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UV–H_2O_2 oxidation of monoazo dyes in aqueous media: a kinetic study

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Abstract

During the past few years attention has been drawn on chemical techniques that could be used to discolour text wastewaters. We have studied the photooxidation of several aqueous monoazodyes solutions in the presence hydrogen peroxide. Irradiation was carried out with a low-pressure mercury lamp. We observed that the reaction pseudo-first-order with respect to the dye concentration. The effects of hydrogen peroxide and dye dosages, tempe ture, pH, and chemical structure of the organic matter were also investigated. Results suggest that molecules, hydr zone form of which predominates, are the most sensitive to °OH oxidation. If a labile hydrogen atom is present in t chromophore, it is the primary target of the attack. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: UV–H_2O_2 oxidation; Monoazodyes; Tautomerism; Kinetic; Textile wastewaters; Discolouration

1. Introduction

During the dyeing of fibres, especially cellulosic ones, substantial amounts of dye are not fixed in the fibres and dyehouse wastewaters usually contain about 10 to 50 mg l^{-1} of dyes, a concentration which is high enough to induce a marked colouration. In a near future, most European countries will issue stricter standards and it is likely that textile industries will be forced to discolour their wastewaters before discharging them in rivers [1]. Conventional biologic methods, used in public sewage treatment plants, have not proven to be particularly effective for coloured effluents. Physical methods, for instance adsorption on activated charcoal or reversed osmosis, can be considered too, but their cost is high.

During the past few years, the so-call Advanced Oxidation Processes (AOP), whe highly oxidizing species, like hydroxyl radicals, a produced, have been used to destroy vario hazardous aromatic pollutants in solutions (ph nols, chlorinated derivatives...) [2]. In the prese study, we have investigated the ability of the o dative UV–H_2O_2 process to discolour aqueo solutions of monoazodyes.

2. Experimental

2.1. Reagents

C.I. Acid Orange 5, 6, 7, 20 and 52 were co mercial products (Aldrich, Fluka). The oth monoazo dyes were purchased from Steiner Co All products were salt free. HPLC analyses reve

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no significant amounts of impurities. Thus the dyes were used without further purification. Some of their colouristic characteristics are summarized in Table 1.

Hydrogen peroxide (30% w/w) was obtained from Prolabo, as were the HPLC grade solvents (methanol and water).

2.2. Photochemical degradation

The reactions were performed in a reversed-immersion photoreactor fitted with a low-pressure mercury lamp (15 W—emission at 253.7 nm). The solution (5 l) was projected at the top of the reactor, forming a thin film at the inner surface of the external tube. The solution was then collected in a 10 l-reservoir, from which it was continuously pumped, as shown in Fig. 1

2.3. Methodology

In our experiments dye concentrations were set at values, in most cases 5.7×10^{-5} mol l^{-1}, within the range of typical concentrations in textile wastewaters. The selected organic compound, at the required concentration level, was dissolved in distilled deionized water. A large excess of hydrogen peroxide in comparison to the dye was added (172 mol:1 mol, or a higher ratio), so that $[H_2O_2]$ could be considered as constant during the whole experiment. The pH of the solution was measured with a TS 70/N-1 Tacussel pH-meter; pH was adjusted to the desired value by addition sodium hydroxide or hydrochloric acid.

A sample was collected every 15 min and t remaining dye content was measured on a Perki Elmer 554 spectrophotometer. Rate constants a order of the reaction were then calculated.

Table 1
Dye characterisation data

C.I. number	Name	λ_{max}	$\varepsilon_{max}\times10^{-3}$ (litre mol^{-1} cm^{-1})	Predominant tautomeric form
13080	AO5	443	17.8	azo
14270	AO6	388	16.3	azo
15510	AO7	483	17.5	hydrazone
15575	AO8	489	19.1	hydrazone
16230	AO10	478	16.9	hydrazone
14600	AO20	475	14.8	hydrazone
13025	AO52	463	27.6	azo
18050	AR1	530	20.7	hydrazone
16255	AR18	507	19.1	hydrazone
18055	AVi7	522	30.5	hydrazone
15670	MVi5	499	13.5	hydrazone

3. Results and discussion

To our knowledge no results have been pu lished on the oxidation of aminoazobenzene dy Thus we decided to study the sensitivity of AO to the UV–H_2O_2 process. Simultaneoulsy, t rates of discolouration of two phenylazonaphtho (AO7 and AO20) were determined, in order emphasize possible variations between the tw types of dyes.

For the three molecules, the action of UV alo or of H_2O_2 in the absence of UV irradiation w negligible. In both cases, more than 99% of t dye remained after 120 mn of treatment. B combined action of UV radiations and hydrog peroxide induced a dramatic decrease in the op cal density of the solutions. For instance in Fig. are shown the results obtained with AO7.

It is indisputable that degradation of the dye due to the hydroxyl radicals generated upon ph tolysis of hydrogen peroxide [3], following t reaction:

$$H_2O_2 \xrightarrow{hv} 2°OH \qquad ($$

This radical is a very powerful oxidizer, able react with inorganic [4,5] as well with aliphat [6,7] or aromatic organic compounds [8,9].

According to the results of Shu et al., [10] t photooxidation reaction is pseudo-first-order wi respect to azo dye concentration. This frequent occurs when the contaminant is very dilute solution. The kinetic constant can also be link to the dye concentration by Eq. (2).

$$\ln\frac{C}{C_0} = -k.t. \qquad ($$

C_0: dye concentration at $t = 0$.
C: concentration at instant t.

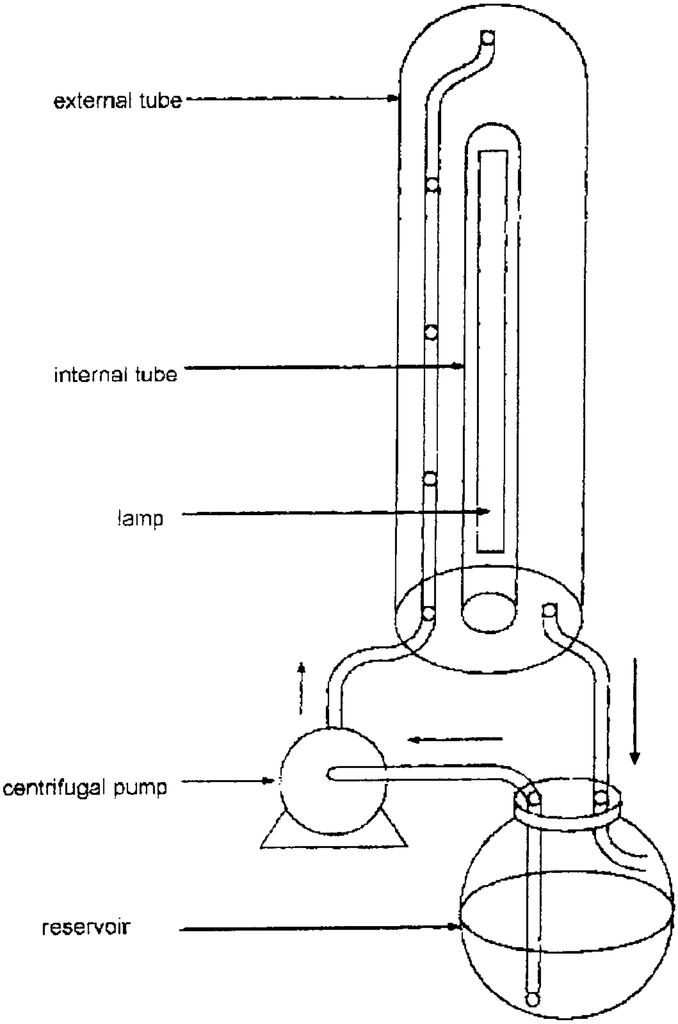


Fig. 1. Configuration of the photoreactor.

Values of the three constants *k* are given in Table 2. Under these conditions, AO52 seems to be less sensitive to OH-induced oxidation, but *k* strongly depends on the reactor configuration and on the experimental conditions. The effects of four variables, including temperature, pH, dye concentration and H_2O_2 concentration, on discolouration kinetics were also investigated for the three molecules. The experiments were conducted by changing one variable at a time while keeping the three other parameters constant.

3.1. Effect of temperature

During the first experiments, the temperature the solutions was not regulated. Therefore, passing repeatedly through the pump and near t lamp, solutions progressively warm up by 2°C 3°C, and finally reach 30°C or 32°C. To make su that this small change in temperature has strong influence on kinetic constant valu experiments were carried out in the temperatu range 22–45°C. Isothermal conditions (with

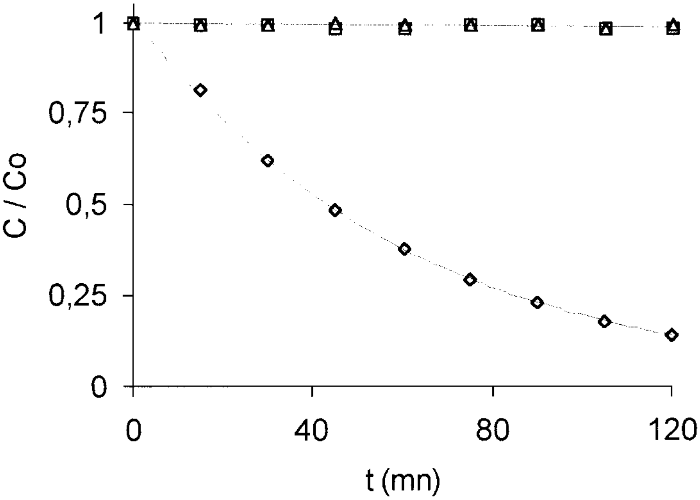


Fig. 2. Effect of H_2O_2 alone (△), of UV alone (□), of the UV/H_2O_2 (◇) association on the rate of degradation of AO7. 32°C; pH 5 $[AO7]_o = 5.7 \times 10^{-5}$ mol l^{-1}; $[H_2O_2]_o = 4.9 \times 10^{-2}$ mol l^{-1}.

temperature precision of ± 0.5°C) were obtained by surrounding the reservoir of the photoreactor by a double boiler.

Fig. 3 shows that reactions are effectively not sensitive to small changes in temperature in the range 22–45°C. This is not surprising, because it is well known that photochemically induced reactions often have a low activation energy [11,12].

3.2. *Effect of pH*

The effect of the pH on the rate of discolouration is illustrated in Fig. 4. The value of the rate at pH ≈6 was used as a reference for every dye. The other rates (at different pH) were determinated comparatively to it.

Generally speaking, the process was more effective in an acid medium (pH ≈ 3–4). However, the behaviour of AO52 is very particular. We have already indicated that, in neutral or slightly alkaline solutions, AO52 was significantly less sensitive to °OH-induced oxidation than hydroxyazo dyes (Table 2). But at lower pH values, its degradation rate rises sharply. This can be explained by a change in the molecule structure. Indeed, when the pH of the solution is lower than the pKa of the dye (pKa = 3.4), AO52 is protonated. As in the majority of aminoazobenzenes, the protonat molecule is subject to ammonium–azonium taut merism and the latter form is stabilized by res nance [13].

The “azonium” configuration presents a sim larity to the hydrazone form of AO20. In bo cases, the β nitrogen atom of the azo bo carries an *H* atom and simultaneously t kinetic constant is very high. Thus we can co clude that the labile *H* atom makes the mol cule of AO52 especially vulnerable towa attack of °OH radicals.

The reaction rates of the three dyes are slow down in alkaline media. This considerat decrease at pH higher than 10.5 is not due to dy but to the oxidative species. In alkaline mediu hydrogen peroxide undergoes decompositi leading to dioxygen and water, rather than pr

Table 2
Kinetic constants of three dyes under the following expe mental conditions: 32°C; pH = 5.9; $[dye]_o = 5.7 \times 10^{-5}$ mol l $[H_2O_2]_o = 4.9 \times 10^{-2}$ mol l^{-1}

Dye	$k \times 1000$ (mn^{-1})
AO7	16.3
AO20	20.9
AO52	5.6

ducing hydroxyl radicals under UV radiations. Therefore the instantaneous concentration in °OH is lower than expected. The base-catalyzed decomposition involves the HO_2^- anion: the conjugated base of H_2O_2 reacts with a non-dissociated molecule of H_2O_2 according to Eq. (3).

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

Furthermore, the desactivation of °OH greater when the pH of the solution is high, t reaction of °OH with H_2O^- being approximate 100 times faster than its reaction with H_2O_2.

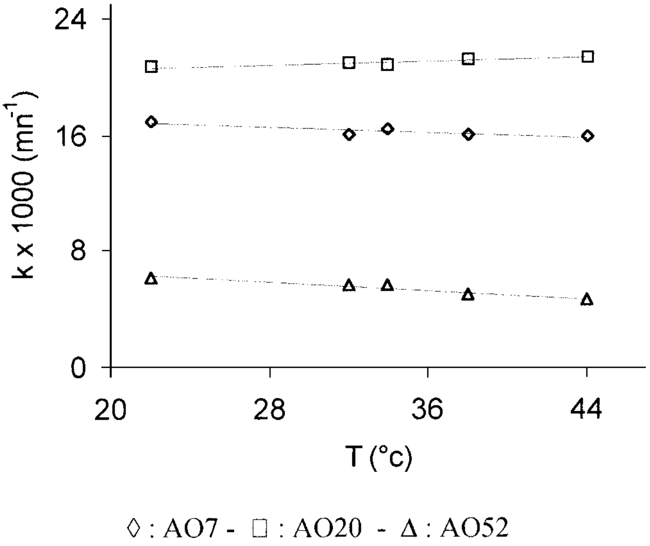


Fig. 3. Effect of temperature on the rate of oxidation of three dyes. pH = 5.9; [dye]o = 5.7×10^{-5} mol l^{-1}; $[H_2O_2]$o = 4.9×10^{-2} l^{-1}.

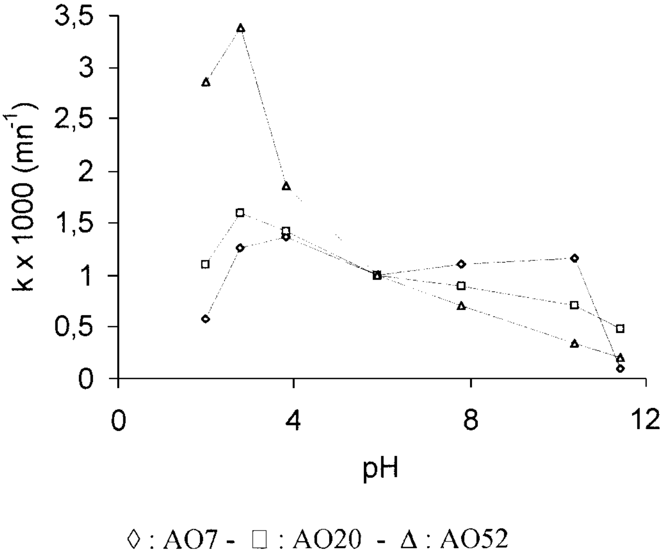


Fig. 4. Effect of pH on the rate of discolouration of the dye solutions. 32°C; pH = 5.9; [dye]o = 5.7×10^{-5} mol l^{-1}; $[H_2O_2]$o 4.9×10^{-2} mol l^{-1}.

$$^{\circ}OH + HO_2^- \rightarrow H_2O + O_2^{\circ -} \qquad k_1 = 7.5 \times 10^9\ \mathrm{l\ mol^{-1}\ s^{-1}} \tag{4}$$

$$^{\circ}OH + H_2O_2 \rightarrow H_2O + HO_2^{\circ} \qquad k_1 = 2.7 \times 10^7\ \mathrm{l\ mol^{-1}\ s^{-1}}\ [14] \tag{5}$$

The reactivity of $HO_2^{\circ -}$ and of its basic form $O_2^{\circ}-$ with organic pollutants is very low. They preferentially disproportionate producing some hydrogen peroxide and dioxygen, according to Eq. (6):

$$HO_2^{\circ -} + O_2^{\circ -} + H_2O \rightarrow H_2O_2 + O_2 + HO^- \tag{6}$$

On the whole, our results demonstrate that it is very important to set a suitable pH in order to optimise the operating conditions.

3.3. Influence of the initial dye concentration

Initial dye concentrations C_0 were set in the range 5–100 mg l^{-1}, as illustrated in Fig. 6.

The relationship between the initial discolouration rate and C_0 can be expressed as Eq. (7). Indeed, a plot of the logarithm of the kinetic constant against the initial concentration of the dyes gives a straight line. Such an evolution is common to the three molecules.

$$k = a\exp(-bC_0) \tag{7}$$

In every experiment, the concentration hydrogen peroxide was high enough not to co stitute a limiting factor (Fig. 6). On the oth hand, the extinction coefficients (ε) of the orgar molecules at 253.7 nm are high, so that an increa in the dye concentration induces a rise of t internal optical density. Dyes react, in fact, like filter. Consequently, the solution becomes mo and more impermeable to UV radiation. Ther fore, the rate of photolysis of hydrogen peroxi directly depends on the incident intensity [15] a especially, in the presence of organic matter, the fraction of radiation absorbed by H_2C defined as follows in Eqs. (8) and (9):

$$f = \frac{\varepsilon_{H_2O_2}\cdot[H_2O_2]}{\sum_i \varepsilon_1\cdot C_i}$$

(

$$-\frac{d[H_2O_2]}{dt} = \frac{\phi P_0}{V} f\left[1 - \exp\left(-2.3\ell \sum_i \varepsilon_i\cdot C_i\right)\right]$$

(

P_0: incident light intensity,
ϕ: quantum yield of H_2O_2 photolysis
V: volume of irradiated solution:

As a consequence, when C_0 rises, f is strong reduced and the production of hydroxyl radica decreases.

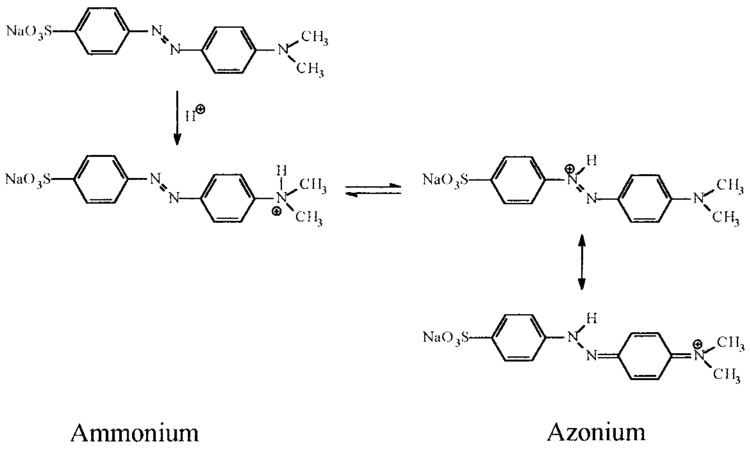


Fig. 5. Ammonium–azonium tautomerism of AO52.

3.4. *Influence of H_2O_2 concentration*

Until now, a very large excess of H_2O_2 in comparison to the dye was introduced in the solutions. Fig. 7 shows that the initial hydrogen peroxide concentration strongly modifies the rates degradation of the organic matter in the U H_2O_2 process.

An increase of the hydrogen peroxide co centration up to 5×10^{-2} mol l^{-1} leads to

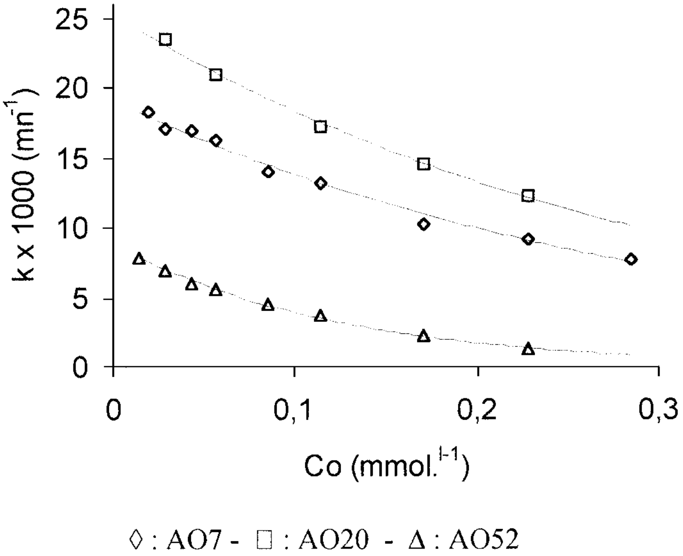


Fig. 6. Effect of the initial concentration of dyes on the kinetics of the degradation. 32°C; pH = 5.9; [dye]o = 5.7×10^{-5} mol l
$[H_2O_2]$o = 4.9×10^{-2} mol l^{-1}.

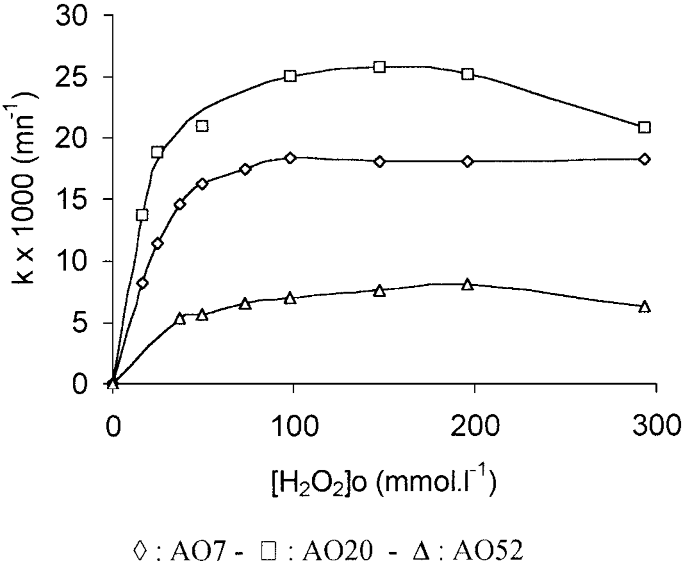


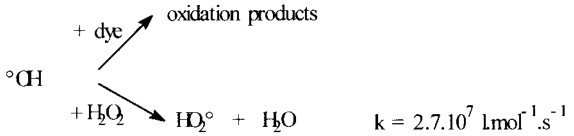
Fig. 7. Effect of the initial hydrogen peroxide concentration on the rate of oxidation of three azodyes. 32°C; pH = 5.9; [dye]o
5.7×10^{-5} mol l^{-1}; $[H_2O_2]$o = 4.9×10^{-2} mol l^{-1}.

Table 3
Numerical values of *a* and *b* coefficients

Dye	*a*	*b*	Correlation coefficient
AO7	19.1	3.2×10^3	0.9945
AO20	25.3	3.2×10^3	0.9984
AO52	8.3	6.7×10^3	0.9966

important rise in the solution discolouration rate. On the other hand, a further increase in the H_2O_2 concentration partly inhibits the oxidation rate. This behaviour is proof of the existence of an optimal dosage in H_2O_2.

We must underline the fact that hydroxyl radicals produced upon photolysis of hydrogen peroxide can react with dye molecules, but also with an excess of H_2O_2.



At low hydrogen peroxide concentrations, formation of °OH is the kinetic determining step. H_2O_2 cannot generate enough hydroxyl radicals and the oxidation rate is logically slow. Further, most of free radicals are directly consumed by the dye. In the presence of high concentration of peroxide, we could expect that more °OH radicals would be produced. However these radicals preferentially react with the excess of H_2O_2. Th undesirable reaction competes with the destru tion of the dye chromophore.

3.5. Influence of the azo-hydrazone tautomerism on the reaction rate

In the present study we tried to find the expe mental conditions to obtain an optimal d colouration rate. However, except in acidic medi the relative constants k_{AO20}/k_{AO7} and k_{AO52}/k_{A} do not markedly depend on values of the fo studied parameters. Thereby, we chose arbitra experimental conditions and we evaluated t degradation rates of a larger number of dyes. T corresponding kinetic constants are summarized Table 4. Dyes have been classified according their predominant tautomeric form in aqueo solution.

On the whole, dyes in which, the hydrazo form predominates, seem to be a little more sen tive to oxidation, but another parameter must al be taken into account. For instance, *k* of AO20 approximately one order of magnitude high than the kinetic constant of AR1 while, in bo cases, the hydrazone structure is dominant [16,1 therefore the nature of the auxiliary substitue attached to the aromatic nuclei certainly influenc reaction rates. Comparison of the reactivity AO5, AO6 and AO52 indicates that aminoaz benzenes are more resistant than hydroxyazo dy to attack by hydroxyl radicals. This result co firms the necessity of a labile *H* atom being ava able on a ring to obtain a noticeable oxidati

Table 4
Photochemical degradation of dyes: 32°C; pH = 5.9; [dye]o = 5.7×10^{-5} mol l^{-1}; [H_2O_2]o = 4.9×10^{-2} mol l^{-1}

Dyes with a predominant hydrazone form	$k\times1000$ (mn^{-1})	Dyes with a predominant azo form	$k\times1000$ (mn^{-1})
AO7	16.3	AO5	4.0
AO8	19.0	AO6	9.3
AO10	15.0	AO52	5.6
AO20	20.9		
AR1	10.8		
AR18	15.9		
AVi7	12.8		
MVi5	18.9		

rate. Consequently, the first step of the degradation probably corresponds, when this is possible, to the abstraction of this labile hydrogen atom.

4. Conclusion

In the present study we have found that monoazo dyes can be destroyed by the UV/H_2O_2 advanced oxidation process. The kinetics of the degradation depends on the dyes, on the hydrogen peroxide initial concentrations, and on the pH of the solution. Temperature does not have a significant influence. From a mechanistic point of view, we have found that the first step of the degradation is related to the abstraction of a labile *H* atom of the organic molecule. However kinetic considerations alone do not permit us to understand the whole mechanism of the degradation.

In further investigations, we will attempt to identify some key intermediate compounds. Among the various possibilities, phenolic derivatives are probably produced, which could be a source of trouble from an environmental point of view.

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