ELSEVIER

Dyes and Pigments 53 (2002) 93–99

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Kinetics of decolorization and mineralization of reactive azo dyes in aqueous solution by the UV/H_2O_2 oxidation

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Received 19 September 2001; received in revised form 21 October 2001; accepted 18 January 2002

Abstract

The photodegradation of three non hydrolysed reactive azo dyes (Reactive red 120, Reactive black 5, Reactive yellow 84) in aqueous solution was investigated in a laboratory-scale batch photoreactor equipped with an immersed low-pressure mercury lamp. Six different doses of hydrogen peroxide, at constant initial concentration of the substrate (100 mg/l) were used. The pseudo-first order rate constants have been calculated from the experimental kinetic curves, for the three azo dyes. These rate constants have extreme values of the order of 0.1 min^{-1} at a H_2O_2 dose of 24.5 mmol/l. The effectiveness of the UV/H_2O_2 process has been evaluated by the degree mineralization of the total organic carbon (TOC), as a complementary indicator of the treatment efficiencies. Our results confirm the suitability of the UV/H_2O_2 process as a textile wastewater pre-treatment step, once optimum operating conditions and cost effectiveness of the method are established. © 2002 Published by Elsevier Science Ltd.

Keywords: Photoreactor; UV/H_2O_2 process; Reactive red 120; Reactive black 5; Reactive yellow 84; Rate constants

1. Introduction

The number of dyes presently used in textile industry is about 10,000. The annual production of these dyes is over 7×10^5 tons [1]. Among these dyes, azo dyes constitute the largest and the most important class of commercial dyes. Anthaquinone dyes constitute the second most important class after azo dyes and are characterized by their good fastness caused by the very stable anthaquinone structure. This work is concerned with another important class of dyes: the reactive azo dyes.

Effluents of textile dyeing and finishing industries are known to contain considerable color, suspended solids, chlorinated organics, surfactants, some heavy metals and to have variable pH, temperature and COD [2]. Particularly reactive azo dyes cause special environmental concern due to their precursors and their degradation products such as aromatic amines are considered highly carcinogenic [3,4]. Most of the dyestuffs used are highly structured polymers with low biodegradability. Their concentration in dye-baths range from 10 to 10,000 mg/l, depending on the strength

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0143-7208/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0143-7208(02)00012-8

Nomenclature

A	substrate
$A(\lambda)$	spectral absorbance
C_{A}	molar concentration, mol/l
c_{A}	concentration of A, mg/l
COD	chemical oxygen demand, mgO_2/l
d	optical pathlength, mm
I_{a}	UV light intensity absorbed, Es/s
k_1	first-order rate constant, s^{-1}
k_2	second-order rate constant, l/mol s
TOC	total organic carbon, mgC/l
X_{DEC}	degree of decolorization,%
X_{MIN}	degree of mineralization,%
τ	irradiation time, s

of the dye and the process in operation. In general, the residual dye solution is diluted by 20–40% upon rinsing and the fabrics absorb 50–70% of the hydrolysed dye molecules during batch-dyeing. The effluent still contains 20% of the unfixed dyes. Numerous biodegradability studies on dyes have shown that azo dyes are not likely to be biodegradable under aerobic conditions [5,6]. They are either sorbed or trapped in bioflocs [3,7]. Thus, ecosystems of streams can be seriously affected. Consequently, dyes have to be removed from textile wastewater before discharge. In the past, effluents containing azo dyes have been treated by adsorption onto activated carbon or by chemical coagulation [8,9]. However, these traditional methods mainly transfer the contaminants from wastewater to solid wastes. Therefore, advanced oxidation is a potential alternative to decolorize and to reduce recalcitrant wastewater loads from textile dyeing and finishing effluents [6].

Our previous experience with the UV/H_2O_2 system in the photodegradation of nitromusks in water [10,11] was an additional support in choosing the approach combining the UV radiation and hydrogen peroxide for degradation of reactive azo dyes in textile wastewater.

In this study, three non hydrolysed reactive azo dyes (Reactive red 120, Reactive black 5, Reactive yellow 84) have been chosen as model substrates for our photodegradation studies. Due to the fact that if real wastewater is used, other organic contaminants will interfere and slow down the reaction performed in this work, we have used aqueous dye solution of Reactive red 120 (RR120), Reactive yellow 84 (RY 84) and Reactive black 5 (RB 5). The main objective of this work was to investigate the degradation kinetics of these three reactive azo dyes (RR120, RY84, RB5) by the UV/H_2O_2. In addition to the conventional parameters, the reaction endproducts have also been determined in order to evaluate the mineralization rate, as an important indicator of the treatment effectiveness.

2. Materials and methods

2.1. Materials

The azo dyes, Reactive yellow 84 (color index, RY 84), Reactive red 120 (color index, RR120) and Reactive black 5 (color index, RB5) were obtained from BASF (Germany) as commercially available dyes and used without further purification. Further characteristics of the azo dyes used as substrates are listed in Table 1. The hydrogen peroxide solution (30%) of analytical grade and all organic components (p.a.) were obtained from Merck, Germany. Aqueous solution containing 100 mg/l azo dye were prepared with ultrapure water (conductivity of 0.056 μS/cm) from Millipore Waters Milli Q purification unit. COD determination was done with commercially available test kits of the company Machery & Nagel, Düren, Germany, by oxidation with potassium dichromate in sulphuric acid and heating for two hours to 421 K.

2.2. Photoreactor and actinometry

The photodegradation experiments were carried out in a stirred batch photoreactor, at 298 K, as described in a previous paper [10]. The UV reactor was loaded with a synthetic reaction mixture consisting of 100 mg/l reactive azo dye and varying concentrations of H_2O_2 (0.0; 1.0; 5.0; 10.0; 24.5; 49.0; 98.0 mmol/l) in order to find out the optimal concentration. A Heraeus UV immersed lamp TN 15/35 with a nominal output of 15 W irradiated

Table 1
Main characteristics of the reactive azo dyes used

Colour index	RY84	RR120	RB5
Trade name	Procion Gelb H-E4R	Procion Rot H-E3B	Basilen Schwarz FB
Chemical formula	$C_{50}H_{24}Cl_2N_{14}$ $Na_{10}O_{30}S_{10}$	$C_{44}H_{24}Cl_2N_{14}Na_6O_{20}S_6$	$C_{26}H_{21}N_5Na_4O_{19}S_6$
Molecular mass (g/mol)	1,922.45	1,469.34	991.8
Water solubility at 293 K (g/l)	70	70	160
Phitotoxicity LC_{50} (mg/l)	>100	>100	100–500
λ_{max} (nm)	406	535	596
Supplier	BASF AG	BASF AG	BASF AG
Purity (%)	80.90	62.19	74.58

the solutions. The incident photonic flux was measured by photolysis of H_2O_2 ($Io = 1.007\ 10^{-5}$ Es/s).

2.3. Analyses

The optical absorption of each azo dye solution was determined and recorded by a UV-vis Cary spectrophotometer (Varian). The concentrations of the unconverted dye in solution were defined as the dye absorption maximum (Table 1) by Eq. (1), and the translucent colour value (TCV) was defined by (2):

$$\frac{C_A}{C_A^0}100 = \frac{\mathrm{TCV}}{(\mathrm{TCV})_{\tau=0}}100 \qquad (1)$$

$$\mathrm{TCV} = A(\lambda)1000d^{-1} \qquad (2)$$

where $A(\lambda)$ = spectral absorbance
d = length of the quarz cell (10 mm).

The phenol, as an intermediate degradation product, was determined photometrically with diazotized 4-nitroaniline in a Nanocolor photometer from Machery-Nagel GmbH, Düren. The analysis of organic acids (oxalic, malic, malonic, formic, acetic, succinic) was performed by the HPICE Dionex model 4000 ion chromatograph (DX 500 Chromathography System, Dionex, Sunnyvale, CA, USA) equipped with an Ion-Pac HPICE–AS6 column (Dionex) and operating in suppressed conductivity detection mode. Samples, injected with a volume of 25 µl by an automatic sampler, were eluted by heptafluorbutyric acid 0.4 mol/l at a flow rate of 1.5 ml/min.

The total organic carbon (TOC) content in solution was determined by Schimadzu model 5050 TOC analyzer. The pH was measured by means of a WTW pH-Meter Multiline P4.

3. Results and discussion

The percentages of unconverted dyes vs. time with different initial hydrogen peroxide doses, determined by Eq. (1) for the three reactive azo dyes, are presented in Tables 2–4. The primary analyses of the experimental results indicate that at least five reactions are to be considered: direct photolysis (3); hydrogen peroxide photolysis (4) generating the highly reactive HO• radicals giving the primary products (5); oxidation of primary products (P) with HO• in the presence of dissolved oxygen to mineral compounds (6), and the reaction of HO• with excess H_2O_2 (7):

Table 2
The effect of H_2O_2 initial concentration ($C^0_{H_2O_2}$, mmol/l) on RY84 decolorization (C_A/C_A^0), at $c_A = 100$ mg/l

Time (min)	$C^0_{H_2O_2}$ (mmol/l)					
	0.0	5.0	10.0	24.5	49.0	98.0
0	100.00	100.00	100.00	100.00	100.00	100.00
5	98.92	97.89	87.24	96.53	90.95	91.58
10	98.79	71.73	68.86	49.74	43.30	70.37
15	97.98	71.38	45.56	33.00	36.05	54.88
30	96.09	40.14	17.35	6.57	4.73	20.40
45	91.65	23.86	8.67	0.42	0.68	4.24
60	87.21	15.25	1.17	n.d.[a]	n.d.	1.41

[a] n.d., Not determined.

Table 3
The effect of H_2O_2 initial concentration ($C^0_{H_2O_2}$, mmol/l) on RR120 decolorization (C_A/C^0_A), at $c_A = 100$ mg/l

Time (min)	$C^0_{H_2O_2}$ (mmol/l)					
	0.0	5.0	10.0	24.5	49.0	98.0
0	100.00	100.00	100.00	100.00	100.00	100.00
5	99.73	94.95	91.84	90.52	90.67	92.82
10	99.59	77.71	76.41	52.37	48.66	56.67
15	99.46	68.49	62.29	31.21	30.92	34.67
30	98.84	50.11	44.02	7.33	6.09	12.67
45	97.78	39.53	32.67	0.47	3.05	1.92
60	96.72	28.96	21.34	n.d.[a]	n.d.	0.18

[a] n.d., not determined.

Table 4
The effect of H_2O_2 initial concentration ($C^0_{H_2O_2}$, mmol/l) on RB5 decolorization (C_A/C^0_A), at $c_A = 100$ mg/l

Time (min)	$C^0_{H_2O_2}$ (mmol/l)				
	0.0	5.0	10.0	24.5	49.0
0	100.00	100.00	100.00	100.00	100.00
5	99.56	83.52	69.45	75.99	84.39
10	99.39	42.19	23.48	21.04	22.78
15	99.21	31.18	9.35	6.70	9.37
30	98.69	8.23	0.25	0.12	0.37
45	98.57	4.36	–	–	–
60	98.44	0.49	–	–	–

$$A + h\nu = \text{Intermediates} \tag{3}$$

$$H_2O_2 + h\nu = 2\ HO\bullet \tag{4}$$

$$A + HO\bullet = \text{products (P)} \tag{5}$$

$$\begin{aligned} &P + HO\bullet = \text{final products} \\ &\quad \left(CO_2,\ H_2O,\ NO_3^-,\ Cl^-,\ SO^{4-2}\right) \end{aligned} \tag{6}$$

$$HO \bullet + H_2O_2 = HO_2 \bullet + H_2O \tag{7}$$

Our results show that direct photolysis of the dye (3) is not negligible but is very slow. The decolorization is enhanced by the presence of H_2O_2 due to the hydroxyl radicals generated during the photochemical reactions (4). The results also show dependence of the decolorizing degree on the initial concentration of the hydrogen peroxide. Increasing $C^0_{H_2O_2}$ beyond a value 24.5 mmol/l accelerates the reaction (7) whose effect is the consumption of the very reactive HO• radicals to give less reactive HO_2• radicals. Thus, H_2O_2 in excess becomes a scavenger of hydoxyl radicals, in accordance with the reaction (7). Further quantitative interpretation of the results requires a kinetic model. The major kinetic pathway of azo dyes degradation could be expressed by Eq. (8):

$$-\frac{dC_A}{d\tau} = k_2 C_A C_{OH\bullet} \tag{8}$$

where C_A represents azo dye concentration and $C_{HO\bullet}$ denotes the hydroxyl radical concentration (mol/L). By the pseudo-stationary hypothesis (i.e. the $C_{HO\bullet}$ can be considered as a constant in the presence of excess hydrogen peroxide) the rate expression (8) is simplified into a pseudo-first order kinetic model (9):

$$-\frac{dC_A}{d\tau} = k_1 C_A \tag{9}$$

The observed pseudo-first order rate constants (k_1, s^{-1}) were calculated by using linear regression from the experimental data given in Tables 2–4. The calculated results are presented in Table 5. It can be concluded that a H_2O_2 dose higher than 24.5 mmol/l corresponds to an unprofitable consumption of hydrogen peroxide. The proposed kinetic model is also in good agreement with our experimental data.

The existence of an optimal dose of H_2O_2 has been previously noticed by numerous authors [12,1]. Shu et al. investigated the decolorization of Acid red 1 and Acid yellow 23 by the UV/ H_2O_2 treatment. They described an optimal dose of 9.8 mmol/l H_2O_2 for a 23.56 μmol/l Acid red aqueous solution with an initial molar ratio H_2O_2/dye of 415.96. Our finding in the case of RY 84, for instance, leads to a ratio of 417.02 mol H_2O_2/mol dye.

In a second series of experiments, the correlation with the irradiation of unconverted dyes, COD, TOC, pH and reaction products (phenol, oxalate, malonate, maliate, formate, acetate, succinate) were determined in the presence of 24.5 mmol H_2O_2/l. The results are presented in Tables 6

Table 5
The pseudo-first order rate constants of the three dyes photodegradation ($c^0_{dye} = 100$ mg/l)

$C^0_{H_2O_2}$ (mmol/l)	k_1 (min^{-1})		
	RY84	RR120	RB5
0.0	0.0021	0.0006	0.0004
5.0	0.0307	0.0211	0.0868
10.0	0.0649	0.0342	0.1853
24.5	0.1079	0.1060	0.2091
49.0	0.1039	0.0823	0.1750
98.0	0.0668	0.0921	n.d.[a]

[a] n.d., Not determined.

and 7 and Fig. 1. After 15 min of irradiation time with a dose of 24.5 mmol H_2O_2/l the decolorization was higher then 65% for all three aqueous dye solutions. A COD reduction of about 70% was observed for RY 84 and RB5, and 40% for RR120 at the same time. The TOC removal rates were 18% for RR120, 28.5% for RY84 and 41% for RB5 under identical operational conditions. Whereas, after 60 min of irradiation time with a same dose of H_2O_2 the decolorization was higher then 99.6% for all three aqueous dye solutions. Due to the production of organic and anorganic acid anions the pH decreased from 6.22–6.90 to 3.38–4.44 during

Table 6
The evolution of TOC, COD and pH with time ($C^0_{H_2O_2} = 24.5$ mmol/l, $c^0_{dye} = 100$ mg/l)

Time (min)	RY 84			RR120			RB 5		
	TOC	COD	pH	TOC	COD	pH	TOC	COD	pH
0	28.52	58	6.89	24.56	107	6.84	23.48	52	6.22
5	25.75	46	5.85	23.79	90	5.70	19.90	47	6.02
10	22.88	35	5.55	22.82	73	4.56	16.23	<15	3.96
15	20.41	17	4.95	20.13	65	4.17	13.89	<15	3.70
30	17.81	<15	4.44	17.15	53	3.77	7.80	–	3.38
45	12.89	<15	–	16.01	27	3.67	6.85	–	3.34
60	11.84	<15	–	11.57	<15	3.57	4.32	–	3.32

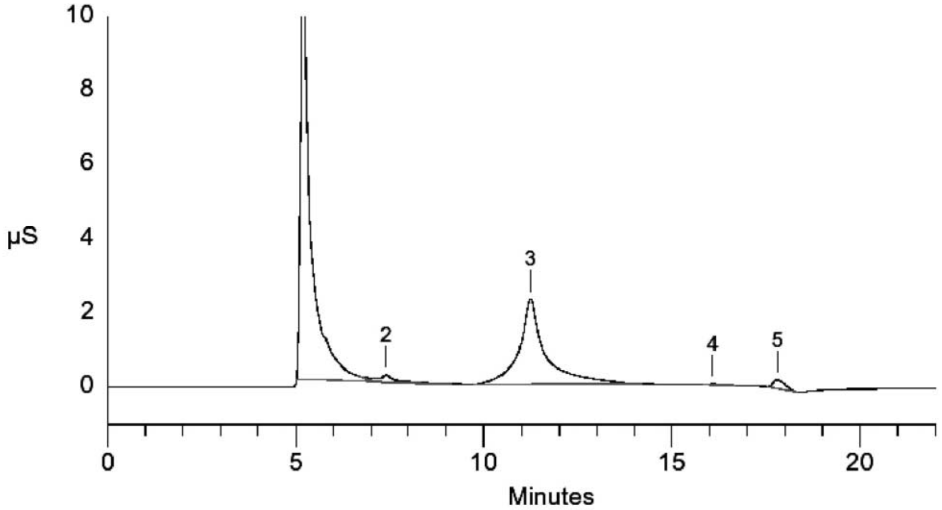

Fig. 1. HPICE analysis of RB5 after 45 min irradiation with 24,5 mmol H_2O_2/l. Peak identities are as follows: 1, oxalate; 2, malonate (trace); 3, formate; 5, acetate.

Table 7
The experimental decolorization (X_{DEC}) and mineralization (X_{MIN}) degrees ($C^0_{\mathrm{H_2O_2}} = 24.5$ mmol/l, $c^0_{\mathrm{dye}} = 100$ mg/l)

Time (min)	RY84		RR120		RB5	
	X_{DEC} (%)	X_{MIN} (%)	X_{DEC} (%)	X_{MIN} (%)	X_{DEC} (%)	X_{MIN} (%)
0	0.00	0.00	0.00	0.00	0.00	0.00
5	13.47	9.71	9.48	3.13	24.01	15.24
10	50.26	19.71	47.63	7.08	78.96	30.87
15	67.00	28.43	68.79	18.04	93.30	40.84
30	93.43	37.55	92.67	30.17	99.82	66.78
45	99.58	54.80	99.53	34.81	n.d.[a]	70.82
60	–	58.48	99.66	52.89	n.d.	81.60

[a] n.d., Not determined.

irradiation time. The TOC removal rates were 53% for RR120, 58.5% for RY84 and 81.6% for RB5 for the same reaction time.

Table 7 presents the decolorization degree (X_{DEC}) and the mineralization degree (X_{MIN}) of the investigated dyes, defined by the Eqs. (10) and (11), and calculated using the data in Tables 2–5.

$$X_{\mathrm{DEC}} = \left(1 - \frac{C_{\mathrm{A}}}{C^0_{\mathrm{A}}}\right)100 \qquad (10)$$

$$X_{\mathrm{MIN}} = \left(1 - \frac{\mathrm{TOC}}{\mathrm{TOC}_0}\right)100 \qquad (11)$$

On the basis of these measurements, the mineralization degree has been calculated for each system at the optimal conditions previously established. The minerilization rates were 58.5% for RY84; 52.9% for RR84 and 81.6% for RB5, respectively. Due to the decreasing value of the pH during the oxidation it can be assumed that the solution contains the analysed organic anions in the form of their corresponding acids. The remaining carbon consisted mainly of oxalic and formic acids and comparatively small quantities of phenol, malonic, acetic, and succinic acids.

4. Conclusions

The results have shown that with a dose of 24.5 mmol/l H_2O_2 and a 60 min irradiation (UV) time the decolorization was higher than 99.6% for all the three aqueous dye solutions. To use a hydrogen peroxide dosage higher than 24.5 mmol/l H_2O_2 is not cost effective. Our results also prove that the pseudo-first order kinetic model is in good agreement with the experimental data.

A second series of experiments have been carried out in order to determine the equation of TOC, COD, pH and the concentration of reaction products such as phenol and organic acids (oxalic, malic, malonic, formic, acetic, succinic). The minerilization rates were 58.5% for RY84; 52.9% for RR84 and 81.6% for RB5, respectively. The remaining carbon consisted mainly of oxalic and formic acids and comparatively small quantities of phenol, malonic, acetic, and succinic acids.

The results have shown that the UV/H_2O_2 process can be a suitable pre-treatment method for complete decolorization and detoxification of effluents from textile dyeing and finishing processes, once the optimum operating conditions are established. The investigations should be continued in order to find the influence of other factors like textile auxiliaries, salts, surfactants and natural impurities on the mineralization degree. Additional determination is also necessary in order to identify the evaluation of the intermediates during the oxidation process.

Acknowledgements

This work was financially supported through grant No. EVK1-CT-2001-50008 from the Commission of the European Communities and has been conducted at the GSF-National Research Center for Environment and Health, Institute of Ecological Chemistry, Neuherberg, Germany.

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