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“Critical” effect of hydrogen peroxide in photochemical oxidative decolorization of dyes: Acid Orange 8, Acid Blue 74 and Methyl Orange

A. Aleboyeh*, H. Aleboyeh, Y. Moussa

Laboratoire Groupe Sécurité Ecologie Chimique, Ecole Nationale Supérieure de Chimie de Mulhouse, Université de Haute Alsace, 3, rue Alfred Werner, 68093 Mulhouse, France

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Abstract

Advanced oxidation processes (AOPs) have proved very effective in treatment of the various hazardous organic pollutants in water. The photochemical decolorization of three dyes, namely Acid Orange 8 (AO8), Acid Blue 74 (AB74) and Methyl Orange (MO) was studied in the UV/hydrogen peroxide process by using a continuous photochemical reactor with a 15 W low pressure mercury lamp. Decolorization was complete in relatively short time and follows apparent first order kinetics with respect of dye concentration. The rate of disappearance of a given dye was monitored spectrophotometrically at the visible maximum absorption wavelength. It was found that the rate of decolorization rises by increasing the initial dosage of H_2O_2 up to a “critical” value at which it is maximum and beyond which it is inhibited. A simple reactions pathway, describing adequately the process, has been studied. Based on this reaction schema, we have established a mathematical relation between the apparent rate constant of the dye removal and applied H_2O_2 dosage presented by the ratio of its initial mass concentration to that of the dye. The rate constant values obtained by model for the three dye solutions are in good agreement with the experimental data. The model parameters have been determined.

Keywords: Dye; Decolorization; UV/H_2O_2; Kinetic; AOP; Hydroxyl radicals

1. Introduction

Synthetic dyes are used extensively in numerous industrial processes including textile dyeing. In the dyeing and finishing processes of textile manufacturing plants, a considerable amount of wastewater containing residual dyes is generated. Some of them are toxic, very difficult to degrade biologically and therefore cannot be treated efficiently using conventional treatment procedures [1–3].

Combining UV radiation and hydrogen peroxide oxidation has been applied successfully in advanced oxidation processes (AOPs) to treat different pollutants in water [4–8].

Galindo and Kalt [9] demonstrated that the UV/H_2O_2 process is able to destroy totally the chromophore structure of azo dyes and the reaction rate of azo dyes depends on the basic structure of

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* Corresponding author. Tel.: +33-3-89-33-68-24; fax: +33-3-89-33-68-15.

E-mail address: a.aleboyeh@uha.fr (A. Aleboyeh).

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the molecule and on the nature of auxiliary groups attached to the aromatic nuclei of dyes. Colonna et al. [8] reported that UV irradiation in the presence of H_2O_2 leads to complete decolorization and mineralization of sulphonated azo and anthraquinone dyes.

The mechanism of dye destruction in AOPs is based on the formation of a very reactive hydroxyl radical ($^{\bullet}OH$), that, with an oxidation potential of 2.80 V [10,11], can oxidize a broad range of organic compounds. Such a process implies relatively simple reactions, such as UV photolysis of H_2O_2.

Furthermore, the UV/H_2O_2 process has the additional advantage of preventing any sludge formation during the different stages of the treatment. It can be carried out under ambient conditions and may lead to complete mineralization of organic carbon into CO_2 [7]. In spite of all its intrinsic advantages, to render AOP competitive with other processes, it is essential that its application represents a low cost operation, which basically implies a careful and continuous control of H_2O_2 concentration. The aim of the present work was to establish a mathematical relation between the rate constant of Acid Orange 8 (AO8), Methyl Orange (MO) and Acid Blue 74 (AB74) removal in the UV/H_2O_2 system and the initial amount of H_2O_2 presented by the ratio of its initial mass concentration to that of the dye. The parameters of the model were determined.

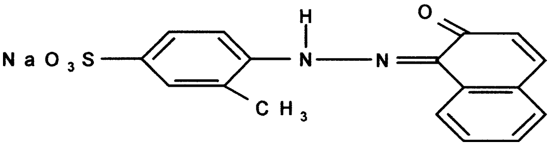
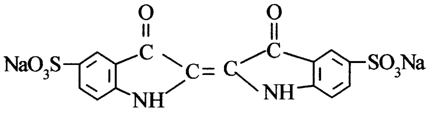
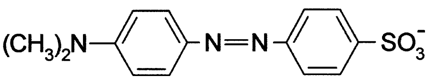
2. Materials and methods

AO 8 (65%), AB 74 (85%) and MO (95%) were obtained from Aldrich Chemical and used without further purification. Galindo [12] has analyzed these dyes by HPLC and has revealed that the dyes did not contain organic impurities in significant amounts. The impurities are mainly salt and water and they are not expected to influence decolorization kinetic. The characteristics of the dyes are given in Table 1.

Hydrogen peroxide (30% w/w) was obtained from Prolabo. The optical absorption spectrum of each dye was recorded on a V-530 UV/VIS spectrophotometer. The reactor used in this study is a continuous column circulation photoreactor fitted with a 15 W electric power low-pressure mercury lamp (Philips emission at 253.7 nm) as shown in Fig. 1. The radiant flux of this lamp was determined by means of the chemical actinometer hydrogen peroxide [13]. The incident photon flux was 6.1×10^{-6} Einstein s^{-1}. This irradiation frequency was selected because a number of papers have reported the efficient degradation of chemicals in water using the same emission (253.7 nm) produced by mercury arcs [14,15].

We determined the following maximum absorption wavelengths (λ_{max}): 488 for AO8, 610 nm for AB74 and 463 nm for MO. Absorption spectra of the dye solutions irradiated by UV light were recorded. It was found that the position of the

Table 1
Some physicochemical characteristics of the three commercial dyes treated

Dye	M_w (g mol^{-1})	λ_{max} (nm)	ε 10^{-3} (l mol^{-1} cm^{-1})	Structure
AO8	364	488	28.12	
AB74	466	610	22.33	
MO	327	463	26.05	

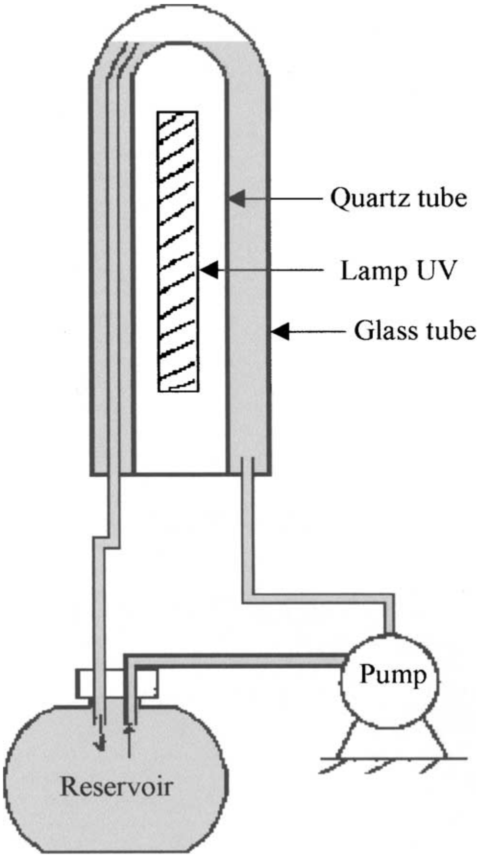


Fig. 1. Continuous circulation photochemical reactor.

maximum absorption wavelengths varied, depending on the solution concentration. In addition, no new absorption peaks occurred near the original maximum. Fig. 2 shows the spectral evolution upon photoirradiation for the dye AO 8 for the time: 0, 2, 5, 8, 10, 12 and 15 min. As a result, we can conclude that the absorption bands are not disturbed by intermediate oxidation products. Furthennore, the molar extinction (ε) of H_2O_2 varies between 15 and 25 (mol l^{-1} cm^{-1}) for the wavelength (λ) between 450 and 650 nm. As a result, the measurement error that might be caused by H_2O_2 in the mixture is low. The photolysis of blank samples containing the same dose of H_2O_2 without dye was carried out, so that the interference due to H_2O_2 could be eliminated. The concentrations of dye solutions irradiated by UV could also be determined by spectrophotometry.

The unit for continuous circulation reactor used in the experiments consisted of a 4.25 cm inner radius glass column with a 3.25 cm outer radius quartz tube. The UV lamp was fitted inside the central column.

A total of 2500 ml of dye solution in the reservoir was used for the treatment while the liquid level in the radiation column was kept constant at 1600 ml. The liquid inside the column was exposed to a 15 W UV lamp. The treated wastewater was returned to the reservoir and then left to circulate back to the reactor column at a constant flow rate of 3.5 l min^{-1}.

The following initial dye concentrations were selected: AO8: 18.2 mg l^{-1}; AB74: 23.3 mg l^{-1} and MO: 19.62 mg l^{-1}. Beer's law applies at these values (Fig. 3). Each selected amount of dye was dissolved in deionized water prior to use. The different initial H_2O_2 dosages were added to each dye solution to prepare the reaction mixtures. The initial pH was measured by a Schott Gerate pH meter CG817T in solution $(4.5 \leqslant pH \leqslant 5.5)$.

Dye decolorization was investigated by using the above reactor. At regular time intervals samples were collected and analyzed by UV/VIS to determine the decolorization rate.

Repeated operations were performed to examine the reproductivity of the results.

For the three dyes studied in this work the action of UV alone or H_2O_2 in the absence of UV irradiation was negligible after three days of treatment. Galindo and Kalt [16] have demonstrated that the photooxidation reactions are indeed not sensitive to small temperature changes in the range 22–45 °C, because the photochemically induced reactions often have a low activation energy.

3. Kinetic

Hydrogen peroxide concentration is an important parameter to adjust and control the decolorization of dyes in the UV/H_2O_2 reactor. Degradation of the color is due to the hydroxyl radicals generated upon photolysis of hydrogen peroxide [5,17], several studies in the past have proposed different reaction mechanisms for this photolysis. It is widely accepted that the main

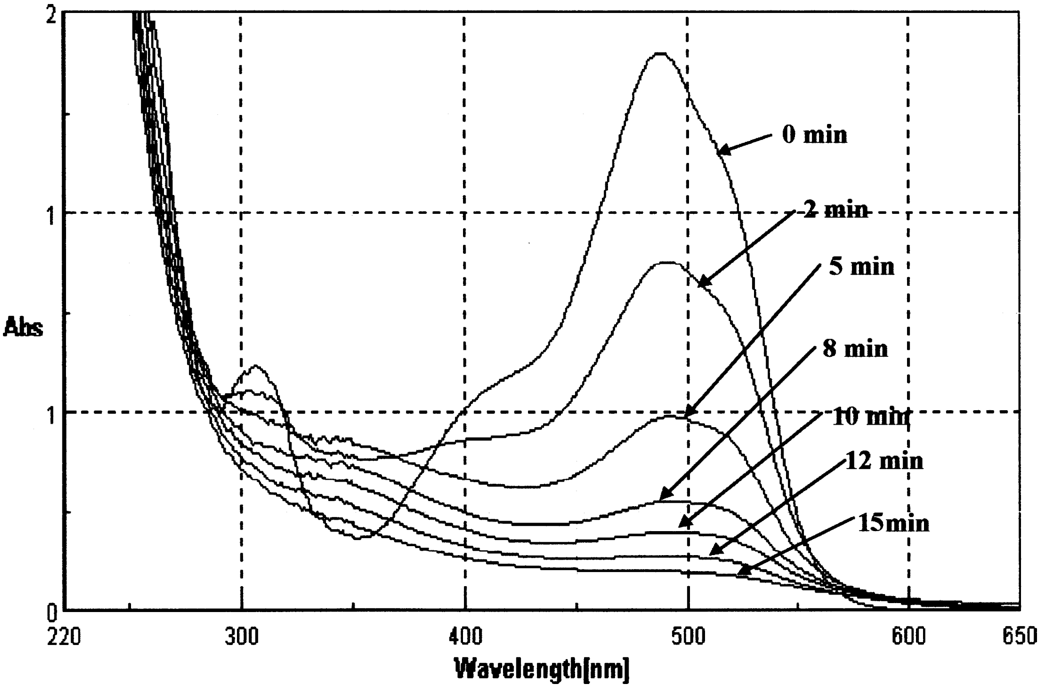


Fig. 2. Spectral evolution upon photoirradiation for the dye Acid Orange 8 for different time of radiation.

interaction between H_2O_2 with UV radiation and free radicals are well represented by reactions 1–6 [18].

Initiation

$$H_2O_2 + h\nu \overset{k_1}{\rightarrow} 2^\bullet OH \tag{1}$$

Propagation:

$$H_2O_2 + {}^\bullet OH \overset{k_2}{\rightarrow} {}^\bullet O_2H + H_2O_2 \tag{2}$$

$$H_2O_2 + {}^\bullet O_2H \overset{k_3}{\rightarrow} {}^\bullet OH + H_2O + O_2 \tag{3}$$

Termination:

$$^\bullet OH + {}^\bullet OH \overset{k_4}{\rightarrow} H_2O_2 \tag{4}$$

$$^\bullet O_2H + {}^\bullet O_2H \overset{k_5}{\rightarrow} H_2O_2 + O_2 \tag{5}$$

$$^\bullet OH + {}^\bullet O_2H \overset{k_6}{\rightarrow} H_2O + O_2 \tag{6}$$

The powerful oxidizing hydroxyl radicals react with dye molecules, resulting in the destruction of their intrinsic color.

Decomposition:

$$RX +^\bullet OH \overset{k_7}{\rightarrow} \text{Products} \tag{7}$$

$$RX +^\bullet O_2H \overset{k_8}{\rightarrow} \text{Products} \tag{8}$$

3.1. Modeling

Dye concentrations in effluent samples were determined by Beer's law, using the optical density (observed at the characteristic wavelength) and the molar extinction coefficient of the dye and a path length of 1 cm:

$$A = l.\varepsilon.C \tag{9}$$

A, Absorbency; l, path length (cm); ε: molar extinction coefficient (l mol^{-1} cm^{-1}); and C, dye concentration at time t (mol l^{-1}).

The primary and principal step for the UV/H_2O_2 degradation has been postulated as the initial attack by photon of H_2O_2 and the formation of $^\bullet OH$ radicals [Eq. (1)].

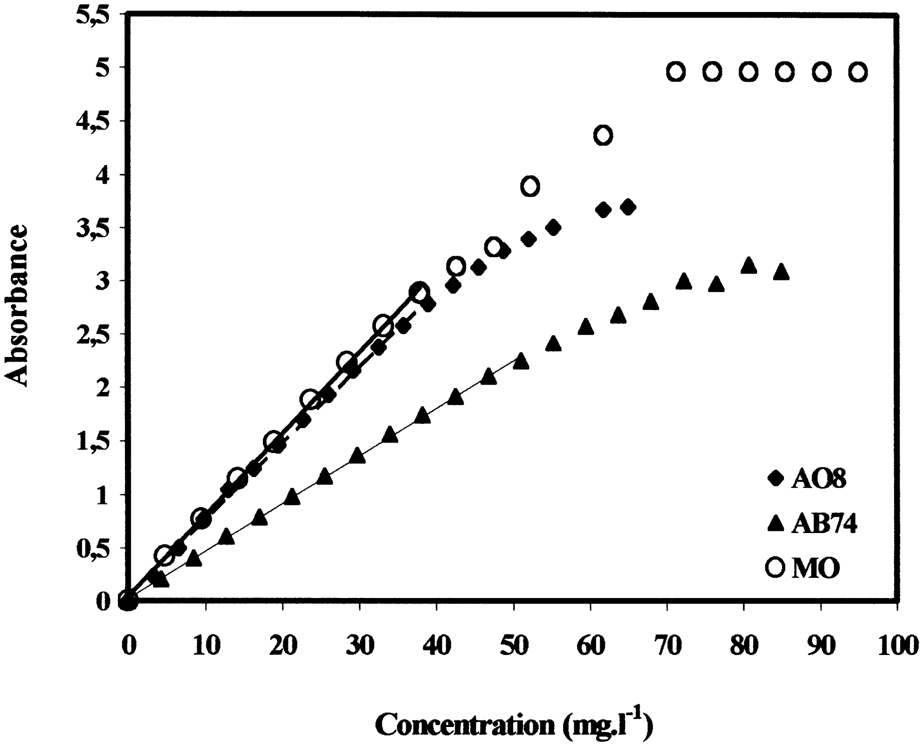


Fig. 3. Absorbance vs. concentration calibration curves for the dyes AO8, AB74, MO.

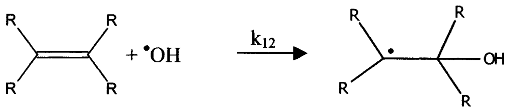
The •OH radicals is capable of oxidizing organic compounds mostly by hydrogen abstraction [Eq. (10)].

$$RH + {}^{\bullet}OH \xrightarrow{k_{10}} R^{\bullet} + H_2O \qquad (10)$$

This reaction generates organic radicals which by addition of molecular oxygen yield peroxyl radicals. These intermediates initiate thermal chain reactions of oxidative degradation leading finally to carbon dioxide, water and inorganic salts [Eq. (11)].

$$R^{\bullet} + O_2 \xrightarrow{k_{11}} RO_2^{\bullet} \rightarrow \rightarrow \text{Products} \qquad (11)$$

Electrophilic addition of •OH radicals to organic π systems constitutes another mechanism of oxidative degradation [Eq. (12)].



(12)

this reaction will lead to organic radicals and the subsequent reactions similar to those mentioned for hydrogen abstraction mechanism.

Finally, electron transfer to hydroxyl radicals [Eq. (13)] is interesting in the case where hydrogen abstraction or electrophilic addition reactions may be disfavored by multiple halogen substitution or steric hindrance [10].

$${}^{\bullet}OH + RX \xrightarrow{k_{13}} RX^{\bullet+} + {}^{-}OH \qquad (13)$$

according to the proposal of Spadaro et al. [19] only an addition of an •OH radical on an aromatic ring of molecules which do not contain a labile H atoms can occur. In the presence of labile H atom, abstraction of a H atom (carried by a nitrogen in the hydrazon from and by an oxygen atom in the azo form) competes with the addition of •OH on phenyl or naphthyl nucleus.

During the experiments, it is observed that a small amount of the color is degradable by alone UV irradiation and by using H_2O_2 in the absence of UV radiation [Eqs. (14) and (15)].

$$\text{Dye} + \text{hv} \xrightarrow{k_0} \text{Products} \quad (14)$$

$$\text{Dye} + H_2O_2 \xrightarrow{k_{15}} \text{Products} \quad (15)$$

Other reactions involved are given by [Eqs. (1)–(8)]. The global reaction of dye removal under UV/H_2O_2 process can be presented by:

$$\text{Dye} + H_2O_2 + h\nu \xrightarrow{k} \text{Products} \quad (16)$$

The photooxidation is supposed to be a pseudo-first order reaction with respect to dye concentration. The kinetic pathway of color degradation could be expressed as follows:

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = kt \quad (17)$$

where k is the global reaction apparent rate constant (min^{-1}); C, the dye concentration at a given time (mol l^{-1}); and t, the exposure time (min).

This equation, after integration with initial condition $C = C_0$ for $t = 0$, leads to:

$$\ln\frac{C}{C_0} = -kt \quad (18)$$

We can justify Eq. (19) by considering that the steady-state approximation may be applied for highly reactive intermediates such as $^{\bullet}OH$ and $^{\bullet}O_2H$ radicals.

$$k = a + \frac{bH}{1 + cH + dH^2} \quad (19)$$

where H is the relative concentration of H_2O_2 expressed as the mass ratio of the H_2O_2 concentration to that of the dye at time zero.

$$H = \frac{[H_2O_2]_0}{[\text{Dye}]_0} \quad (20)$$

a, b, c and d are the model parameters.

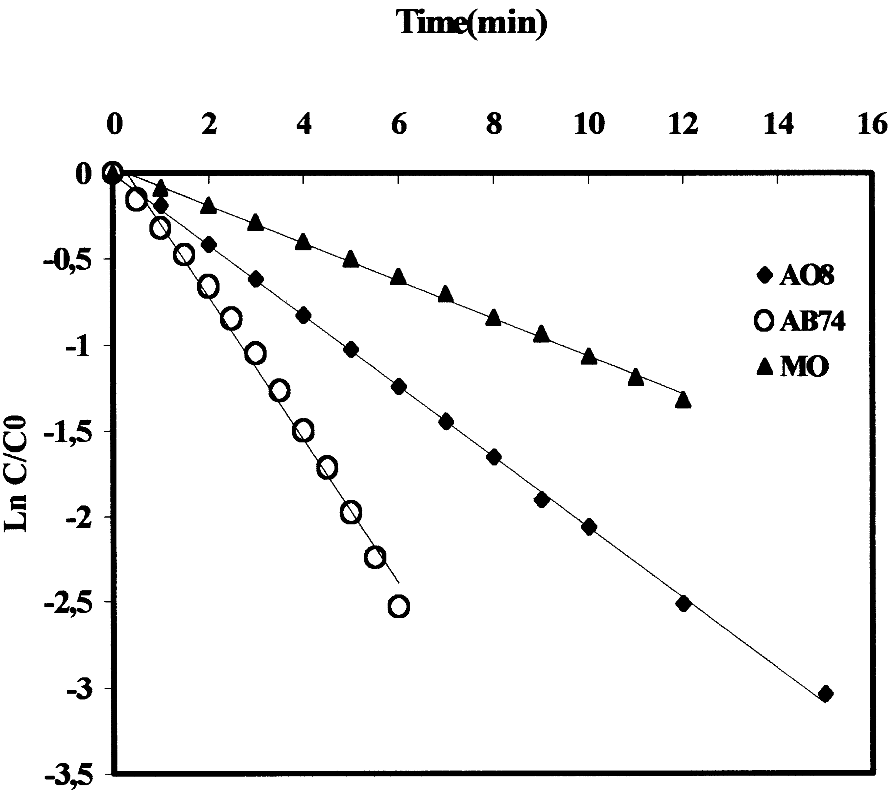


Fig. 4. First order plot of color degradation with time under the following experimental conditions. [AO8 = 18.2 mg l^{-1}, [AB74] = 23.3 mg l^{-1}, [MO] = 19.62 mg l^{-1}. [H_2O_2] = 2665.6 mg l^{-1}, $4.5 \leqslant \text{pH} \leqslant 5.5$, 2500 ml treated.

a and b depend to the rate of photon absorption, c and d depend to the constant k_2, k_3, k_7 and k_8.

If we present the observed value of the photodegradation rate constant in the absence of H_2O_2 by k_0. From Eq. (19) we can deduce:

$$k = a = k_0 \tag{21}$$

Table 2
Kinetic constants of three dyes under the following experimental conditions

Dye	k (min^{-1})	R^2
Acid Orange 8 (AO8)	0.2060	0.9993
Acid Blue 74 (AB74)	0.4182	0.9913
Methyl Orange (MO)	0.1098	0.9976

[AO8] 48.2 mg l^{-1}, [AB74] = 23.3 mg l^{-1}, [MO] = 19.62 mg l^{-1} and [H_2O_2] = 2665.6 mg l^{-1}, 4.5 ⩽ pH ⩽ 5.5, 2500 ml treated.

Eq. (19) can be presented as follows:

$$k = k_0 + \frac{bH}{1 + cH + dH^2} \tag{22}$$

4. Results and discussion

A typical first order plot of color degradation with time under UV irradiation is shown in Fig. 4. For each of the three dyes the color removal rate constants were evaluated using a linear regression. R^2 is the correlation coefficient that can explain the fitting extent of the function equation and the experimental data. k And R^2 values are given in Table 2. These R^2 values are superior to 0.99 in all cases and confirm the goodness of the assumed kinetics for the global decolorization reaction.

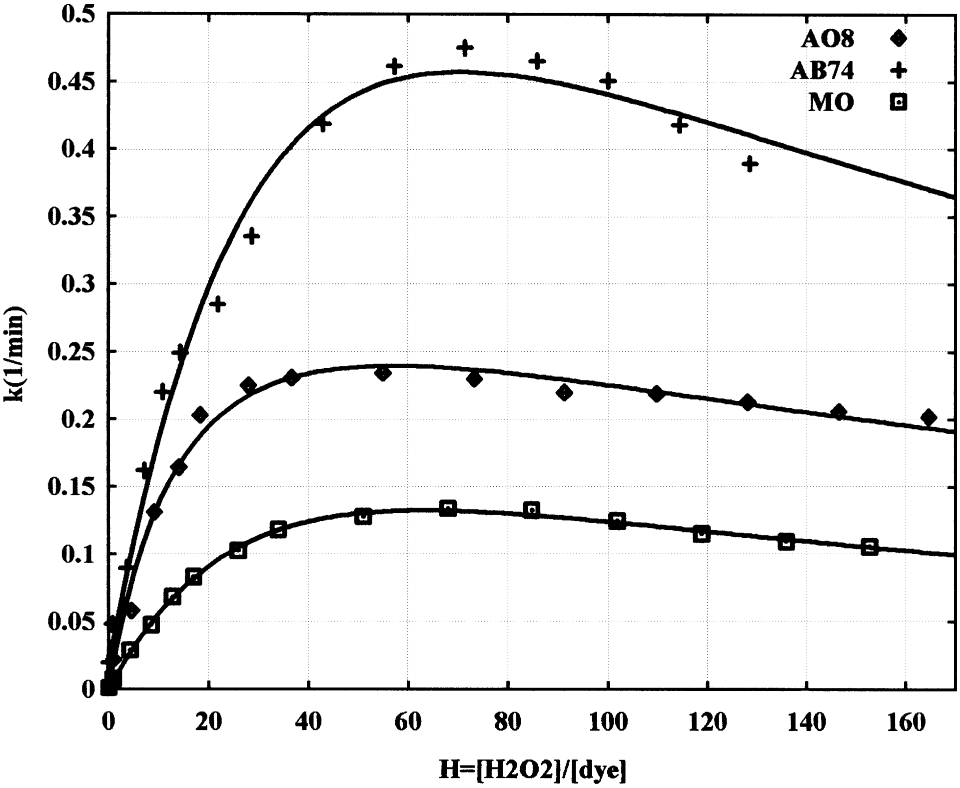


Fig. 5. First order decolorization rate constant of the dye as function of relative concentration of H_2O_2 to that of dye. The solid line represents a nonlinear regression fit to the data by use of Eq. (22). [AO8] = 18.2 mg l^{-1}, [AB74] = 23.3 mol l^{-1}, [MO] 19.62 mol l^{-1}, 4.5 ⩽ pH ⩽ 5.5, 2500 ml treated.

Table 3
Model parameters allowing to predict the first order decolorization rate constant of Acid Orange 8, Acid Blue 74 and Methyl Orange by Eq. (18)

Dye	σ	$k_{0\ (\mathrm{exp})}$ (min^{-1})	$k_{0\ (\mathrm{model})}$ (min^{-1})	b	c	d
AO8	0.009	0.0012	0.0017	0.0216±0.0020	0.0554±0.0098	0.0003
AB74	0.018	0.0195	0.0225	0.0199±0.0019	0.0165±0.0057	0.0001
MO	0.002	0.0008	0.0011	0.0067±0.0002	0.0191±0.0021	0.0002

σ Is the sum of the squared differences between the input data point and the function values, evaluated at the same place. $k_{0\ (\mathrm{exp})}$: k_0 experimental, $k_{0\ (\mathrm{model})}$: calculated by Eq. (22).

Results obtained with the model are in good agreement with the experimental data and are presented in Fig. 5.

Evaluations of model parameters are listed in Table 3. It is observed that the degradation of color increases with an increase in the initial mass ratio of H_2O_2, but a very high relative concentration of hydrogen peroxide retards the reaction.

From Fig. 5, it is observed that the k values shows a maximum around $H=70$, 65 and 55 for AB74, MO and AO8, respectively. These values are in good agreement with the experimental data of 71.36, 67.93 and 54.92. These different critical levels may be explained by the different molar extinction coefficients and structure [9]. Beyond these points, degradation of color decreases. This phenomenon could be explained by considering the two opposing effects of H_2O_2 in the photo-oxidation reaction, explained as follows:

1. When increasing quantities of H_2O_2 are added to the solution, the fraction of light absorbed by the photo-decomposition increases, and, consequently, so does its photolysis rate (reaction 1). More hydroxyl radicals are available for dye oxidation.
2. If additional of H_2O_2 is used, H_2O_2 acts as a scavenger of highly reactive OH free radicals to form oxygen and peroxyl radicals [Eq. (2)] which are much less reactive. In addition, $^\bullet$OH radicals, generated at high local concentration, will readily dimerize to H_2O_2 [Eq. (4)] [20]. As a consequence, there should be a favorable hydrogen peroxide concentration for the effective removal of dyes, corresponding to the maximum color degradation, so an optimum hydrogen peroxide concentration exists. Thus if H_2O_2 concentration is increased above this limiting value, competition for $^\bullet$OH can be anticipated. These predictions are in good agreement with the experimental data.

The model [Eq. (22)] allows to predict the first order decolorization global rate constant and to determine the most "effective level" of H_2O_2 at which the color degradation rate constant is maximum.

5. Conclusion

The impact of H_2O_2 initial concentration in color removal kinetics under UV/H_2O_2 process for three typical dyes was investigated. Our results prove that the pseudo-first order kinetic model is in good agreement with the experimental data. A set of parameters for the model depicting this degradation were determined. These parameters will naturally vary with the operating conditions, such as UV irradiation intensity, but also the chemical characteristics (such as dye structure, pH, concentrations...) of the effluents tested.

An increase in H_2O_2 concentration leads to a faster degradation up to a critical value; at a higher ratio the degradation process becomes slower.

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