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Dyes and Pigments 58 (2003) 245–252

DYES and PIGMENTS

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Comparison of H_2O_2/UV, H_2O_2/O_3 and H_2O_2/Fe^{2+} processes for the decolorisation of vinylsulphone reactive dyes

Tanja Kurbus[a], Alenka Majcen Le Marechal[a,*], Darinka Brodnjak Vončina[b]

[a]*Faculty of Mechanical Engineering, Smetanova 17, 2000 Maribor, Slovenia*
[b]*Faculty of Chemistry and Chemical Engineering, Smetanova 17, 2000 Maribor, Slovenia*

Received 13 March 2003; received in revised form 5 April 2003; accepted 28 April 2003

Abstract

Six vinylsulphone reactive dyes were decolorised using three oxidation processes (H_2O_2/UV, H_2O_2/O_3 and H_2O_2/Fe^{2+}). The efficiency of decolorisation was measured by decolorisation time, absorbance, COD and TOC and the three methods of decolorisation are compared.

Keywords: Vinylsulphone dyes; Decolorisation; Hydrogen peroxide; UV irradiation; Ozone; Reactive dyes

1. Introduction

Effluents from the textile industry commonly contain high concentrations of organic and inorganic chemicals and are characterized by high COD and TOC values as well as strong color [1]. The major concern with color is its aesthetic character at the point of discharge with respect to visibility in rivers [2]. Dyes from dyeing operations are the major source of colour in textile effluents and reactive dyes pose serious environmental problems, because these particular types of dye can display low fixation to cellulosic fibres [3].

The dyeing of cellulose fibres with vinylsulphone reactive dyes is carried out with additions such as NaOH, NaCl, urea, etc. These chemicals help to optimise the covalent bonding of the dyes to the substrate. The dyeing process is performed in an alkaline medium, which is needed to create the covalent bond between the dye molecule and the ionised hydroxyl group of cellulose. NaOH is responsible for the formation of the nucleophile (Cell–O^-) and its addition to the double bond of the vinylsulphone group of the dye. As the mechanism is AdN1, so it takes place in two steps, the first step is the elimination of H_2SO_4 and the formation of the double bond and the second step comprises the addition of the Cell–O^- to the double bond in the dye [4].

NaCl promotes dye exhaustion by reducting the water solubility of the dye resulting in the accelerated transition of aggregates of dye molecules from the solution the substrate. It is very important to use optimal amounts of electrolyte; too little brings no effect, while an excess may lead to a

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* Coresponding author. Fax: +386-2-220-7990.
E-mail address: alenka.majcen@uni-mb.si (A. Majcen Le Marechal).

0143-7208/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0143-7208(03)00085-8

high degree of dye aggregation, and as a consequence, dye precipitation.

Dyeing with reactive dyes also involves the use of urea, which is used to swell the cellulosic substrate and to dissagregate the dye (leading to increased solubility) resulting in improved diffusion of the dye within the fibre [5].

To eliminate the color from textile effluents, oxidation processes are most widely used. Various physical/chemical processes (coagulation, flocculation, adsorption on activated carbon, reverse osmosis) and biological processes have been used for wastewater decolorisation. Biological processes are not effective enough to decolorize dyes of high photostability while physical/chemical processes are not strong enough to decompose the dye. Hence sludge generation and adsorbent regeneration are the principal weaknesses of these processes [6]. Advanced oxidation processes (AOP) decompose the chromophore of the dye and consequently realise complete decolorisation. These processes comprise the activation of hydrogen peroxide with UV light, ozone or Fenton‘s reagent [7–20]. Hydroxyl radicals, formed after activation, have a higher oxidation potential (2.8 V) than hydrogen peroxide (1.78 V) and so dye decolourisation is feasible.

The objective of this research was to find out which of the advanced oxidation processes needs the least time to decolour model wastewater solutions derived from the dyeing of cellulosic fibres with vinylsulphone reactive dyes. The following advanced oxidation processes were chosen, namely H_2O_2/UV, H_2O_2/O_3 and H_2O_2/Fe^{2+} and the efficiency of decolourisation in the shortest possible time was verified using pollution parameters such as absorbance, COD and TOC.

2. Experimental

Six vinylsulphone dyes were used as follows: C.I. Reactive Blue 220, C.I. Reactive Black 5, Remazol Dark Black N (C.I. is not known), C.I. Reactive Blue 28, C.I. Reactive Red 22, C.I. Reactive Yellow 15. All dyes were used without purification. Hydrogen peroxide solution (35% w/w, with $\rho = 1{,}23$ g/ml) of analytical grade was obtained from Belinka.

The chemical structures of C.I. Reactive 5, C.I. Reactive Red 22 and C.I. Reactive Yellow 15 are known (Figs. 1–3), while the chemical structures of the other dyes are not disclosed.

Decolourisation with H_2O_2/UV was performed on a pilot plant manufactured by Solvay Interox (Fig. 4). A 6 l dyebath was pumped into the reservoir; the water flow was 3 dm^3 min^{-1}, the dosage of hydrogen peroxide was 4.5 ml l^{-1}, and the UV lamp ($\lambda = 254$ nm) was set to 1400 W (Table 1). After decolourisation, the absorbance, COD and TOC of

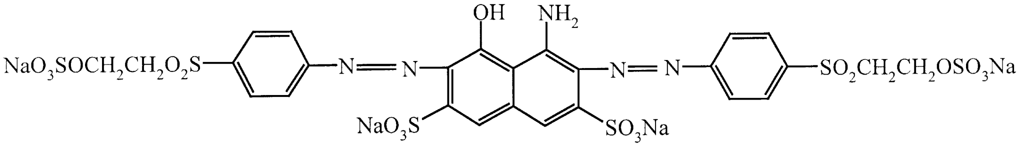

Fig. 1. Chemical structure of the reactive vinylsulphone dye with C.I. Reactive Black 5.

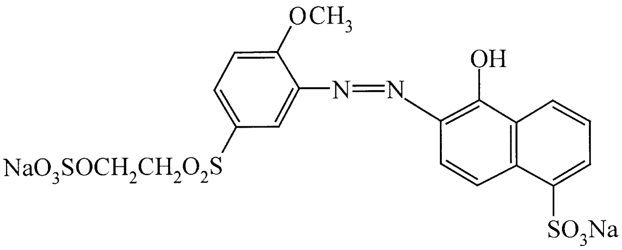

Fig. 2. Chemical structure of the reactive vinylsulphone dye with C.I. Reactive Red 22.

Table 1
The input variables of H_2O_2/UV, H_2O_2/O_3 and H_2O_2/Fe^{2+} decolourisation

Process	Concentration				Reaction conditions			
	dye [mg l^{-1}]	NaCl [g l^{-1}]	NaOH [ml^{-1}]	Urea [g l^{-1}]	H_2O_2 [ml l^{-1}]	UV [W]	O_3 [mol m^{-3}]	Fe^{2+} [g l^{-1}]
H_2O_2/UV	200	3	1.7	10	4.5	1400	–	–
H_2O_2/O_3	200	3	1.7	10	4.5	–	0.0813	–
H_2O_2/Fe^{2+}	200	3	1.7	10	4.5	–	–	0.7278

samples were measured. Decolourisation was performed in an alkaline medium (pH = 12).

Decolourisation with H_2O_2/O_3 was performed in an ozonizer (Fig. 5). An 800 ml dyebath was used to which 4.5 ml l^{-1} of hydrogen peroxide was added. Air was pumped into the ozononizer, to produce ozone. During decolourisation the flow of air with ozone was 100 dm^3 h^{-1} and the overpressure in the Hg manometer was 488 Pa (Table 1). After decolourisation, the absorbance, COD and TOC of samples were measured as described at the end of the experimental part. Decolourisation was performed in an alkaline medium (pH = 12).

Decolourisation with H_2O_2/Fe^{2+} (Fenton's reagent) was performed as shown in Fig. 6. Decolourisation with Fenton's reagent was performed in an acid medium (pH = 3). Dyebath (1 l) was used, set at pH 3 using 10% sulphuric acid, and $FeSO_4$ (0.7278 gl $^{-1}$) and hydrogen peroxide (4.5 ml l^{-1}) were added. After decolourisation, the absorbance, COD and TOC of samples were measured.

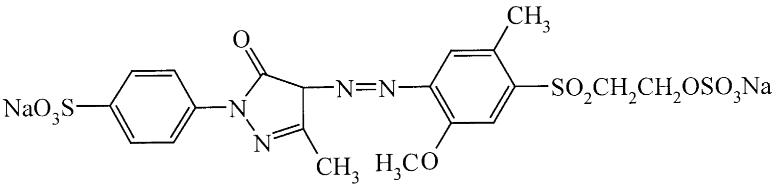

Fig. 3. Chemical structure of the reactive vinylsulphone dye with C.I. Reactive Yellow 15.

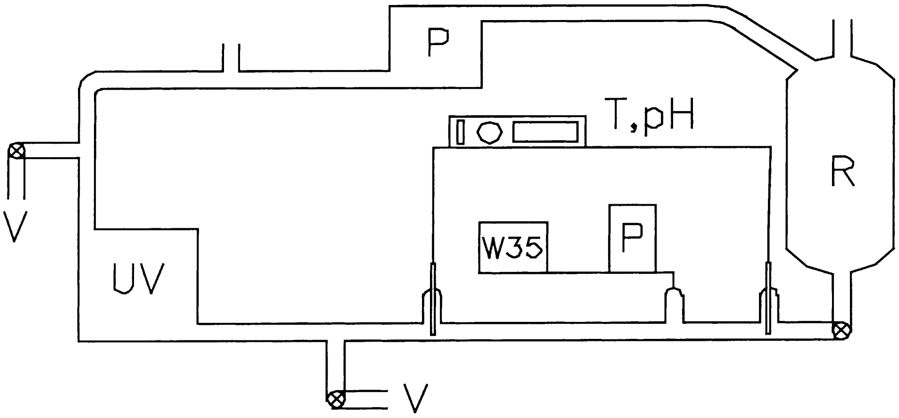

Fig. 4. Scheme of the pilot plant used for decolourisation with the H_2O_2/UV process.

The absorbance, COD and TOC were measured before and after decolourisation as described below. To measure the absorbance before the decolourisation process, the samples were diluted with distilled water in the ratio of 1:10.

Absorbance was measured on a Cary 50 Spectrophotometer, at the wavelength of maximum absorbance for each dye: C.I. Reactive Blue 220 at 610 nm, C.I. Reactive Black 5 at 600 nm, C.I. Reactive Blue 28 at 575 nm, C.I. Reactive Red 22 at 620 nm, C.I. Reactive Yellow 15 at 415 nm.

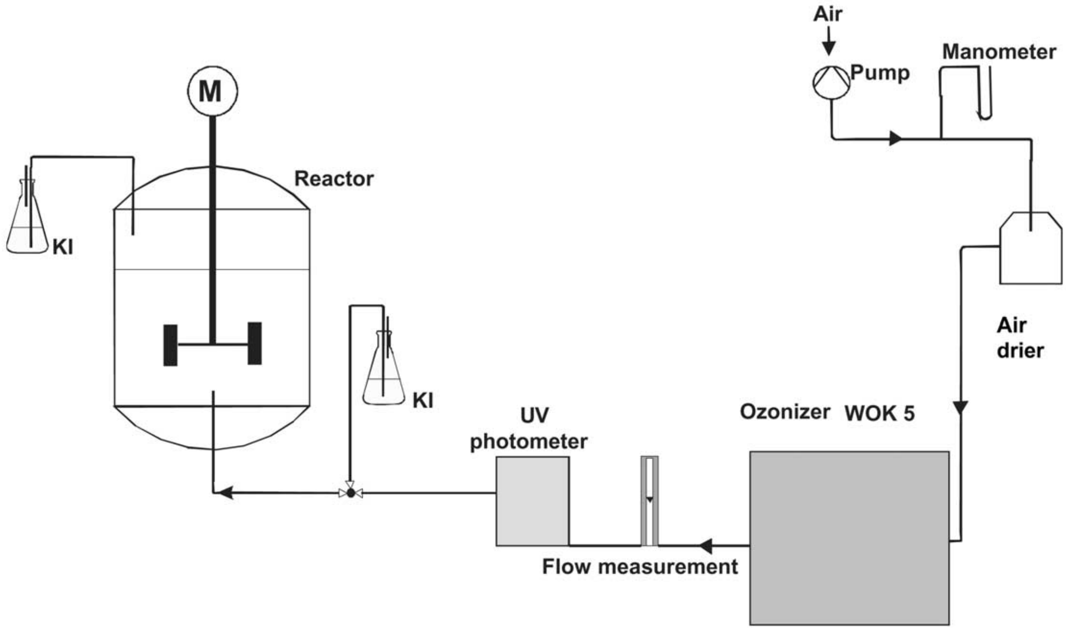

Fig. 5. Ozonizer used for decolourisation with the H_2O_2/O_3 process. M = mixer, KI = potassium iodide.

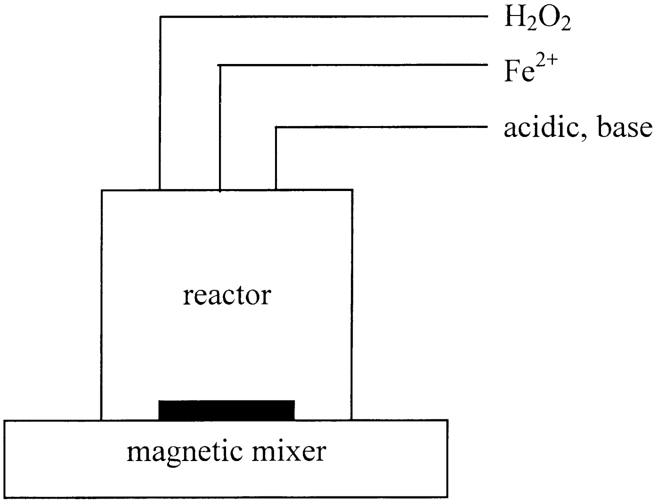

Fig. 6. Scheme of the apparatus used for decolourisation with the H_2O_2/Fe^{2+} process.

Chemical oxygen demand (COD) was measured using a Thermoreactor CR 2010 and Multilab P5, following ISO 6060 standard.

Total organic carbon (TOC) was measured on TOC 5000A Shimadzu analyzer. Because of the linear range of analytical method, samples were diluted with distilled water 10 times.

3. Results and discussion

The objective of the work was to decolorize the previously mentioned dyes using three advanced oxidation processes (H_2O_2/UV, H_2O_2/O_3 and H_2O_2/Fe^{2+}). Decolourisation was determined by absorbance measurements. The moment the dye solution was visually colourless, the decolourisation process was halted and the absorbance, COD and TOC were measured. Prior to decolourisation, the model solutions were prepared so as to reach the closest possible similarity to real wastewater solutions. The data were obtained using 60% dye exhaustion and 75% squeezing effect.

The results obtained are given for each dye in Figs. 7–9. Table 2 shows the values of absorbance both before and after decolourisation from which it is evident that decolourisation was either complete or nearly complete for each of the three systems used.

After decolourisation, the values of absorbance were zero or approximately zero after 20–120 min. The C.I. Reactive Blue 220 (its structure is not known in detail) was the most difficult to decolorize, whilst C.I. Reactive Yellow 15 displayed the shortest decolourisation time. The quickest decolourisation was obtained when H_2O_2 was activated by Fenton's reagent (average time 30 min), and the longest when H_2O_2 was activated by ozone (about 90 min); satisfactory decolourisation times were achieved using H_2O_2/UV (about 60 min). Fig. 7 shows the decolourisation time obtained for each dye using the three oxidation processes.

The differences in decolourisation times can be partly explained by the pH at which the decolourisation process was achieved.

Decolourisation with Fenton's reagent was performed in an acidic medium (pH = 3), whilst docolourisation with UV and ozone took place in an alkaline medium (pH = 12). Hydrogen peroxide can react with NaOH using alkaline conditions, resulting in the formation of sodium peroxide (Na_2O_2). As a result, lower concentrations of hydrogen peroxide are available for the formation of hydroxyl radicals. Oxidation with H_2O_2 should therefore be performed in an acidic medium, but acidification and neutralization increase the cost of such processes. Flocculates that are produced as a result of neutralization using the H_2O_2/Fe^{2+} process can precipitate non-decomposed dye.

Values of chemical oxygen demand (COD) indicate how much oxygen is needed for the complete oxidation of a substance in a specific volume of an aqueous sample. The values of COD depend

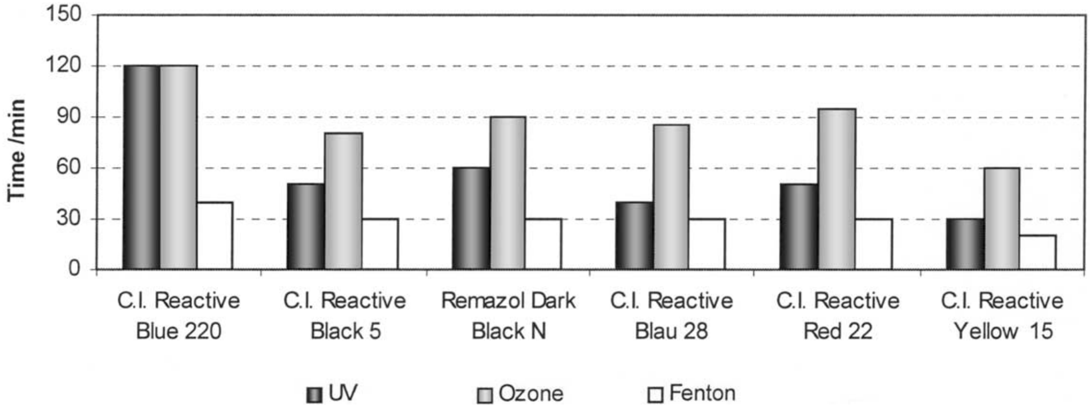

Fig. 7. Decolourisation time of dyes obtained by H_2O_2/UV, H_2O_2/O_3 and H_2O_2/Fe^{2+}. Ozone, values of ecological parameters after decolourisation with H_2O_2/O_3 process. Fenton, values of ecological parameters after decolourisation with H_2O_2/Fe^{2+} process.

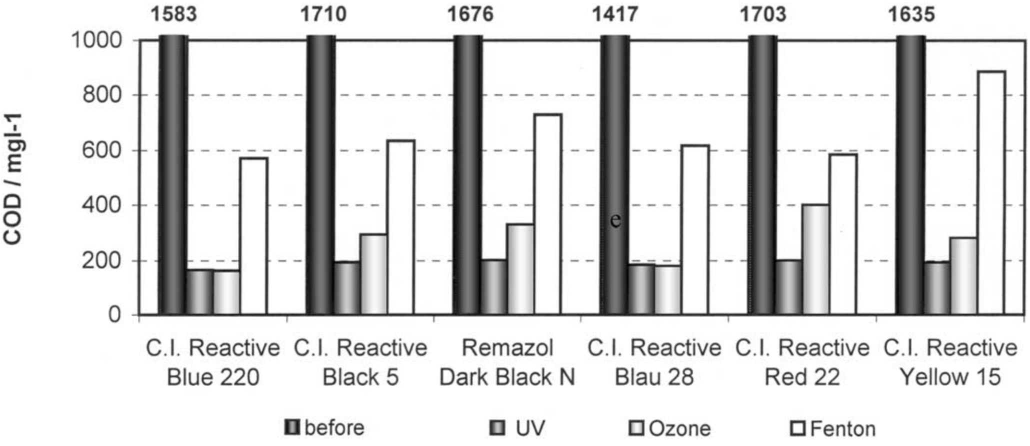

Fig. 8. COD values for each dye obtained by H_2O_2/UV, H_2O_2/O_3 and H_2O_2/Fe^{2+} processes. Before, values of ecological parameters before decolourisation. UV, values of ecological parameters after decolourisation with H_2O_2/UV process. Ozone, values of ecological parameters after decolourisation with H_2O_2/O_3 process. Fenton, values of ecological parameters after decolourisation with H_2O_2/Fe^{2+} process.

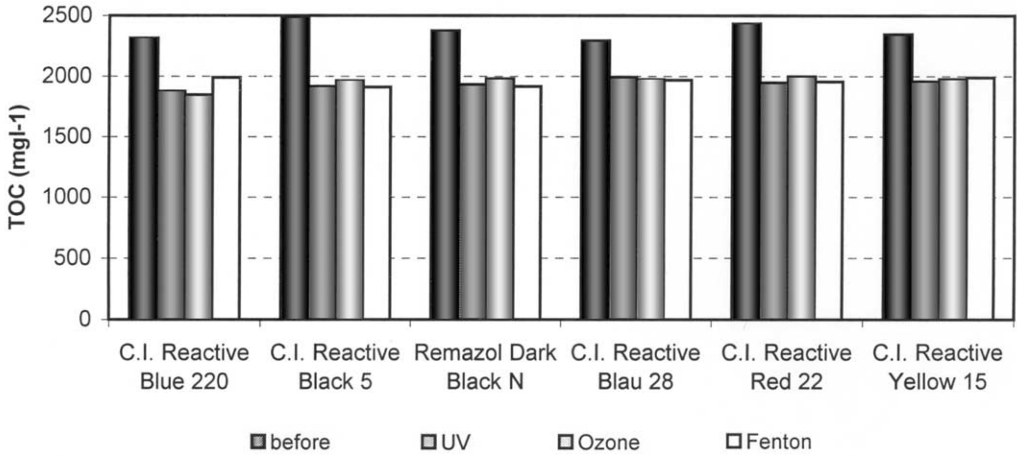

Fig. 9. TOC values for each dye obtained by H_2O_2/UV, H_2O_2/O_3 and H_2O_2/Fe^{2+} processes. Before, values of ecological parameters before decolourisation. UV, values of ecological parameters after decolourisation with H_2O_2/UV process. Ozone, values of ecological parameters after decolourisation with H_2O_2/O_3 process. Fenton, values of ecological parameters after decolourisation with H_2O_2/Fe^{2+} process.

on the initial dye concentration, its chemical structure and decolourisation time. Fig. 8 shows COD values for each dye bath before and after decolourisation. The average COD values obtained after decolourisation with H_2O_2/UV were 190 mg l^{-1}, which are below the limit value allowed by Slovenian environmental regulations (200 mg l^{-1}). The COD values obtained using the H_2O_2/Fe^{2+} decolourisation process were high and reach at an average value of 670 mg l^{-1}. The COD values of the dyes C.I. Reactive 220 and C.I. Reactive Blue 28 obtained after H_2O_2/O_3 decolourisation were also below the allowed limit (170 mg l^{-1} on average), but the COD values of the other dyes exceeded the allowed limit value (330 mg l^{-1} on average).

The high COD values obtained after the use of Fe^{2+} and ozone reveal that only partial oxidation

Table 2
The values of absorbance before and after decolourisation

Processes		H_2O_2/UV			H_2O_2/O_3			H_2O_2/Fe^{2+}		
Dyes	λ [nm]	A before[a]	A after[b]	% decol.	A before	A after	% decol.	A before	A after	% decol.
C.I. Reactive 220	610	2307	0.010	99.6	2307	0.031	99	2307	0	100
C.I. Reactive 5	600	5811	0	100	5811	0	100	5811	0	100
Remazol Dark Black N	481	2357	0.012	99.5	2357	0.013	99.5	2357	0.009	99.6
	600	3259	0	100	3259	0	100	3259	0	100
C.I. Reactive 28	575	1978	0	100	1978	0	100	1978	0	100
C.I. Reactive 22	520	3631	0	100	3631	0	100	3631	0	100
C.I. Reactive 15	415	2430	0034	99	2430	0.036	99	2430	0.045	98

[a] Absorbance before decolourisation.

[b] Absorbance before decolourisation.

of organic substances took place. Thus although decolourisation was achieved in the shortest possible time, this was not sufficient for the effective oxidation of organic substances. The observed high COD values can be partly explained by the presence of H_2O_2, which reacts with the substances used for the determination of COD such as potassium dichromate (VI) which reacts with H_2O_2 in an acidic medium to yield the unstable, peroxy dichromic acid; being unstable, this immediately degrades into Cr (III) salts (Eqs. (1) and (2)).

$$H_2Cr_3O_7 + 5H_2O_2 \rightarrow H_2Cr_2O_{12} + 5H_2O \tag{1}$$

$$H_2Cr_2O_{12} + 8H_2O_2 \rightarrow Cr_2O_3 + 9H_2O + 8O_2 \tag{2}$$

However, H_2O_2 is present in each of the three advanced oxidation processes and the COD values resulting from H_2O_2/UV decolourisation were satisfactory. It may be concluded that UV is more effective in the formation of hydroxyl radicals and that UV light itself activates the bonds of organic molecules for further degradation (photochemical reactions); Fe^{2+} and O_3 lack this ability.

Total organic carbon (TOC) is a measure of the quantity of organically bound carbon that can be oxidised to CO_2. The TOC values decreased little after decolourisation (Table 9) and exceeded, considerably, the limit value allowed by Slovenian regulations (60 mg l^{-1}). The average TOC values, obtained using each of the three decolourisation processes, were slightly above 1900 mg l^{-1}. The observed high TOC values can be explained by the fact that during decolourisation, new organic substances were formed (not identified), which were no longer coloured, but needed more time for degradation.

4. Conclusions

Six vinylsulphone reactive dyes were used to determine the effectiveness of three advanced oxidation processes (H_2O_2/UV, H_2O_2/O_3 and H_2O_2/Fe^{2+}). Prior to decolourisation, the dyebath samples were prepared so that the concentrations of the dye and other chemicals were similar to those in a typical dyebath after dyeing. The decolourisation process was halted the moment the solution became visually colourless. Decolourisation was achieved in 20–120 min. C.I. Reactive Blue 220 was the most difficult to decolorize, and C.I. Reactive Yellow 15 the easiest. The H_2O_2/Fe^{2+} process achieved decolourisation in 20 min, the H_2O_2/UV process in about 60 min, and the H_2O_2/O_3 process in about 90 min. The selected dyes were efficiently decolorized by all of the three advanced oxidation processes, their absorbance values after decolourisation being zero or approximately zero. The COD values obtained after decolourisation with H_2O_2/UV were low (about 190 mg l^{-1}) while the COD values obtained after H_2O_2/O_3 decolourisation were higher (about 300 mg l^{-1}), but the

COD values obtained after H_2O_2/Fe^{2+} decolourisation were very high (about 670 mg l^{-1}). The TOC values obtained in all of the three decolourisation processes were high (about 1900 mg l^{-1}).

Although decolourisation with H_2O_2/Fe^{2+} was fastest, and the costs of such a process are low, it is not really suitable for environmental reasons, namely the formed sludge needs to be removed.

Although decolourisation with H_2O_2/O_3 yields lower COD values, it causes additional water pollution because of ozone; the disadvantages of this procedure are high investment and operating costs.

Decolourisation with H_2O_2/UV is an environment-friendly procedure. It causes no sludge and no additional water pollution because of the physical activation of hydrogen peroxide while the COD values were low, but investment and operating costs are high.

In further investigations we will compare the current advanced oxidation processes and other processes, such as biological treatment.

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