOH doesn't have significant influence also at minimum level in the case of Blue R can also be explained by differences in commercial product.

Comparison of variables' effects on TOC values for both dyes (Table 4) shows, that only urea has the same influence and effect for both dyes. Similar is also effect of decoloration time, only in the case of Blue R time has negative effect also at maximum level.

UV irradiation and NaOH both have positive effect on TOC values also at minimum level, which in the case of Blue VR was negative. If we take into account the explanation given for influences of UV irradiation and NaOH for Blue VR, we can

conclude, that different effect at minimum level for dye Blue R is a consequence of different commercial product as well. Same is valid for the rest of the variables, i.e. H_2O_2 , dye and NaCl. In the case of NaCl we can also conclude, that with this commercial product salt does not increase aggregation of dye molecules substantially, when salt is at minimum level, since its effect on TOC values is positive, meaning some of dyes' degradation intermediates can oxidize already during the treatment. With increased concentrations of salt also higher aggregation occurs, which results in decreased pre-oxidation of intermediates during the treatment itself (thus higher TOC values in TOC test).

If we compare effects of variables on TIC values for both dyes (Table 4) we can see, that influences of NaCl, NaOH, urea and decoloration time are the same as for Blue VR.

Effects of UV irradiation and dye are still positive, only for dye Blue VR this happens at maximum levels, while for dye Blue R the effect is positive at minimum levels. The conclusion may therefore, be reverse, namely, for these two variables there is a limit above which slight changes in their values do not influence TIC values substantially.

Influence of H_2O_2 at maximum level is insignificant also for Blue R, but inverse at minimum level. Namely, in the case of Blue R effect of peroxide is positive. This difference as well can only be explained by different stabilizers added to the commercial product, which in the case of Blue R don't hinder oxidation of (bi)carbonates to CO_2 already during the treatment.

5. Conclusions

The intensity of UV irradiation has mainly significant influence on all ecological parameters at both levels and for both dyes. Its effect is positive, with the exception of influence on TOC values at minimum level for Blue VR. 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.

For both dyes urea has a positive effect only on absorbance, while COD, TOC and TIC values are

affected negatively by this chemical. Also this is an expected result, since urea is an organic compound that (i) needs more oxygen to completely oxidize and (ii) has organically bonded carbon that increases TOC values and produces larger quantities of (bi)carbonates, that influence TIC values.

Decoloration time affects positively absorbance and COD values, influence on TOC is negative, while TIC is not significantly effected by the time of treatment. From this we can conclude, that longer decoloration times favor degradation of dye into intermediates, that are no longer visible and need smaller amounts of oxygen to completely oxidize, while at the same time these intermediates cause higher TOC values.

The rest of the variables (H_2O_2 , dye, NaCl and NaOH) have very different influences on ecological parameters. Their influences also differ between the both dyes. If we take into account, that for both dyes the influences are the same only on absorbance and TIC (and even this only for 4 variables), we can conclude, that even if Duractive Brilliant Blue VR and Goldenzol Brilliant Blue Special R have the same chemical structure, the commercial products differ quite a lot. Such conclusion means, that based only on obtained results, it would be hard to state which variable one should pay attention to during decoloration process the most, in order to clean waste water in the most efficient and fastest way. In order to be able to make such predictions, more experiments need to be carried out.

References

- [1] Završnik T. Čiščenje tekstilnih odpadnih vod s poučkom na odstranjevanju barvil. *Tekstilec* 1992;7–8:321–4.
- [2] Zollinger H. *Color chemistry*, 2nd ed. Germany: VCH; 1991.
- [3] Griffiths J. *Colour and constitution of organic molecules*. London: Academic Press, Inc; 1976.
- [4] Yang Y, Xu L. Reusing hydrolyzed reactive dye-bath for nylon and wool dyeing. *American Dyestuff Reporter* 1996; 3:27–34.
- [5] Strickland AF, Perkins WS. Decoloration of continuous dyeing wastewater by ozonation. *Textile Chemist and Colorist* 1995;27(5):11–15.

- [6] Slokar YM, Majcen Le Marechal A. Methods of decoloration of textile wastewaters. *Dyes and Pigments* 1998; 37:338–40.
- [7] Cripps C, Bumpus JA, Aust SD. Biodegradation of azo and heterocyclic dyes by *phanerochaete chrysosporium*. *Appl Environ Microbiol* 1990;1114–8.
- [8] Slokar YM, Zupan J, Majcen Le Marechal A. The use of artificial neural network (ANN) for modeling of the H_2O_2 /UV decoloration process. *Dyes and Pigments* 1999;42: 123–35.
- [9] Dobovišek Ž. Tehniške meritve v strojništvu: Univerza v Mariboru; 1991. p. 26.
- [10] Slokar YM. Optimiranje razbarvanja tekstilnih reaktivnih barvil s H_2O_2 /UV. Doktorska disertacija 2000. p. 79–80.
- [11] Hamlin JD, Phillips DAS, Whiting A. UV/visible spectroscopic studies of the effects of common salt and urea upon reactive dye solutions. *Dyes and Pigments* 1999;41:137–42.
- [12] Majcen-Le Marechal A, Slokar YM, Taufer T. Decoloration of chlorotriazine reactive azo dyes with H_2O_2 /UV. *Dyes and Pigments* 1997;33:286.