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Decoloration of Chlorotriazine Reactive Azo Dyes with H_2O_2/UV

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ABSTRACT

We describe an environmentally friendly process of oxidative decoloration of chlorotriazinyl reactive azo dyes with hydrogen peroxide, activated with UV irradiation. A comparison of this process with other oxidative decolorations is given. The influence of the synthetic route, the dyebath components, and the reaction conditions of the decoloration process is described. Decoloration efficiency is evaluated with respect to the time-dependent reduction of the color intensity, as well as with ecological parameters such as COD, BOD_5 and TC. The method proved to be suitable for the decoloration of reactive azo dyes of triazinyl type. © 1997 Elsevier Science Ltd

Keywords: ecology, decoloration, hydrogen peroxide, UV irradiation, reactive dye, ecological parameters.

INTRODUCTION

Awareness of ecological problems principally arose during the 1970s,[1] and currently, in the context of the coloration industry, waste water contamination is of particular concern.[2]

This study is concerned with impurities originating from dyestuffs and their oxidative elimination from waste waters. There are in the region of 3000 different dyes available on the commercial market,[3] and more than half of these dyes are azo compounds, followed by groups of dyes with a common structural element containing, e.g. an anthraquinone, triphenylmethane or phthalocyanine moiety. The biological activities of dyes can differ greatly in spite of their similar structure, so their toxicological properties cannot be generalised by reference to one group only. Toxicological characteristics of any individual substances can only be determined through experimental work. Since the presence of a dye in an effluent can be observed at very low concentrations (1 mg/liter can be seen, 0.1 mg/liter can be determined analytically), the production and application of dyes represent an especially important area. The pertinent effects on the environment are most often assessed by ecological parameters such as chemical oxygen demand, biochemical oxygen demand, total carbon and adsorbable organic halogen.

THEORY

The ecological approach to the synthesis and use of dyes can be implemented before, during or after dyeing. In the latter the process is called *decoloration.* Because of its numerous advantages and easy handling, the technique most often used is chemical treatment, i.e. oxidation with hydrogen peroxide. Of all chemical oxidants the presence of hydrogen peroxide in the waste water is the least questionable[4] and in addition, the supply of oxygen needed for aerobic biological cleaning is greater.

Hydrogen peroxide is stable when pure, which is why oxidation of organic substances is often very difficult or, under usual waste water treatment conditions, even impossible without the presence of appropriate catalysts.[5] A catalyst is needed for the formation of hydroxyl radicals (eqn 1), whose oxidation potentials are much higher than that of hydrogen peroxide.

$$\mathrm{HO{:}OH} \rightarrow 2\,{}^{\cdot}\mathrm{OH}. \qquad (1)$$

The following activators are used for the decoloration with H_2O_2:

(a) Fe(II) salts, i.e. Fenton's reagent;
(b) UV irradiation;
(c) ozone.

A comparison of these individual processes is given in Table 1.[6]

This paper describes a process of waste water decoloration using UV/H_2O_2, in which the role of UV irradiation is of prime importance, since this catalyses the chemical oxidation of organic compounds in two ways:[7]

(a) the toxic substances absorb the energy of the UV irradiation, which then changes their chemical structure and increases their reactivity with oxidants;
(b) even more important is the formation of hydroxyl radicals which have, as already mentioned, high oxidation potential.

TABLE 1
Technical Comparison of Oxidative Decolorations

Process	*Advantages*	*Disadvantages*
Fenton	– Simple equipment and easy implementation – Reduction of COD (except with reactive dyes)	– Sludge formation – Long reaction times – Salt formation – Hazardous waste
FSR[a]	– Simple equipment and implementation – Reduction of COD (except with reactive dyes)	– Salt formation – Formation of gases (H_2, O_2 during electrolysis)
UV/H_2O_2	– No sludge formation – No salt formation – Considerable safety, easy operation – Short reaction times – Reduction of COD	– Not applicable for all dye types – Requires separation of suspended solid particles
O_3/H_2O_2	– No sludge formation – No salt formation – Short reaction times – Very short reaction times for reactive dyes	– Not applicable for all dye types – Toxicity, hazard, problematic handling – No COD reduction – Additional load of water with ozone

[a] FSR, Fenton Sludge Recycling System is a process using oxidative decoloration with Fenton's reagent and a subsequent sludge recycling. Disposal of sludge is ecologically objectionable.

The dye used for the decoloration experiments was the chlorotriazine reactive azo dye C.I. Reactive Red 120 (Fig. 1), prepared following four different synthesis routes.

The standard route for the dye **1A**[8] was modified as follows:

(a) **2A**: instead of acetone, a non-ionic wetting agent Kieralon D (BASF) was used as a solvent medium for trichloro-*s*-triazine and phenylene diamine;
(b) **3A**: H-acid was added all at once and not progressively;
(c) **4A**: for salting out, surplus NaCl from the waste water after the first synthesis was used.

The impact of these procedures on the decomposition of dyes was studied. The results were compared to those of the commercial dye Cibacron Brilliant Red 4G-E (Ciba). In addition, the influence of chemicals usually added to dyebaths when dyeing with this dye was investigated, as well as the influence of decoloration reaction conditions. The results were evaluated with

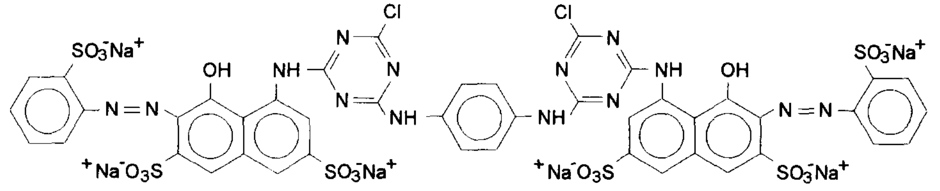

Fig. 1. Bifunctional reactive dye with C.I. Reactive Red 120.

TABLE 2
Composition of Decolorizing Baths

Bath	*Concentration*				
	Dye (mg/liter)	*NaCl (g/liter)*	*NaOH*[a] *(ml/liter)*	*Oxidizing agent*[b] *(g/liter)*	H_2O_2[c] *(ml/6 liters)*
1	100	—	—	—	4
2	100	4	—	—	4
3	100	—	1.5	—	4
4	100	—	—	0.2	4
5	100	4	1.5	0.2	4

[a] $w(\mathrm{NaOH}) = 32.5\%$.
[b] Lamberti Redoks L2C (*m*-nitrobenzene sulfonate, anion active).
[c] $w(H_2O_2) = 35\%$.

time-dependent color intensity reduction and with the ecological parameters COD, BOD_5 and TC.

EXPERIMENTAL

Preparation of decolorizing baths

Dyebaths for dyeing with reactive dyes also contain an alkali (NaOH), salt (NaCl) and an oxidizing agent (Lamberti Redoks L2C).[9] Our intention was to find out in what way these individual chemicals, and all chemicals together, affect the decoloration process. For this purpose the baths were prepared as presented in Table 2.

Our intention was to approach the concentrations of dyes and chemicals remaining in the bath after dyeing as close as possible, so the additions were calculated with respect to 75% exhaustion of the dye at 2% coloring depth. It was also foreseen that, in an industrial process, a mix can be made of after-dyeing baths with other baths (e.g. washing baths), so the decolorizing

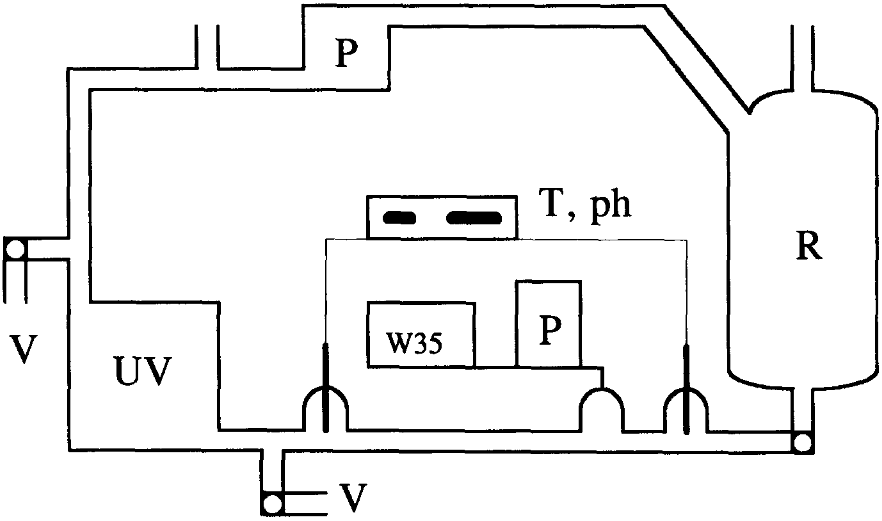

Fig. 2. Schematic presentation of the plant for decoloration with H_2O_2/UV: P, pump; UV, HP reactor; R, reservoir; W35, peroxide; V, sample draw.

TABLE 3
Reaction Conditions During the Decolorizing Processes

Bath	*1600 W + H_2O_2*	*800 W + H_2O_2*	*1600 W*
1	+	+	+
2–5	+	–	–

baths were 2.5-times diluted. The effect of chemicals was studied on dye **1A** at concentration 100 mg/liter, using a 1600 W UV lamp.

Equipment and techniques

Decoloration was performed on the pilot plant Solvay Interox GmbH (Fig. 2).[10]

The first sample was taken prior to decoloration (time 0) and after switching the UV reactor on, samples were taken every minute. To determine the effect of the reaction conditions during the decoloration process, Bath 1 (Table 2) was decolorized at a lower radiation flux (800 W) and at a higher one (1600 W) without the addition of hydrogen peroxide (Table 3).

The decoloration of dyebaths was followed spectrophotometrically on the HP Diode Array Spectrophotometer 8452A. The absorbancy was measured at the maximum wavelength of the dye, which was in an acid medium (Baths 1, 2 and 4) 514 nm and in an alkaline medium (Baths 3 and 5) 508 nm.

The results were expressed as a percentage of the color intensity. The absorbancy of the first sample had 100% intensity, the samples that followed had correspondingly lower values. The ecological parameters of pollution (COD, BOD_5 and TC) were determined for starting and end samples.

RESULTS

Since the reactivity of hydrogen peroxide depends on the medium's pH value, it was measured first. The pH values ranged from 5.2 to 6.2 in Baths 1, 2 and 4, and from 11.2 to 11.5 in Baths 3 and 5. In all dyebaths where the decoloration started in an acid medium, the pH value dropped after the treatment, while in an alkaline medium it remained unchanged.

When decoloration was complete, the quantity of the residual hydrogen peroxide was determined. In alkaline medium the concentration of hydrogen peroxide was considerably lower, so we conclude that part of the hydrogen peroxide reacted with NaOH to form sodium peroxide (eqn 2).[11]

$$H_2O_2 + 2NaOH + 6H_2O \rightarrow Na_2O_2 \times 8H_2O. \qquad (2)$$

Decoloration

It is shown in Fig. 3 that the shortest times of decoloration were obtained with dye **2A** (5 min) while about 20% longer times were needed for decoloration of other dyes. A similar situation was observed with the synthesized waste water. The fastest to decolorize was the effluent leaving process **2A**. It can be concluded that the wetting agent facilitated the decoloration process.

The chemicals that were fed into the bath containing C.I. Reactive Red 120 have, with the exception of salt, a markedly negative effect on the decoloration (Fig. 4).

The addition of alkali greatly inhibited the rate of decoloration, as was expected. It has already been mentioned that a part of the H_2O_2 probably reacts with NaOH, implying that there is less H_2O_2 available for the formation of radicals, which in turn are needed in the decoloration.

Even longer times were needed for the complete decoloration in solutions that contained just an oxidizing agent or, in another case, those which contained all chemicals. Because almost identical decoloration curves were obtained from these two treatments, it can be concluded that the oxidizing agent influences the reaction times more than the alkalis. If we bear in mind that the oxidizing potential of a redox system (eqn 3), with H_2O_2 as the oxidizing agent, totals 1.78 V, while in system (eqn 4), where H_2O_2 acts as a

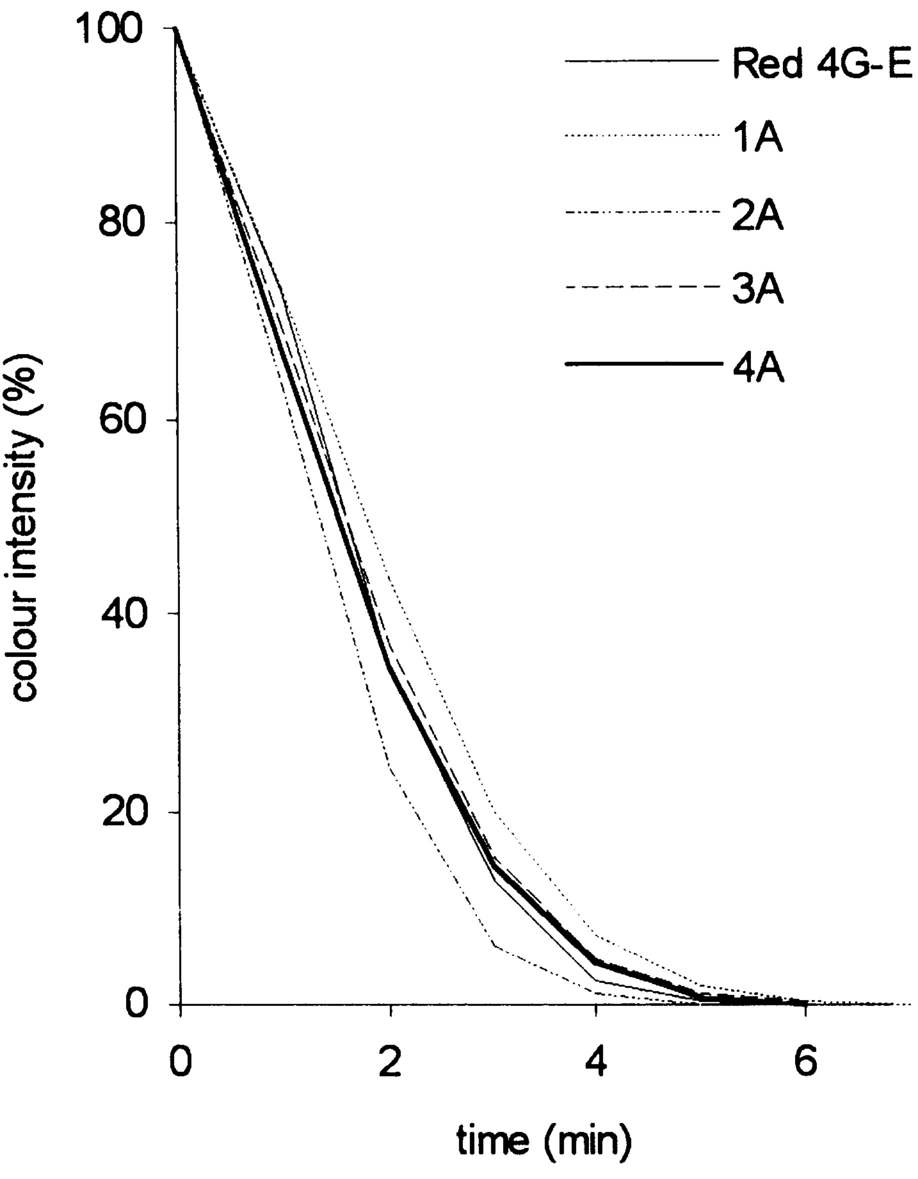

Fig. 3. Time dependent color intensity reduction in relation to different synthesis routes (100 mg/liter, 1600 W + H_2O_2).

reducing agent, it is only 0.68 V,[12] then evidently Lamberti Redoks L2C is a stronger oxidizing agent than H_2O_2. In the decoloration process, therefore, the latter no longer has the ability to oxidize. This was confirmed by the results.

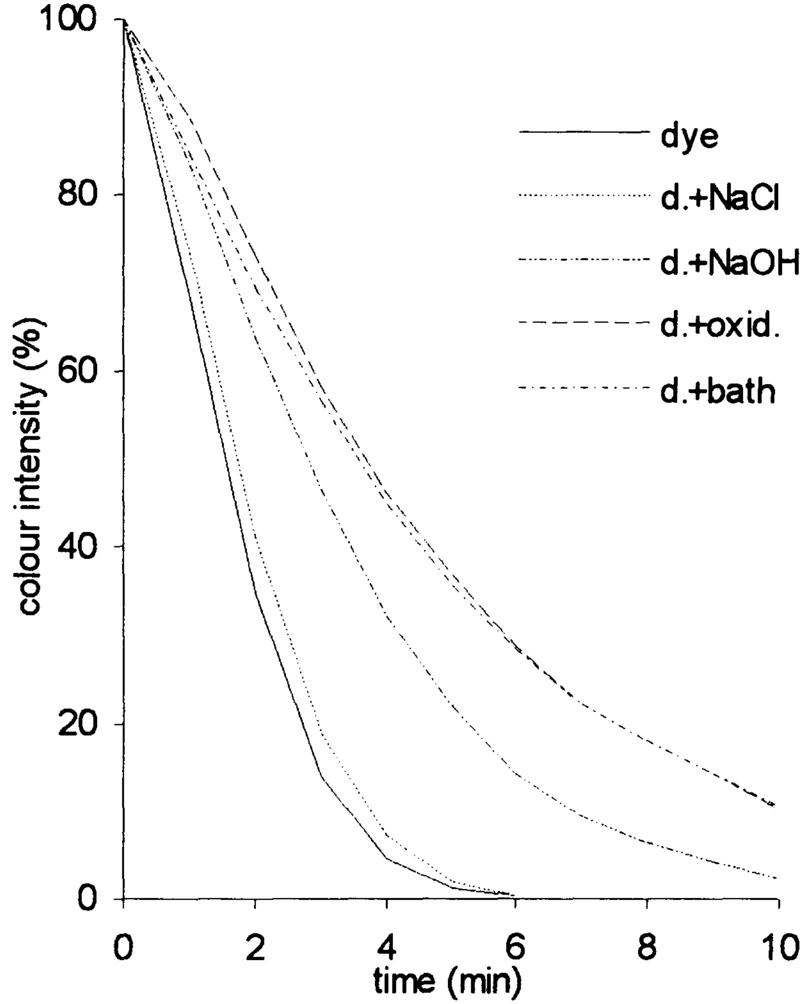

Fig. 4. Time-dependent color intensity reduction in relation to added chemicals (1600 W + H_2O_2).

$$H_2O_2 \cdot 2H^+/2H_2O \tag{3}$$

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-. \tag{4}$$

In this respect, there arises the question of whether the addition of the oxidizing agent in the dyeing process can be avoided. Oxidizing agents are added to prevent possible reduction of the reactive dye during the dyeing process. Since the reduction does not take place under the controlled dyeing conditions in a laboratory, the addition of an oxidizing agent is not essential. It is required in an industrial process, however, where larger quantities of water are used and where certain compounds (for example, the use of non-demineralized water) could start the reduction process. The problem could be solved by using a more appropriate oxidizing agent that would still play its role in a dyeing process, but would have no negative effect on the subsequent cleaning treatment.

shows that color intensity reduction depends heavily on the UV output irradiation, since the reaction times at lower output (800 W) are longer by up to 70%. If no hydrogen peroxide is present, the decoloration process does not reach completion even after 10 min.

Two conclusions can be drawn. First, color intensity reduction takes place even without the addition of H_2O_2, since bond cleavage obviously occurs by the UV light alone. If no H_2O_2 is added, reaction times should be considerably prolonged, which is uneconomical. Second, it has been confirmed that H_2O_2 has an oxidizing capacity large enough to break the bond in a dye molecule, which is why the water after the decoloration process is no longer colored.

Ecological parameters

Through decoloration, the COD and TC values are reduced irrespective of the synthesis used (Figs 6 and 7).

A difference can be noticed, especially in COD values: the concentration of oxygen, required for a complete oxidation of organic matter at the highest capacity of the reactor, is reduced on average by 97%. The reduction of total carbon is considerably smaller (by 40% on average). Since COD is a measure of the presence of organic matter, which is environmentally harmful, and TC represents a measure of carbon compounds, which can be oxidized to CO_2, there are two possibilities for such a result:

(a) compounds formed through oxidation can easily be broken down into forms that do not harm the environment, which is why the final COD values are low;
(b) carbon compounds in the form of carbonates are present; they cannot be tracked by means of a detector, because at that pH they are not transformed to CO_2.

However, the obtained end values are no longer objectionable and the decolorized water can be discharged.

In addition, the COD and BOD_5 values were determined in the synthesis waste waters. The COD:BOD_5 ratio is a typical characteristic of a waste water[2]. It represents its ability for biological degradation (the lower the ratio, the better the biological degradation). Figures 8 and 9 show that waste water **4A** is the easiest to degrade biologically, but none of the final pollution parameters exceeded the allowed maximum values (160 mg/liter for COD and 30 mg/liter for BOD_5).[13]

Contrary to what was observed in the decoloration, the addition of chemicals had no such negative effect on the pollution parameters. Their values after the decoloration reduced considerably (Figs 10 and 11).

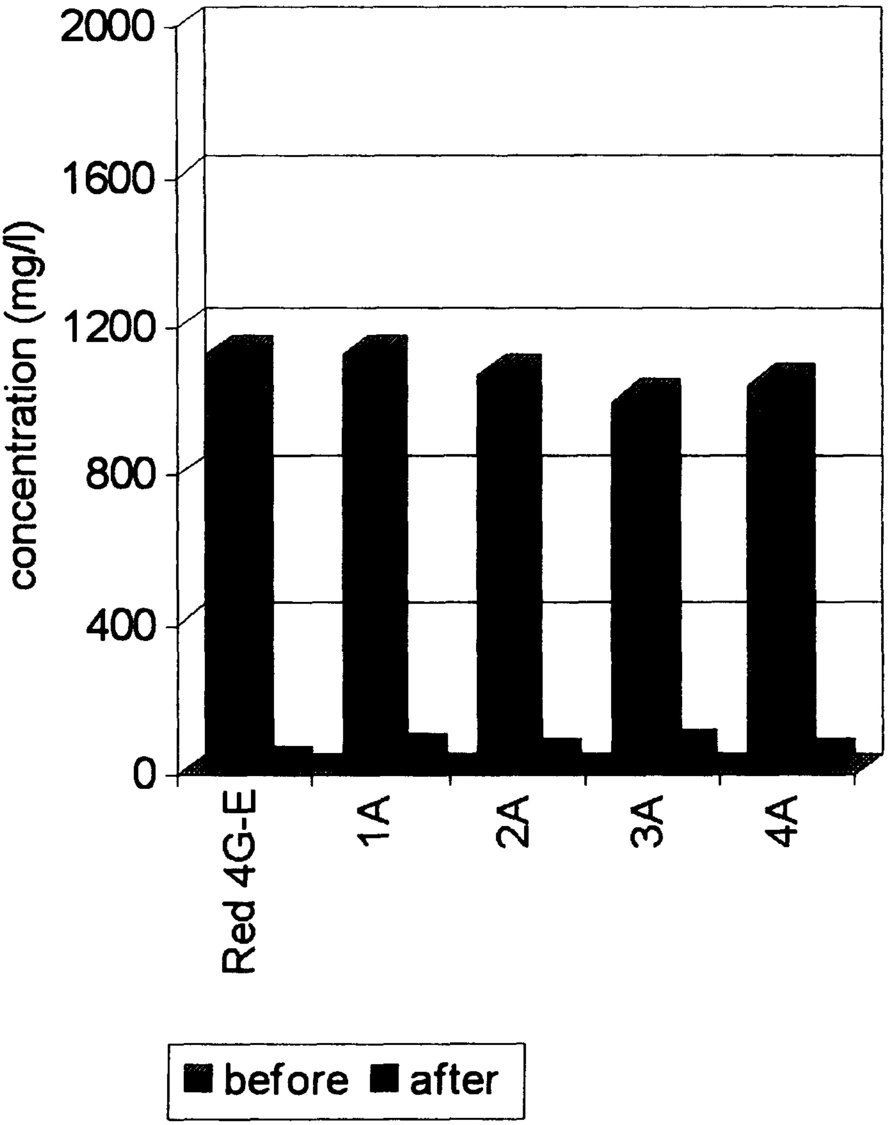

Fig. 6. COD values in starting and end samples in relation to different synthesis routes (100 mg/liter, 1600 W + H_2O_2).

In all baths, irrespective of the chemical added, the COD values were reduced by more than 85%. It is interesting that COD reduction in a bath containing all chemicals was minimal (19%). In view of the previous findings it can be concluded that it comes to a synergy between all the chemicals present.

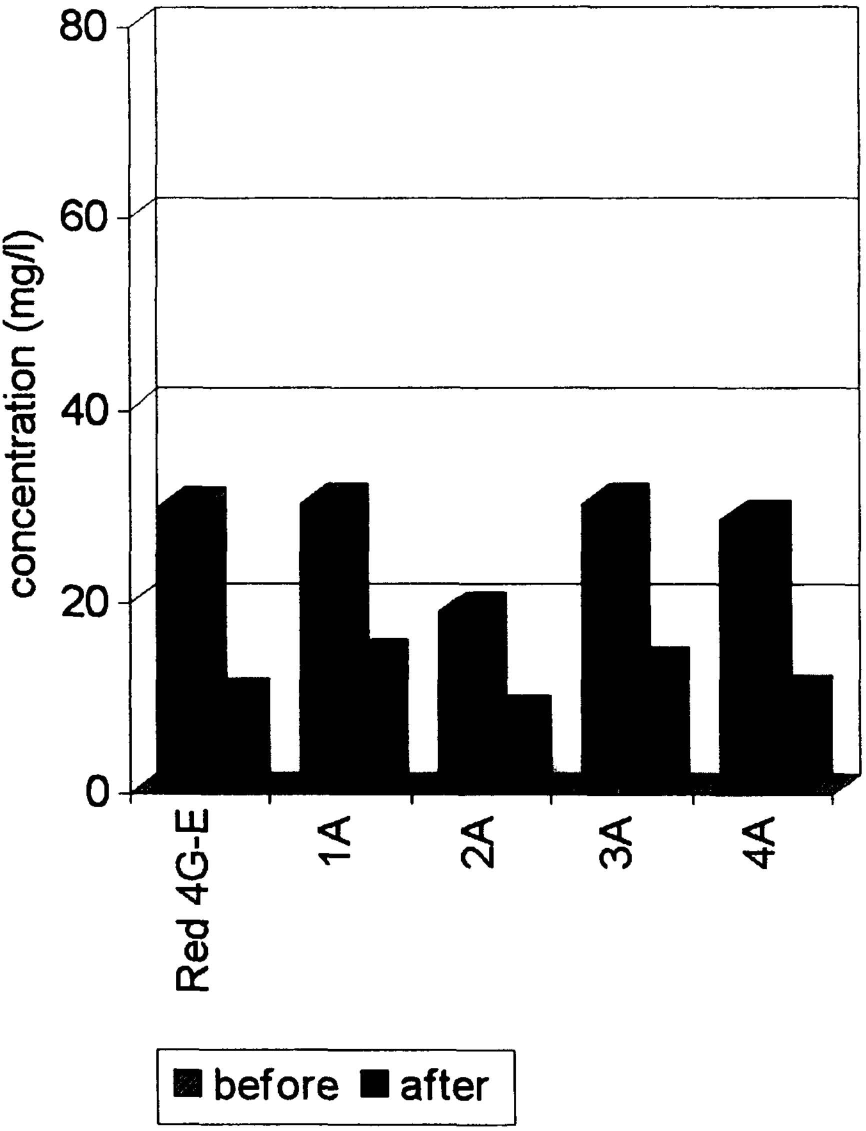

Fig. 7. TC values in starting and end samples in relation to different synthesis routes (100 mg/liter, 1600 W + H_2O_2).

The reduction of TC in baths that contained chemicals was smaller than the reduction in baths containing only a dye. In the bath containing alkali the TC value was reduced by 118%, in the bath containing the oxidizing agent it was reduced by 16%, while in the presence of all chemicals the reduction was just 15%.

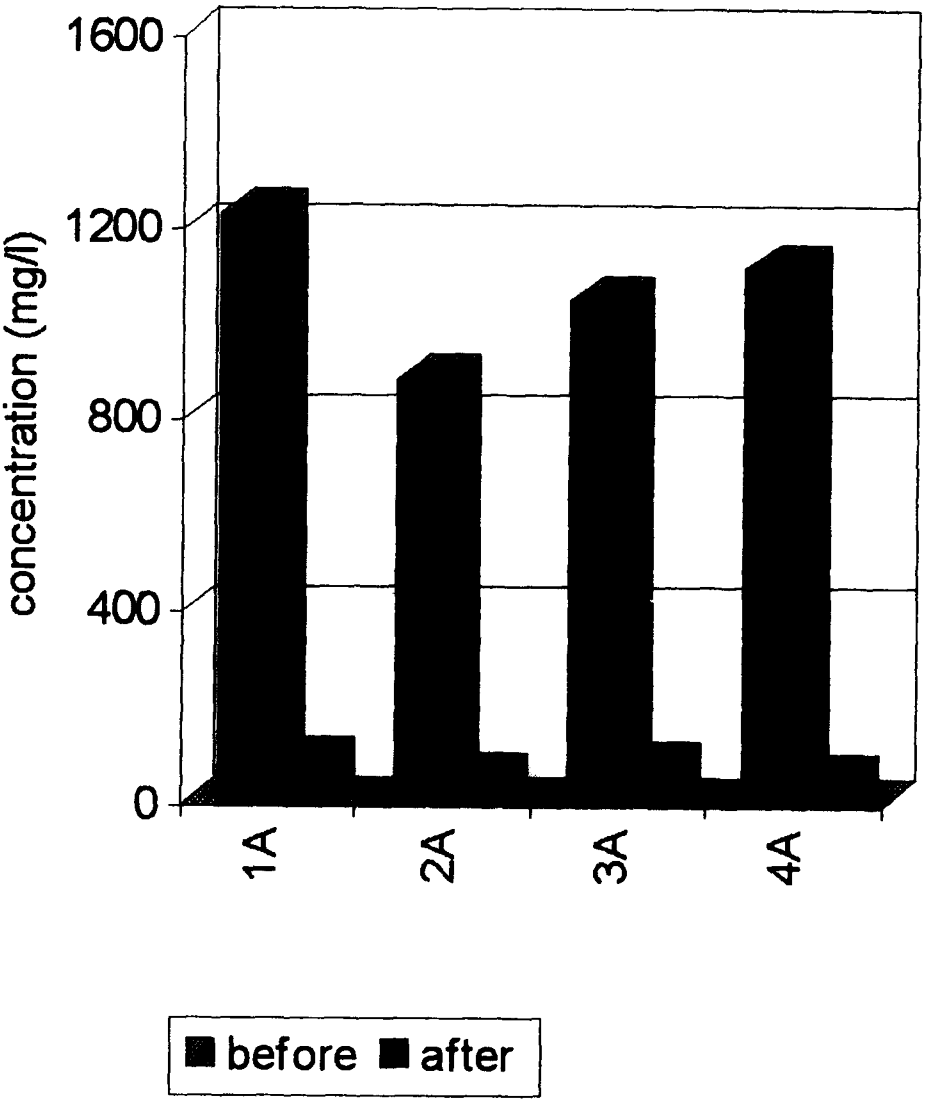

Fig. 8. COD values in the waste waters of synthesized dyes in starting and end samples in relation to different synthesis routes (50 mg/liter, 1600 W + H_2O_2).

From Figs 12 and 13, showing the comparison of pollution parameters at different decoloration reaction conditions, it can be seen that the addition of H_2O_2 reduced the pollution parameters: COD by 94% and TC by 50%. This result corresponds with the findings concerning the color intensity reduction in relation to the said reaction conditions. The reduction of COD and TC

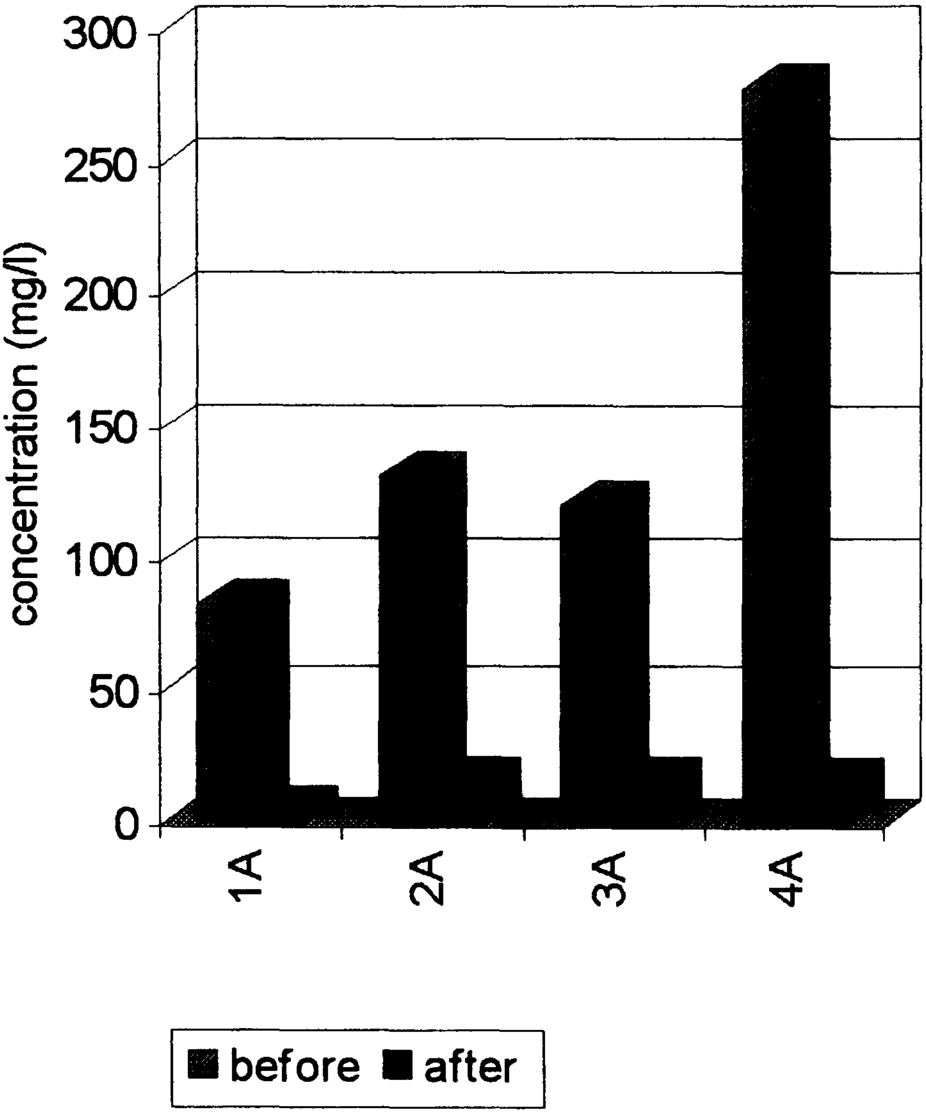

Fig. 9. BOD_5 values in the waste waters of synthesized dyes in starting and end samples in relation to different synthesis routes (50 mg/liter, 1600 W + H_2O_2).

end values in all dyes was the smallest in decoloration tests where no H_2O_2 had been added (14% COD and 11% TC). The reduction in pollution parameters at 800 W was slightly smaller than the reduction at 1600 W, the differences were evident especially in TC values (in the presence of hydrogen peroxide the reduction of TC totalled 60% at 1600 W and 40% at 800 W).

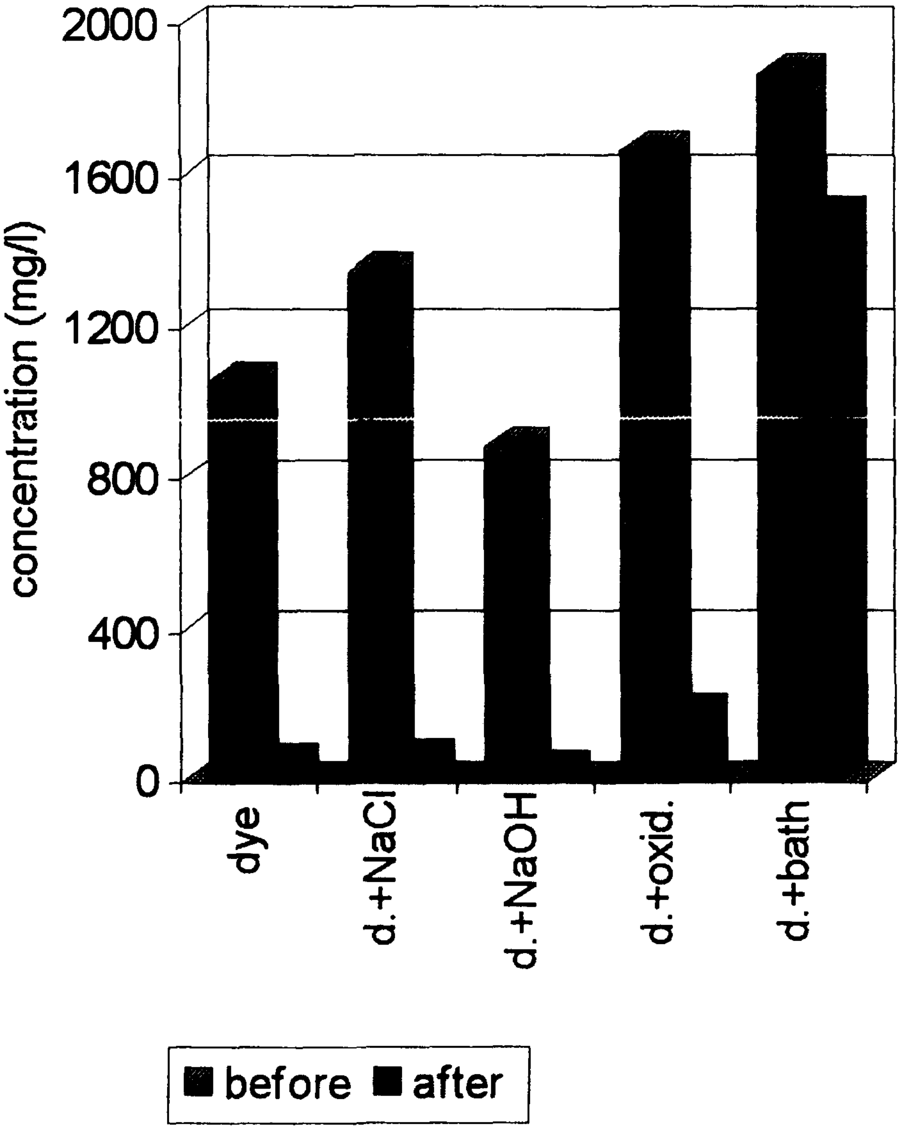

Fig. 10. COD values in starting and end samples in relation to the addition of chemicals (1600 W + H_2O_2).

Of special interest was the difference in the starting COD values between baths with peroxide and those without peroxide. One of the chemicals used in the determination of COD is potassium dichromate(VI). In an acid media, hydrogen peroxide reacts with dichromate ions to form peroxy-dichromic acid (eqn 5), which is not stable and decomposes immediately into Cr(III) salts (eqn 6).[12]

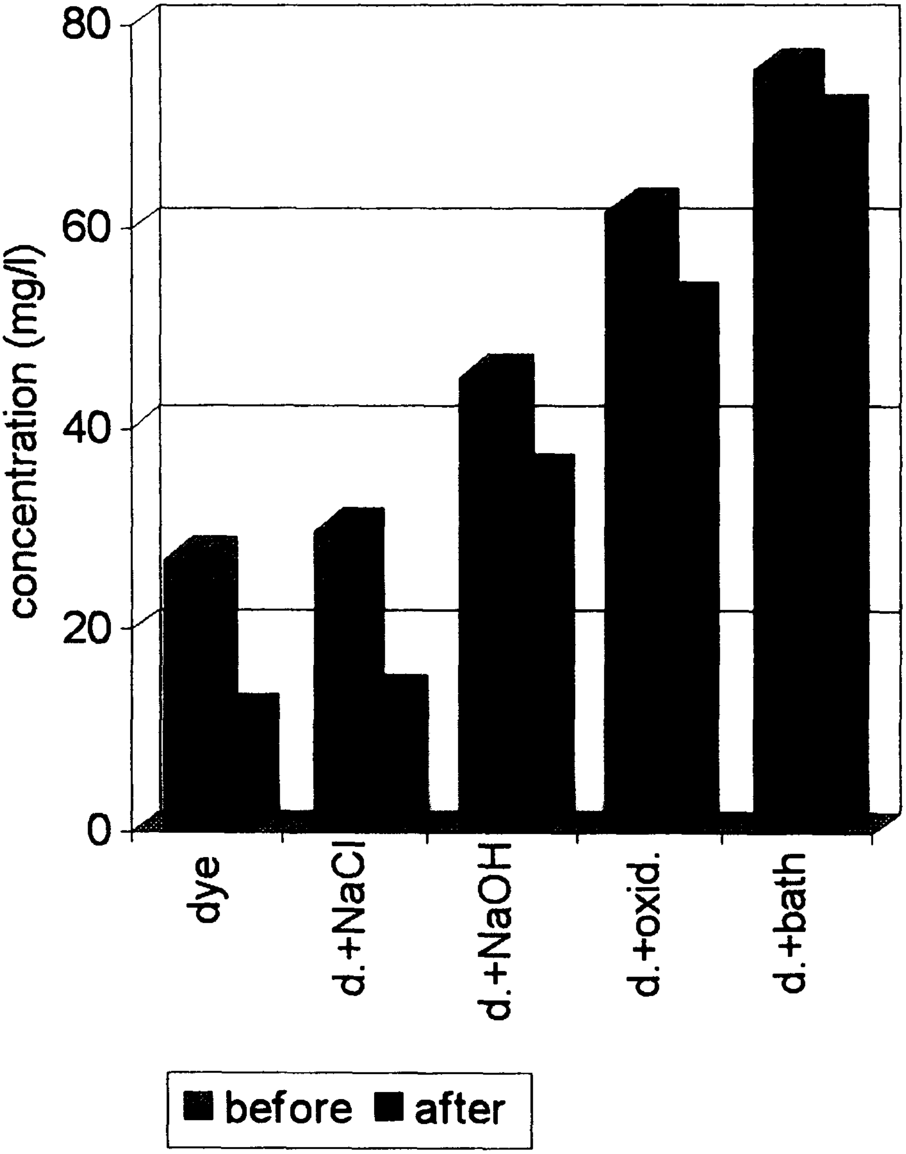

Fig. 11. TC values in starting and end samples in relation to the addition of chemicals (1600 W + H_2O_2).

$$H_2Cr_2O_7 + 5H_2O_2 \rightarrow H_2Cr_2O_{12} + 5H_2O \tag{5}$$

$$H_2Cr_2O_{12} + 8H_2O_2 \rightarrow Cr_2O_3 + 9H_2O + 8O_2. \tag{6}$$

When determining the actual value it is therefore necessary to take into account a correction factor: for 1 mg/liter of peroxide, this factor amounts to 0.25 mg/liter COD.

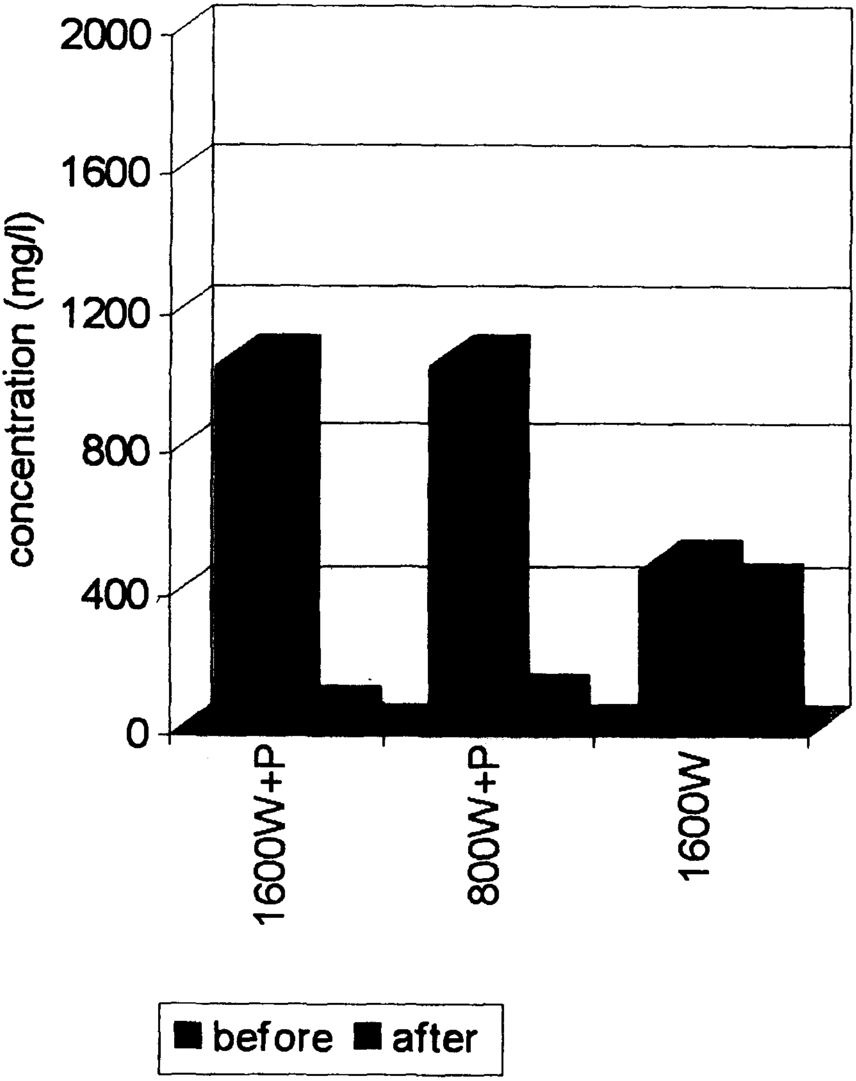

Fig. 12. COD values in starting and end samples in relation to the reaction conditions (100 mg/liter).

It is evident from Fig. 13 that the presence of H_2O_2 causes the reduction of the initial TC values. In a bath where peroxide had not been present this value was higher by 16%. The reason for this is the reaction between hydrogen peroxide and a part of the organic compounds that can be oxidized to CO_2. Because of this some of the carbon is removed during the preparation of decoloration baths.

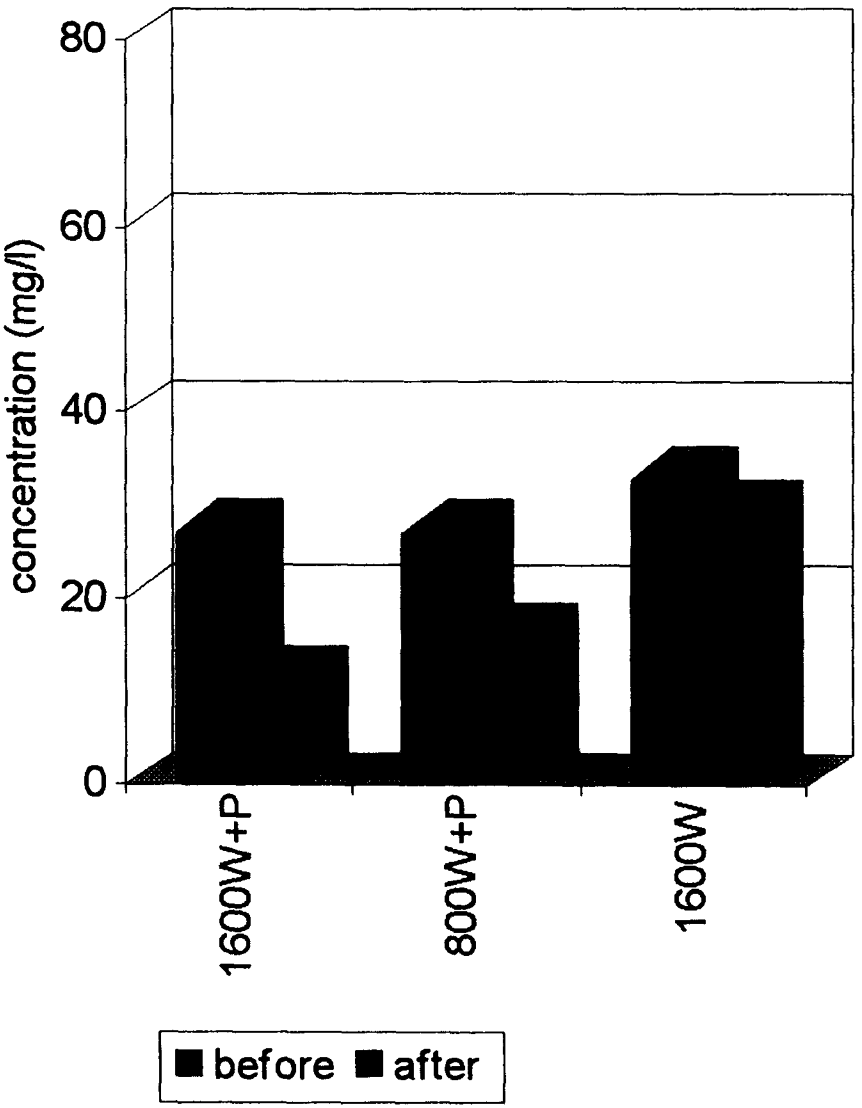

Fig. 13. TC values in starting and end samples in relation to the reaction conditions (100 mg/liter).

CONCLUSION

The efficiency of decoloration of commercial and synthesized dyes with H_2O_2/UV was examined by time-dependent color intensity reduction, as well as by determining ecological parameters such as COD, BOD_5 and TC. A comparison of four different syntheses showed that the addition of a wetting agent accelerates the decoloration process and reduces the pollution parameters most. Biological degradation of the mentioned dye is good. In general, none of the dyes remained environmentally objectionable after the decoloration process. Both COD and BOD_5 values were below the limits set by Slovenian regulations (160 mg/liter for COD and 30 mg/liter for BOD_5).

It was found that chemicals used in the dyeing process reduced the efficiency of the decoloration process. The effect of oxidizing agent or NaOH was especially notable. Concerning the reaction conditions, it was further observed that the rate of decoloration was proportional to the output of the UV irradiator.

The results show that the decoloration process using UV activated H_2O_2 is very suitable for treating triazine reactive azo dyes, since a decrease was noted both in the intensity of the color and in the values of the ecological parameters.

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