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Decolorization of the textile azo dye Reactive Orange 16 by the UV/H_2O_2 process

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Abstract: The photochemical decolorization of C.I. Reactive Orange 16 (RO16), a reactive textile azo dye, by the UV/H_2O_2 process was studied using a batch photoreactor with UV lamps emitting at 253.7 nm. Complete decolorization of 50.0 mg dm^{-3} initial dye concentration was achieved in less than 6 min under optimal conditions (25 mM initial peroxide concentration, at pH 7.0 and with a UV light intensity of 1950 μW cm^{-2}). The effects of experimental variables, such as initial pH, initial concentration of H_2O_2, initial dye concentration, and the intensity of UV light were studied. The highest decolorization rates were realized at a peroxide concentration in range from 20 to 40 mM, above which decolorization was inhibited by the scavenging effect of the peroxide. The decolorization was more efficient in neutral pH values. The efficiency of the process was improved with lower initial dye concentrations and at higher intensities of UV light.

Keywords: Reactive Orange 16; UV/H_2O_2 process; decolorization.

INTRODUCTION

Colored effluent from the textile industry is becoming more and more apparent as one of the major environmental problems associated with this industry. It is estimated that 15 % of total production of colorants may be released to wastewater during synthesis and processing operations.[1] Dyes in wastewaters cause aesthetic problems, absorb and scatter sunlight and thus affect the aquatic ecosystem.[2] Azo compounds represent the largest group of colorants with respect to both the number and production volume. These compounds contain one or more azo groups (–N=N–), mostly linked to benzene or naphthalene rings.[1] Some azo dyes, *via* metabolic cleavage of the azo linkage, can produce potentially car-

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cinogenic aromatic amines.[3] This is one more reason for the open concern about the release of azo dyes to the environment. According to their mode of application, textile dyes can be classified as acid, reactive, metal complex, disperse, vat, mordant, direct, basic and sulfur dyes.[4] The research on textile effluent decolorization has focused on fiber reactive dyes for the following reasons. Reactive dyes are most commonly in use today, especially for dyeing cellulosic fibers, such as cotton and wool. Reactive azo dyes possess a low fixation rate and up to 50 % of the applied reactive dye is usually discharged as a deeply colored effluent.[4] In the reactive dyeing process, ten times more water is consumed on average for the preparation, dyeing, washing, and rinsing stages than during dyeing with other dye types.[4] Therefore, it is necessary to remove reactive azo dyes from effluents before their discharge.

Conventional methods for water treatment (activated carbon adsorption, coagulation, flocculation, reverse osmosis and ultrafiltration) are non-destructive and just transfer contaminants from one phase to another and form secondary waste.[5] Recently, advanced oxidation processes (AOPs) have been used as techniques which are alternative to physico–chemical phase transfer methods. These techniques are successfully applied for the complete mineralization of organic pollutants in water.[6–8] AOPs involve different processes, such as H_2O_2/UV, O_3/UV, H_2O_2/O_3/UV, TiO_2/UV, H_2O_2/Fe^{2+}, UV/H_2O_2/Fe^{2+}, H_2O_2/Fe^{3+}, Fe^{2+}/oxalate/UV, H_2O_2/Fe^{3+}/oxalate, H_2O_2/Fe^{3+}/oxalate/UV, Mn^{2+}/oxalic acid/O_3 and $H_2O_2/Fe^{2+}/Fe^{3+}$/UV. In these processes, a complex set of reactions occur, which imply generation of oxidizing species, such as $^{\bullet}OH$ radicals and hydroperoxyl radicals.[9] These species, especially radicals that have an oxidation potential of 2.8 V, are powerful oxidizing agents able to degrade a variety of organic water contaminants.[10] Some of the advantages of use of UV/H_2O_2 in comparison to other AOPs are a considerably safe and easy operation, a reduction of the chemical oxygen demand (COD) and a short reaction time.[11] The reaction of hydroxyl radicals, generated by photolysis of H_2O_2, with organic contaminant includes three different mechanisms: hydrogen abstraction, electrophilic addition, and electron transfer.[10]

The aim of this study was to investigate the efficiency of decolorization of the widely used textile azo dye C.I. Reactive Orange 16 (RO16) with UV radiation in the presence of H_2O_2. The decolorization rate of this process depends on many parameters, such as initial pH, initial azo dye concentration, initial H_2O_2 concentration, UV light intensity, which were varied in order to determine the optimal operating conditions.

EXPERIMENTAL

Reagents

The azo reactive dye Reactive Orange 16 (50 %) was obtained from Farbotex (Italy) and used without further purification. The H_2O_2 solution (30 %), analytical grade, was purchased from Merck (Germany). All other used reagents were of analytical grade. All solutions were prepared with deionized water.

Photoreactor

All photochemical experiments were performed in a batch photoreactor, schematically shown in Fig. 1. Low-pressure mercury vapor lamps, with a maximum emission primarily at 253.7 nm (28 W, UV-C, Philips, Holland), were used as the light source. Ten UV lamps were fixed parallel in a reflector at the top of the photoreactor. An air cooling system, with electrical fans, was used to vent the heat outside of the reactor and to prevent the lamps from overheating. The interior surface of the photoreactor was made of highly polished stainless steel, because of light reflection. Intensity of UV radiation was measured by a UV radiometer Solarmeter model 8.0 UVC (Solartech, USA). The total UV intensity was controlled by turning on a different number of UV lamps, from 2 up to 10 lamps, which gave intensity from 730 up to 1950 μW cm^{-2} (with all ten UV lamps on) at the distance of 220 mm from the working solution surface. Some of the experiments were conducted using the lowest UV light intensity in order to reduce the decolorization rate of the dye for a better observation of the effects of some parameters.

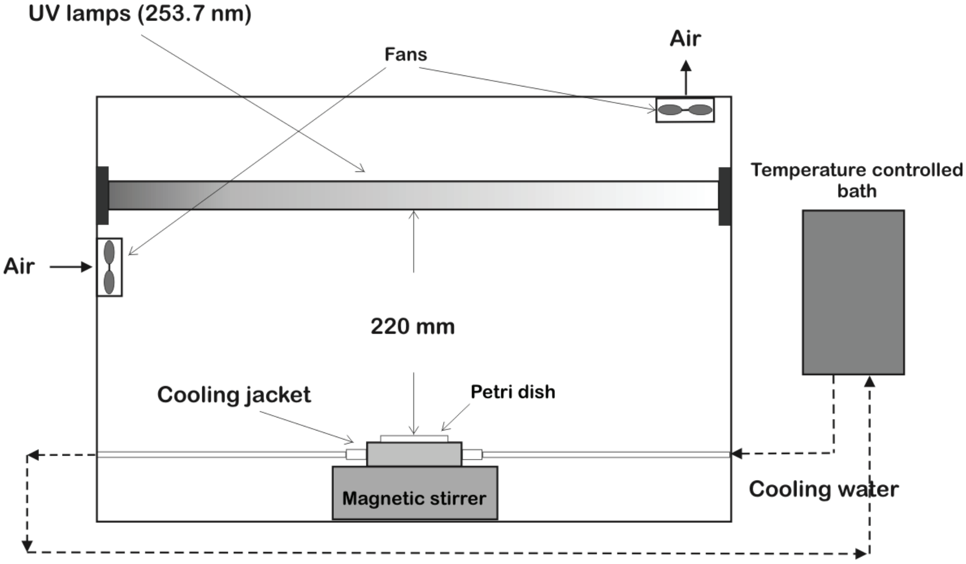

Fig. 1. Scheme of the batch photoreactor.

Procedure

In each experiment, 100 ml of dye solution of the desired initial concentrations of dye and H_2O_2 and appropriate pH value was irradiated. During the irradiation, the solution was magnetically stirred at a constant rate and the temperature was maintained at 25±0.5 °C by thermostating. The pH of the solution was measured using a HACH SensIon3 pH meter and adjusted by the addition of aqueous NaOH or dilute mineral acids. Simultaneously, the photolysis of a blank sample containing the same amount of peroxide and at the same pH but without dye was carried out. This was done in order to avoid interference due to H_2O_2, which may absorb light in the range from 190 to 450 nm. At certain reaction intervals, a 5 ml aliquot was withdrawn, analyzed by UV–Vis spectrophotometry (Carry 50, Varian) and returned back to the photoreactor. Dye concentrations were calculated from the calibration curve established by relating the concentration to the absorbance measured at 494 nm. The absorbance at 494 nm is due to the color of the dye solution (n→π* transition in –N=N–) and it was used to monitor the decolorization of the dye. All experiments were performed at least in triplicate and the results are presented as mean value ±*SD*.

RESULTS AND DISCUSSION

Three preliminary experiments were performed in order to investigate the effect of UV radiation only, hydrogen peroxide without UV radiation, and UV irradiation plus H_2O_2. The solution of RO16 dye (50.0 mg dm^{-3}) without peroxide was irradiated for 24 h to examine the effect of UV light radiation alone. When the irradiation of dye solution was performed in the absence of H_2O_2 there was no observable decrease of the residual dye concentration (results not shown). This indicated that the direct photolysis of RO16 dye by UV irradiation was slow (reaction (1)):

$$\text{Dye} + h\nu \rightarrow \text{Products} \tag{1}$$

A solution with only peroxide was left in the dark for 24 h. The dye removal efficiency in this case was also negligible (results not shown). However, if hydrogen peroxide was applied in combination with UV radiation, the residual dye concentration rapidly decreases (Fig. 2). Complete decolorization was obtained in less than 6 min, with an initial dye concentration of 50.0 mg dm^{-3} in the presence of 25 mM H_2O_2 and under 1950 μW cm^{-2} light intensity. This can be related to the generation of highly reactive $^{\bullet}OH$ radicals by direct photolysis of the added hydrogen peroxide, as shown by reaction (2):

$$H_2O_2 + h\nu \xrightarrow{k_1} 2^{\bullet}OH \tag{2}$$

These radicals undergo radical-chain reactions with the aromatic rings and probably also with the –N=N– double bond of the azo dye RO16, thereby forming new products (reaction (3)):

$$^{\bullet}OH + \text{Dye} \xrightarrow{k_2} \text{Products (P)} \tag{3}$$

The new products also have high reactivity towards the $^{\bullet}OH$ radicals as the starting compound (reaction (4)):

$$\text{Products (P)} + {}^{\bullet}OH \xrightarrow{k_3} \text{Products (P}_i\text{)} \tag{4}$$

According to reaction (3), the kinetic expression for the decolorization of the azo dye RO16 can be presented as:

$$-\frac{\mathrm{d}c_\mathrm{d}}{\mathrm{d}t} = kc_\mathrm{OH}c_\mathrm{d} \tag{5}$$

where c_d is the initial dye concentration; c_{OH} is the hydroxyl radical concentration; k is the second order rate constant and t is the reaction time.

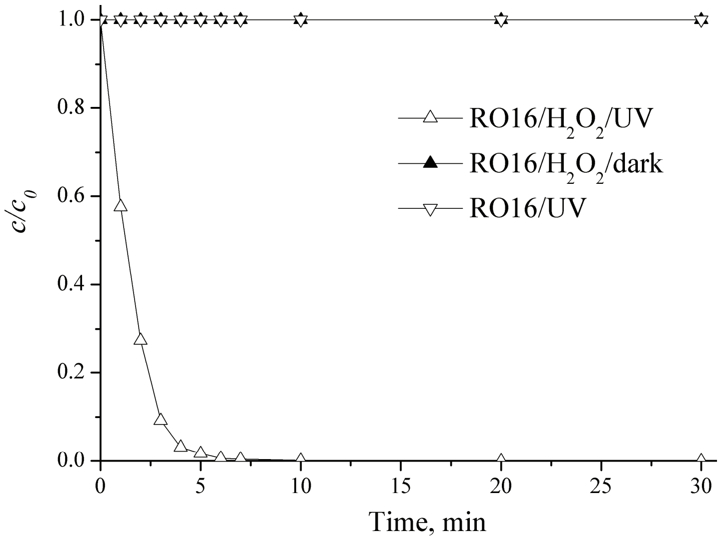

Fig. 2. Effect of UV radiation, H_2O_2 and UV/H_2O_2 on the decolorization of RO16. c_0(RO16) = 50.0 mg dm^{-3}, $c_0(H_2O_2)$ = 25.0 mmol dm^{-3}, pH 7.0±0.2, UV light intensity: 1950 μW cm^{-2}, temperature: 25±0.5 °C.

Many models have been postulated to describe the kinetics of these reactions using the steady-state approximation, in which the concentration of hydroxyl radicals does not change with the reaction time.[12,13] In this way, the non-measurable concentration of the radicals was correlated as a function of hydrogen peroxide concentration.

According to the steady-state approach, the assumption that the rate of production of an intermediate ($^{\bullet}$OH) is equal to the rate of its consumption can be used (reaction (6)):[14]

$$k_1 c_{H_2O_2} = k_2 c_{OH} c_d + k_3 c_p c_{OH} \tag{6}$$

From Eq. (6), the steady state concentration of $^{\bullet}$OH radicals is obtained:

$$c_{OH} = \frac{k_1 c_{H_2O_2}}{k_2 c_d + k_3 c_p} \tag{7}$$

If the reactivity of $^{\bullet}$OH towards the different organic compounds present in solution is assumed to be approximately of the same order of magnitude and if a large quantity of H_2O_2 compared to dye was used so that the change in peroxide concentration is insignificant, after integration the exponential time dependence is obtained:

$$\ln\left(c_t / c_0\right) = -k_{\text{app}} t \tag{8}$$

where c_t is the concentration of dye after irradiation time t, c_0 is the dye concentration at $t = 0$ and k_{app} (min^{-1}) is the apparent pseudo-first order rate constant. The apparent reaction rate constants k_{app} for the decolorization of RO16 were calculated from semi-logarithmic graphs of $\ln(c_t/c_0)$ *vs*. time, using the linear regression method. For all the experimental results, the values of the square of the relative correlation coefficients (R^2) were higher than 0.98, which confirmed the proposed kinetic model.

UV–Vis spectral changes

The typical spectrum of RO16 is characterized by two bands in the visible region, with their maxima at 494 and 386 nm, and by two bands in the ultraviolet region, located at 297 and 254 nm. The absorbance peaks at 254 and 297 nm are due to $\pi\rightarrow\pi^*$ transitions in the benzene and naphthalene rings of RO16, respectively,[15] and decreases in the absorbance in this region indicate degradation of the aromatic part of the dye. The two bands in the visible region are due to $n\rightarrow\pi^*$ transitions in the azo linkage and are attributed to the presence of two forms of the dye molecules, the azo and the hydrazone form. The band at 386 nm corresponds to the azo form, while the band at 494 nm is linked to the hydrazone form of the azo dye, which is favored by water.[16] These forms originate from intramolecular hydrogen bonding tautomeric interaction between the oxygen of the naphthyl group and the β-hydrogen of the corresponding azo-linkage. The disappearance of absorption peaks in the visible region indicates that the main chromophores of the dye were destroyed and for this reason, dye solutions become decolorized. The changes in the UV–Vis absorption spectra of RO16 solutions during UV irradiation in presence of H_2O_2 at different irradiation time are shown in Fig. 3. It is obvious that the intensity of peaks in the visible region, as well as the intensity of peaks in the ultraviolet region, rapidly decreased with irradiation time and after 6 min of irradiation, no absorption peaks were observed. Thus, the UV/H_2O_2 process provides not only decolorization of the azo dye RO16, but also an appreciable degree of decomposition of the aromatic rings in the dye molecules.

Changes of pH and conductivity in the UV/H_2O_2 process

The changes in the pH of dye solutions as a function of the irradiation time for different initial pH values are shown in Fig. 4. After 40 min of irradiation, the pH decreased from 6.86 to 4.31 in neutral medium, from 5.36 to 3.69 in weak acidic medium and from 8.86 to 6.92 in weak basic medium. However, in strong basic (pH 10.12) and strong acidic media (pH 2.08 and 3.2), no significant changes in pH were observed after 40 min of irradiation. Previous reports[17,18] indicated that low molecular weight organic acids, such as oxalic, acetic, formic, maleic, malonic, fumaric and succinic acid, are formed during UV irradiation of dyes. Hence, the significant drops of the solution pH in neutral medium by 2.5 pH units and in weak acidic and basic medium by almost 2 pH units are probably due to the formation of organic and inorganic acids as degradation products of RO16. The effect of these degradation products on the solution pH was more prominent in neutral and weak acidic medium, which could be expected. On the other hand, in strong basic medium, weak organic acids were not formed in sufficient amounts for neutralization of the base.

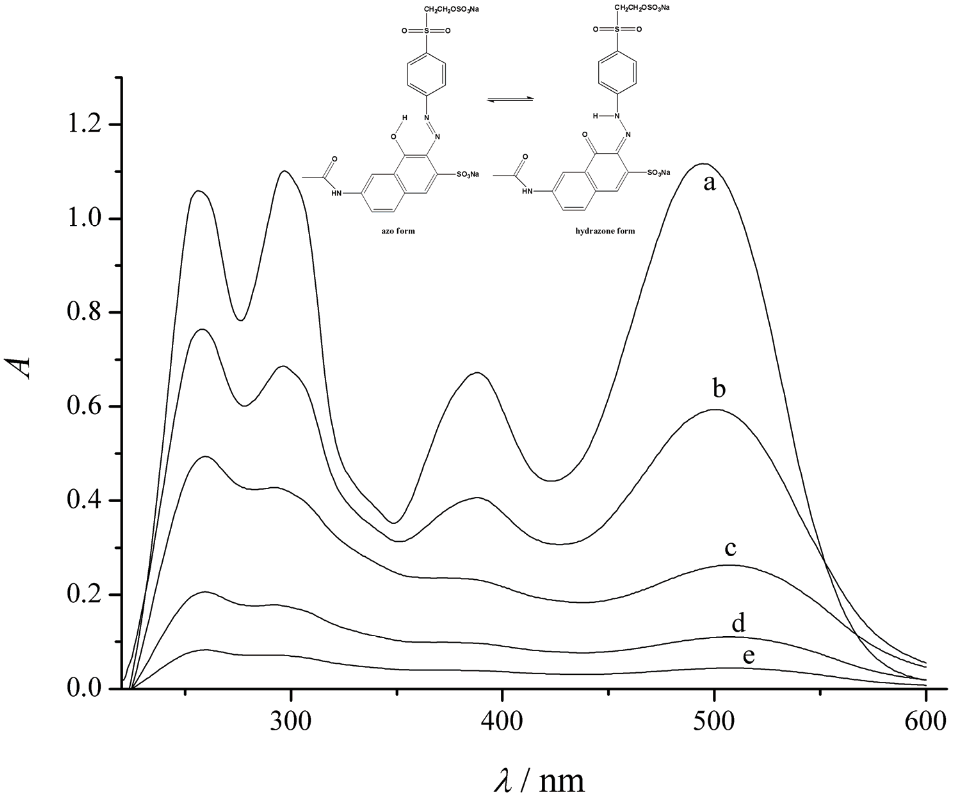

Fig. 3. UV–Vis spectral changes of RO16 as a function of irradiation time: a) 0, b) 1, c) 2, d) 3 and e) 4 min. c_0(RO16) = 50.0 mg dm^{-3}, c_0(H_2O_2) = 25.0 mmol dm^{-3}, pH 7.0±0.2, UV light intensity: 1950 μW cm^{-2}, temperature: 25±0.5 °C. Inset: tautomeric forms of RO16.

The conductivity of the dye solution was found to increase progressively during the irradiation from 39 to 102 μS cm^{-1} (Fig. 5). In the first 4 min of irradiation, when the dye solution was still colored, the conductivity slightly increased from 39 to 42.3 μS cm^{-1}; however, after complete decolorization had been achieved (about 6 min) and the main chromophore (–N=N–) in the dye molecules destroyed, the conductivity rapidly increased and reached a value of 102 μS cm^{-1} at the end of the experiment. The increase of conductivity with time can also be associated with the formation of the above-mentioned acid products in solution as well as with the formation of other mineralization products, such as NH_4^+, NO_3^-, NO_2^- and SO_4^{2-}.[18]

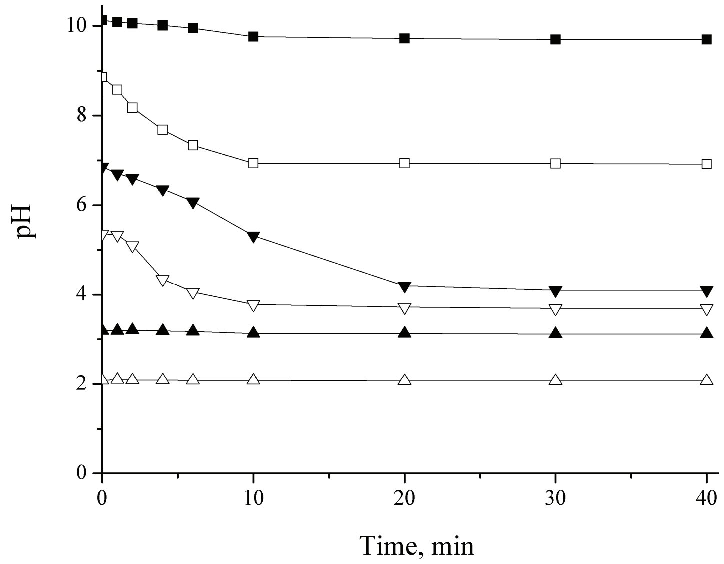

Fig. 4. Changes in pH during irradiation. c_0(RO16) = 50.0 mg dm^{-3}, $c_0(H_2O_2)$ = 25.0 mmol dm^{-3}, UV light intensity: 1950 μW cm^{-2}, temperature: 25 ± 0.5 °C.

The effect of the initial H_2O_2 concentration

The concentration of hydrogen peroxide is an important parameter that influences the efficiency of dye removal by the UV/H_2O_2 process. Due to the low molar absorption coefficient of H_2O_2 at 254 nm (18.6–19.6 L mol^{-1} cm^{-1}),[19] an excess of H_2O_2 is theoretically required to produce sufficient $^{\bullet}OH$ radicals. Numerous authors have reported that the concentration of H_2O_2 may either enhance the photoreaction rate or inhibit it due to the scavenging action of peroxide, depending on the concentration.[20–24] Therefore, an optimum concentration of H_2O_2 in the reaction course must be reached. In order to determine the effect of H_2O_2 concentration on the decolorization rate, doses of H_2O_2 in range of 10 up to 100 mM were added. The applied UV light intensity was 730 μW cm^{-2}, because of the very fast decolorization at the maximal value (1950 μW cm^{-2}), which made the investigation of this operational parameter difficult. The other parameters were kept constant. The apparent rate constants *vs*. different initial concentrations of H_2O_2 are summarized in Fig. 6. This plot shows that k_{app} considerably increased from 0.142 to 0.331 min^{-1} with increasing hydrogen peroxide concentration from 10 to 20 mM. At the low concentration of H_2O_2, a relatively low concentration of hydroxyl radicals was formed for dye oxidation, which resulted in a low decolorization rate. However, with increasing peroxide concentration, more hydroxyl radicals were generated upon its photodissociation (reaction (2)). On further increasing of the peroxide concentration to 40 mM, the apparent constant rate reached a plateau and stayed almost unchangeable.

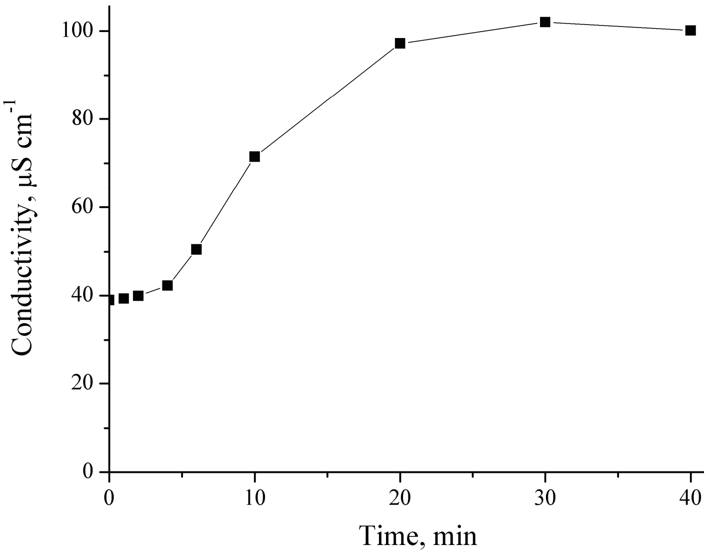

Fig. 5. Changes in conductivity during irradiation. c_0(RO16) = 50.0 mg dm^{-3}, $c_0(H_2O_2)$ = 25.0 mmol dm^{-3}, UV light intensity: 1950 μW cm^{-2}, pH 7.0±0.2, temperature: 25 ± 0.5 °C.

At an initial peroxide concentration above 40 mM, the apparent rate constant decreased from 0.329 to 0.18 min^{-1} on decreasing the H_2O_2 dose from 40 to 100 mM. When the initial peroxide concentration was very high, the generated $^\bullet$OH radicals mostly reacted with the excess peroxide and produced hydroperoxyl radicals $HO_2^\bullet$ (reaction (9)), which are less reactive than $^\bullet$OH, and the rate of dye removal decreased:[25]

$$H_2O_2 + {}^\bullet OH \rightarrow H_2O + HO_2^\bullet,\ k = 2.7\times10^7\ M^{-1}\ s^{-1} \tag{9}$$

The generated $^\bullet$OH can also react with $HO_2^\bullet$ and produce water and oxygen (reaction (10)) or dimerize to H_2O_2 (reaction (11)).[25,26] In this way, the concentration of $^\bullet$OH available for dye degradation also decreased:

$$^\bullet OH + HO_2^\bullet \rightarrow H_2O + O_2,\ k = 6.6\times10^9\ M^{-1}\ s^{-1} \tag{10}$$

$$^\bullet OH + {}^\bullet OH \rightarrow H_2O_2,\ k = 5.5\times10^9\ M^{-1}\ s^{-1} \tag{11}$$

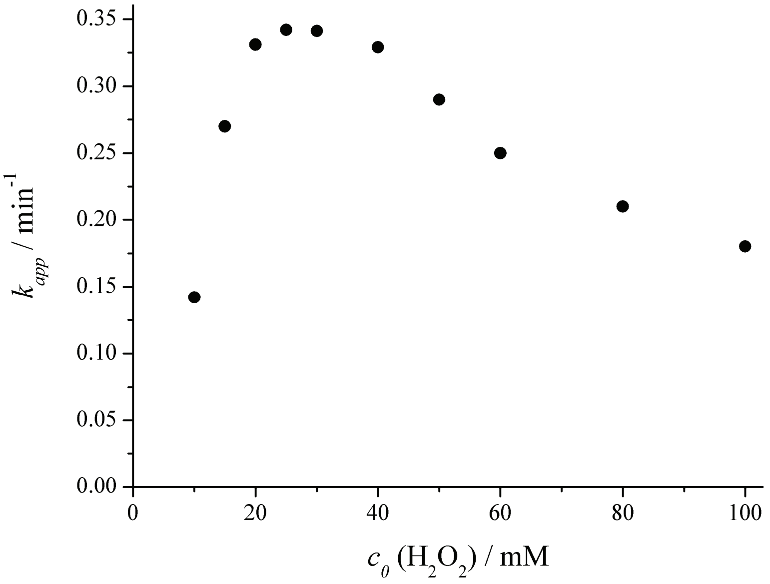

Fig. 6. The effect of the initial H_2O_2 concentration on the rate of RO16 decolorization. c_0(RO16) = 50.0 mg dm^{-3}, pH 7.0±0.2, UV light intensity: 730 µW cm^{-2}, temperature: 25±0.5 °C.

Therefore, the optimum range of the hydrogen peroxide concentration giving the maximum RO16 decolorization rate was from 20 to 40 mM. These values are related to the optimum value of relative molar ratio of the H_2O_2 concentration to that of the dye (H_2O_2/RO16) between 246 and 493. Many authors noticed the existence of an optimal molar ratio between peroxide and dye that leads to a faster decolorization rate. Muruganandham and Swaminahan[27] reported that the optimal initial peroxide concentration for the decolorization of the chlorotriazine reactive azo dye, Reactive Orange 4, in a batch photoreactor was about 20 mM ($[H_2O_2]_0/[RO4]_0 = 40$, $c(RO4) = 5\times10^{-4}$ mol L^{-1}, pH 3.0, UV light power: 64 W). Neamtu *et al.*[28] reported approximately the same optimal concentration of peroxide (24.5 mM) for the decolorization of 100 mg L^{-1} initial concentration of three reactive azo dyes, Reactive Red 120, Reactive Black 5 and Reactive Yellow 84 ($[H_2O_2]_0/[RR120]_0 = 360$, $[H_2O_2]_0/[RB5]_0 = 243$, $[H_2O_2]_0/ [RY14]_0 = 470$, respectively) in a batch photoreactor. On the other hand, Aleboyeh *et al.*[22] investigated the critical effect of the peroxide concentration in the decolorization of the three commercial dyes (Acid Orange 8, Methyl Orange, Acid Blue 74) in a continuous photoreactor and found that the optimal peroxide/dye molar ratio was different in each case ($[H_2O_2]_0/[AO8]_0 = 55$, $[H_2O_2]_0/[MO]_0 = 65$, $[H_2O_2]_0/ /[AB74]_0 = 70$). This confirms the importance of determining the optimal initial peroxide concentration for UV/H_2O_2 decolorization for each dye and for every experimental condition. In this study, an initial H_2O_2 concentration of 25 mmol dm^{-3} was used in all the subsequent experiments.

The effect of pH

The initial pH of dye solutions is also an important parameter for optimizing the operational conditions, since the colored effluent from textile industry could have different pH values. The influence of pH on the rate of decolorization of the RO16 azo dye by UV/H_2O_2 process was investigated at seven different pH values: 2.0, 3.0, 4.0, 5.0, 7.0, 9.0, and 10.0 during 10 min of treatment time, using 50 mg dm^{-3} dye solutions and 25 mM H_2O_2. The first tests run were realized by adjusting the acidic pH (2.0, 3.0, 4.0 and 5.0) with four inorganic acids (HCl, HNO_3, H_2SO_4 and H_3PO_4) and the changes in the decolorization rate are shown in Fig. 7. In all cases, a decrease of the decolorization rate from pH 5 to 2 is evident. On acidification of the solution, amount of added conjugated bases increased (Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}). These anions are able to react with hydroxyl radicals leading to inorganic radical ions which exhibit a much lower reactivity than $^\bullet OH$, hence they did not participate in the dye decolorization. There is also a drastic competition between the dye and the anions with respect to $^\bullet OH$:

$$Cl^- + {}^\bullet OH \rightarrow ClHO^{\bullet -} \tag{12}$$

$$HNO_3 + {}^\bullet OH \rightarrow NO_3^\bullet + H_2O \tag{13}$$

$$HSO_4^- + {}^\bullet OH \rightarrow SO_4^{\bullet -} + H_2O \tag{14}$$

$$H_2PO_4^- + {}^\bullet OH \rightarrow HPO_4^{\bullet -} + H_2O \tag{15}$$

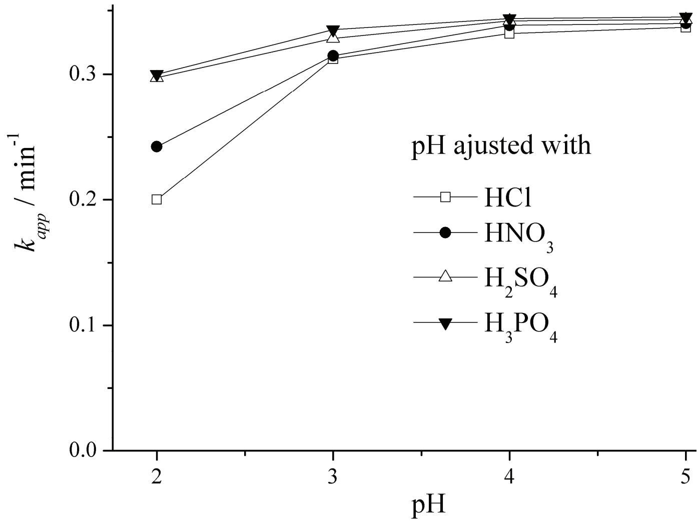

Fig. 7. Effect of pH adjustment with different mineral acids on the rate of RO16 decolorization. c_0(RO16) = 50.0 mg dm^{-3}, $c_0(H_2O_2)$ = 25.0 mmol dm^{-3}, UV light intensity: 730 μW cm^{-2}, temperature: 25±0.5 °C.

The lowest values of the apparent rate constant in all cases were obtained at pH 2, where the greatest concentration of inorganic anions was added to adjust the pH. On increasing the pH value from 3.0 to 5.0, the concentrations of added inorganic anions decreased and, as a result, the values of k_{app} increased slightly. Hence, the scavenging effect decreases with decreasing concentration of added inorganic anions. A comparison of the process efficiency in the pH range from 2 to 5 suggests the following increasing scavenging effect phosphate < sulfate < nitrate < chloride.

Jaysona *et al.*[29] reported that the rate constant for the interaction between $^{\bullet}$OH and Cl^- was $k = 4.3\times10^9$ M^{-1} s^{-1} (reaction (12)). Katsumura *et al.*[30] investigated the reactivity of $NO_3^{\bullet}$ and obtained a value for the rate constant for the reaction $^{\bullet}$OH with NO_3^- of 1.3×10^8 M^{-1} s^{-1} (reaction (13)). The results of Jiang *et al.*[31] and Maruthamuthu *et al.*[32] showed that HSO_4^- and $H_2PO_4^-$ react with $^{\bullet}$OH at a lower rate ($k = 4.7\times10^5$ M^{-1} s^{-1} and $k = 2\times10^4$ M^{-1} s^{-1}, respectively) than NO_3^- (reactions (14) and (15)). Therefore, the obtained scavenging effects of the anions used in this study are in agreement with the values of the rate constants given in the mentioned literature.[29–32]

On the other hand, in a study of Galindo *et al.*[33], which considers the photochemical degradation of Acid Blue 74, a different order of scavenging effects of the anions was shown. They found that the sulfate anion was the strongest $^{\bullet}$OH scavenger, followed by nitrate and phosphate anions, while the chlorides were the weakest scavenger. This decay in the rate of Acid Blue 74 degradation in the presence of sulfate anions was explained by possible aggregation of dye molecule, when a strong electrolyte such as sulfuric acid was added. $^{\bullet}$OH radicals show less affinity to aggregated dye than to single molecules. The results of the present investigation demonstrated that the scavenging effect of the anions was predominant, as no significant effect of aggregation of the dye molecules could be expected with the applied concentrations of the mineral acids.[34]

The other test runs were performed by adjusting the pH with NaOH at 7.0, 9.0 and 10.0 (Fig. 8). A decline of apparent rate constants from 0.342 min^{-1} at pH 7 to 0.151 min^{-1} at pH 10.0 was observed, which can be a consequence of the following possible reasons.

First, at alkaline pH, the concentration of the conjugate base of H_2O_2 increases (reaction (16)):

$$H_2O_2 \rightarrow HO_2^- + H^+,\ pK_a = 11.6 \tag{16}$$

This anion (HO_2^-) reacts with a non-dissociated molecule of H_2O_2, which leads to oxygen and water, instead of producing hydroxyl radicals under UV radiation (reaction (17)). Therefore, the instantaneous concentration of $^{\bullet}$OH is lower than expected:

$$HO_2^- + H_2O_2 \rightarrow H_2O + O_2 + OH^- \tag{17}$$

Furthermore, the deactivation of $^{\bullet}OH$ is more important when the pH of the solution is high. The reaction of $^{\bullet}OH$ with HO_2^- is approximately 300 times faster than its reaction with H_2O_2 (reactions (18) and (19)).

$$^{\bullet}OH + HO_2^- \rightarrow H_2O + O_2^{\bullet -},\ k = 7.5\times10^9\ M^{-1}\ s^{-1} \quad (18)$$

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet},\ k = 2.7\times10^7\ M^{-1}\ s^{-1} \quad (19)$$

The reactivity of $O_2^{\bullet -}$ and $HO_2^{\bullet}$ with organic pollutants is much lower than that of $^{\bullet}OH$. They preferentially disproportionate and produce hydrogen peroxide and dioxygen (reaction (20)):

$$O_2^{\bullet -} + HO_2^{\bullet} + H_2O \rightarrow H_2O_2 + O_2 + OH^- \quad (20)$$

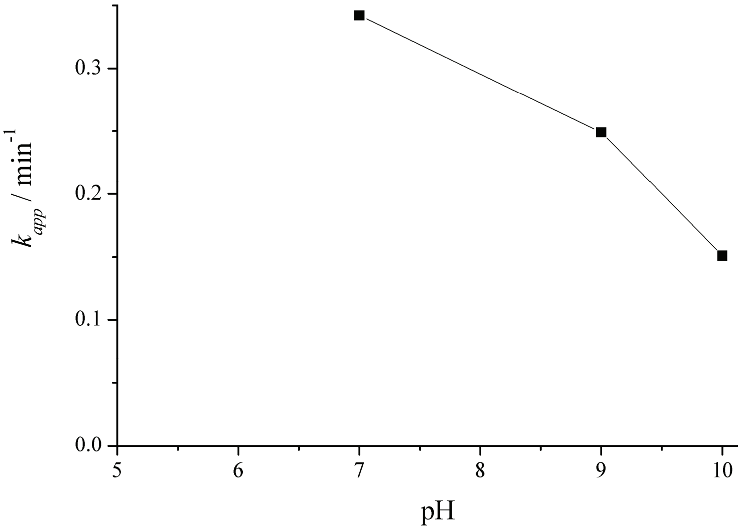

Fig. 8. Effect of pH on the rate of RO16 decolorization. c_0(RO16) = 50.0 mg dm^{-3}, $c_0(H_2O_2)$ = 25.0 mmol dm^{-3}, UV light intensity: 730 μW cm^{-2}, temperature: 25±0.5 °C.

On the other hand, several authors have reported that the peroxide self-decomposition rate, which is strongly pH dependent, partly contributes to the decrease of the k_{app} values in alkaline medium (reaction (21)):[27,35]

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2 \quad (21)$$

Chu[36] investigated the self-decomposition rate of peroxide and found that its first order self-decomposition constants are 2.29×10^{-2} and 7.4×10^{-2} min^{-1} at pH 7.0 and 10.5, respectively. The photodecomposition of peroxide by UV light at the same pH values was also investigated by this author. By comparing the results at alkaline pH values, it was concluded that the decrease of the H_2O_2 concentration was significantly caused by its self-decomposition; hence, a decay pathway not involving free radicals must occur.

Both of the two proposed peroxide decomposition pathways in alkaline medium, the first leading to the formation of the HO_2^- and the second the self decomposition of H_2O_2 leading to the formation of water and oxygen, can occur simultaneously, which results in a decrease in the $^{\bullet}OH$ concentration and, consequently, a decrease in the dye decolorization rate.

It is important to note that the pH of the dye bath for reactive dyes depends on the textile fiber and in industrial applications, the dyeing of cellulosic fibers is performed in alkaline dye baths, while dye baths for wool are acidic. The results presented in this paper indicated that removal efficiency of RO16 dye is higher at neutral pH values; hence, effluents from the textile industry must be neutralized for treatment by the UV/H_2O_2 process in order to achieve the maximal decolorization rate.

The effect of initial dye concentration

The effect of the initial RO16 concentration on the efficiency of dye degradation was investigated in the concentration range from 20–80 mg dm^{-3} and the results are presented in Fig. 9. It appears that with increasing initial dye concentration, the efficiency of dye removal almost linearly decreases. The results indicate that the apparent rate constant decreases from 0.382 min^{-1} for a dye concen-

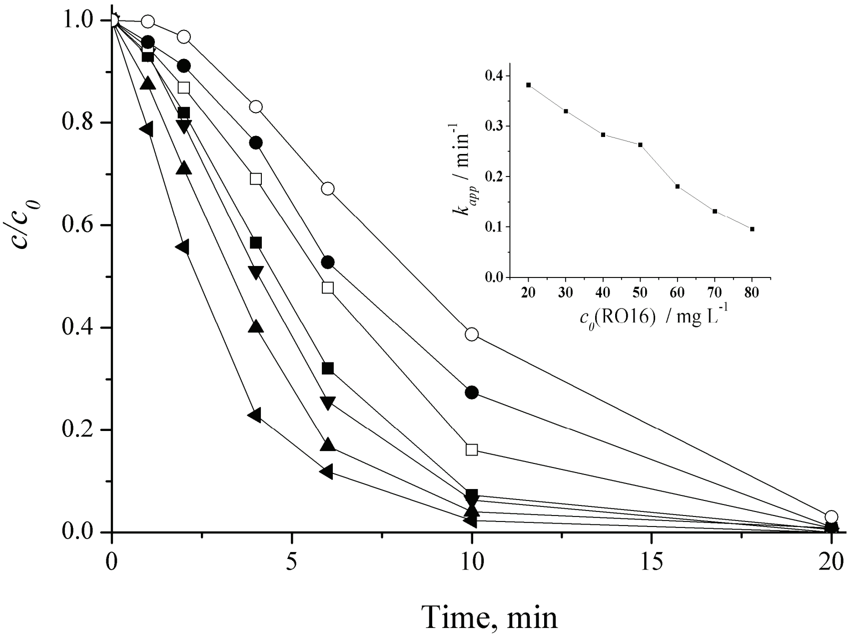

Fig. 9. Effect of the initial concentration of RO16, 20 (◀), 30 (▲), 40 (▼), 50 (■), 60 (□), 70 (●) and 80 mg dm^{-3} (○) on its decolorization. $c_0(H_2O_2)$ = 25.0 mmol dm^{-3}, pH 7.0±0.2, UV light intensity: 730 μW cm^{-2}, temperature: 25±0.5 °C. Inset represents k_{app} at different initial dye concentrations.

tration of 20 mg dm^{-3} to 0.096 min^{-1} for a dye concentration of 80 mg dm^{-3}. Similar results were already reported by Behnajady *et al.*[37] At high dye concentrations, most of the UV light was absorbed by the dye instead of by the peroxide because of its higher molar extinction coefficient at 253.7 nm. Hence, the dye solution becomes increasingly impermeable to UV light, which inhibits photolysis of the peroxide. This is very important from the application point of view and the UV/H_2O_2 system would be more effective for relatively dilute dye solutions.

The effect of UV light intensity

The influence of UV-light intensity on the decolorization of RO16 azo dye was monitored by varying the light intensity from 730 up to 1950 μW cm^{-2} and the results are shown in Fig. 10. It is evident that the apparent rate constant increased linearly with increasing UV light intensity. This result is consistent with those of previous studies, in which an increase in the decolorization rate with increasing UV light intensity was generally observed.[38] Such an effect is expected because photodissociation of peroxide is initiated by its absorption of UV light; hence, increases in the UV light intensity enhance the production of hydroxyl radicals.

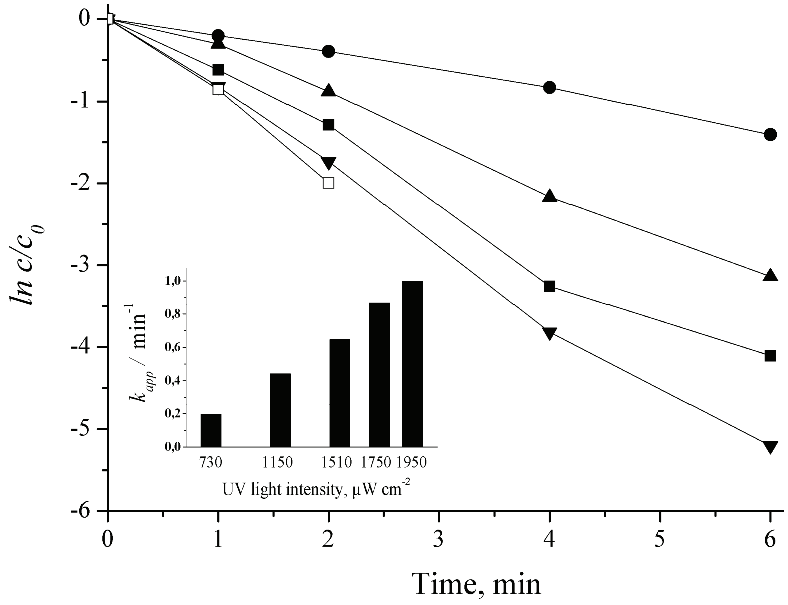

Fig. 10. Effect of UV light intensity, 730 (●), 1150 (▲), 1510 (■), 1750 (▼) and 1950 μW cm^{-2} (□) on the decolorization of RO16. c_0(RO16) = 50.0 mg L^{-1}, $c_0(H_2O_2)$ = 25.0 mmol dm^{-3}, pH 7.0±0.2, temperature 25±0.5 °C. Inset represents k_{app} at different UV light intensities.

CONCLUSIONS

The results presented in this paper showed that the UV/H_2O_2 process could be efficiently used for the decolorization of aqueous solutions of the azo dye Reactive Orange 16. It was found that the rate of decolorization is significantly affected by the initial pH, the initial hydrogen peroxide concentration, the initial dye concentration and the UV light intensity. The decolorization follows pseudo first order reaction kinetics. Peroxide concentrations in the range from 20 to 40 mM appear as optimal. Color removal was observed to be faster in neutral pH solutions than in acidic and basic ones. The hydroxyl radical scavenging effect of the examined inorganic anions increased in the order phosphate < sulfate < nitrate < chloride. Pseudo-rate constant (k_{app}) decreased as the initial dye concentration increased, but it increased linearly with increasing UV light intensity and attained a maximal value at the highest applied intensity. The complete removal of color, after selection of optimal operational parameters, was achieved within 6 min of UV irradiation, which indicates that it is a highly efficient process.

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ИЗВОД

ОБЕЗБОЈАВАЊЕ ТЕКСТИЛНЕ АЗО БОЈЕ РЕАКТИВНИ ОРАНЖ 16 UV/H_2O_2 ПРОЦЕСОМ

ЈЕЛЕНА МИТРОВИЋ, МИЉАНА РАДОВИЋ, ДАНИЈЕЛА БОЈИЋ, ТАТЈАНА АНЂЕЛКОВИЋ,
МИЛОВАН ПУРЕНОВИЋ и АЛЕКСАНДАР БОЈИЋ

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У раду је проучавана ефикасност деколоризације реактивне азо боје реактивни оранж 16 (RO16) UV/H_2O_2 процесом у фотореактору са UV лампама максимума емисије на 253,7 nm. При оптималним условима (25 mM иницијална концентрација пероксида, pH 7, интензитет UV зрачења 1950 μW cm^{-2}) потпуно уклањање иницијалне концентрације боје (50,0 mg dm^{-3}) је постигнуто за мање од 6 min. Испитиван је утицај параметара UV/H_2O_2 процеса, као што су иницијална pH вредност, иницијална концентрација водоник-пероксида, иницијална концентрација боје и интензитет UV зрачења на ефикасност деколоризације боје. Највећа ефикасност процеса постигнута је при иницијалној концентрацији пероксида у распону од 20 до 40 mM, изнад које је процес инхибиран његовим ефектом хватача радикала. Процес деколоризације је ефикаснији у неутралној средини. Са повећањем иницијалне концентрације боје расте и ефикасност процеса као и са повећањем интензитета UV зрачења.

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REFERENCES

1. H. Zollinger, *Color Chemistry: Syntheses, Properties and Applications of Organic Dyes and Pigments*, Wiley–VCH, Weinheim, Germany, 2003, p. 579
2. L. G. Devi, S. G. Kumar, K. M. Reddy, C. Munikrishappa, *J. Hazard. Mater.* **164** (2009) 459

3. M. H. Habibi, A. Hassanzadeh, S. Mahdavi, *J. Photochem. Photobiol., A* **172** (2005) 89
4. *Advanced oxidation processes for water and wastewater treatment*, S. Parsons, Ed., IWA Publishing, London, 2004, p. 302
5. M. A. Behnajady, N. Modirshahla, H. Fathi, *J. Hazard. Mater., B* **136** (2006) 816
6. M. Muruganandham, M. Swaminathan, *Dyes Pigm*. **68** (2006) 133
7. E. Kusvuran, O. Erbatur, *J. Hazard. Mater., B* **106** (2004) 115
8. K. H. Wong, S. Tao, R. Dawson, P. K. Wong, *J. Hazard. Mater., B* **109** (2004) 149
9. F. S. Garcia Einschlag, J. Lopez, L. Carlos, A. L. Capparelli, A. M. Braun, E. Oliveros, *Environ. Sci. Technol*. **36** (2002) 3936
10. O. Lergini, E. Oliveros, A. M. Braun, *Chem. Rev*. **93** (1993) 671
11. A. M. Marechal, Y. M. Slokar, T. Taufer, *Dyes Pigm*. **33** (1997) 281
12. A. M. El-Dein, J. A. Libra, U. Wiesmann, *Chemosphere* **52** (2003) 1069
13. X. Dong, W. Ding, X. Zhang, X. Liang, *Dyes Pigm*. **74** (2007) 470
14. A. Aleboyeh, Y. Moussa, H. Aleboyeh, *Sep. Purif. Technol*. **43** (2005) 143
15. S. M. Milosavljević, *Structural methods of instrumental analysis*, Faculty of Chemistry, Belgrade, 1994, p. 35 (in Serbian)
16. A. S. Ozen, P. Doruker, V. Aviyente, *J. Phys. Chem., A* **111** (2007) 13506
17. M. Stylidi, D. I. Kondarides, X. E. Verykios, *Appl. Catal., B* **47** (2004) 189
18. Z. He, L. Lin, S. Song, M. Xia, L. Xu, H. Ying, J. Chen, *Sep. Purif. Technol*. **62** (2008) 376
19. K. Li, D. R. Hokanson, J. C. Crittenden, R. R. Trussell, D. Minakata, *Water Res*. **42** (2008) 5045
20. W. Abdel-Alim Sadik, A. W. Nashed, *Chem. Eng. J*. **137** (2008) 525
21. D. Jiraroj, F. Unob, A. Hagege, *Water Res.* **40** (2006) 107
22. A. Aleboyeh, H. Aleboyeh, Y. Moussa, *Dyes Pigm*. 57 (2003) 67
23. N. Daneshvar, M. Rabbani, N. Modirshahla, M. A. Behnajady, *Chemosphere* **56** (2004) 895
24. N. H. Ince, *Water Res.* **33** (1999) 1080
25. G. V. Buxton, C. L. Greenstock, W. P. Helman, A. B. Ross, *J. Phys. Chem. Ref. Data* **17** (1988) 513
26. K. Schested, O. L. Rasmussen, H. Fricke, *J. Phys. Chem*. **72** (1968) 626
27. M. Muruganandham, M. Swaminathan, *Dyes Pigm*. **62** (2004) 269
28. M. Neamtu. I. Siminiceanu, A. Yediler, A. Kettrup, *Dyes Pigm*. **53** (2002) 93
29. G. G. Jaysona, B. J. Parsons, A. J. Swallow, *J. Chem. Soc., Faraday Trans*. (1973) 1597
30. Y. Katsumura, P. Y. Jiang, R. Nagaishi, T. Oishi, K. Ishigure, *J. Phys. Chem*. **95** (1991) 4435
31. P. Y. Jiang, Y. Katsumura, R. Nagaishi, M. Domae, K. lshikawa, K. Ishigure, Y. Yoshida, *J. Chem. Soc., Faraday Trans*. **88** (1992) 1653
32. P. Maruthamuthu, P. Neta, *J. Phys. Chem*. **82** (1978) 710
33. C. Galindo, P. Jacques, A. Kalt, *J. Photochem. Photobiol., A* **141** (2001) 47
34. M. H. Habibi, A. Hassanadeh, A. Z. Isfahani, *Dyes Pigm*. **69** (2006) 111
35. H.Y. Shu, M. C. Chang, *J. Hazard. Mater., B* **125** (2005) 96
36. W. Chu, *Chemosphere* **44** (2001) 935
37. M. A. Behnajady, N. Modirshahla, M. Shokri, *Chemosphere* **55** (2004) 129
38. M. W. Chang, C. C. Chung, J. M. Chern, T. S. Chen, *Chem. Eng. Sci*. **65** (2010) 135.