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The Kinetic Study of the AZo Dye Decolourisation By Advanced Oxidation Process

Azam ALEBOYEH*[*] and Hamid ALEBOYEH

Ecole Nationale Supérieure de Chimie de Mulhouse, Université de Haute Alsace
3 rue Alfred Werner, 68093 Mulhouse, France. Tel: (+33) 3 89 33 68 24, Fax: (+33) 3 89 33 68 15.

ABSTRACT

In the present study, advanced oxidation treatment, UV/H_2O_2 was applied to decolourisation of Acid Orange8 (AO8). The UV radiation was carried out with a 15 W low-pressure mercury lamp. Kinetic model for the decolourisation of the dye was developed based on experimental results and known chemical and photochemical reactions. The observed kinetic reaction constant was determined and correlated as a function of H_2O_2 concentration. The rate of colour removal has been studied by measure of the absorbency at characteristic wavelength. The decolourisation reaction is pseudo-first order with respect to the dye concentration. The rate increases nonlinearly with increasing H_2O_2 concentration. Increasing the [H_2O_2] can increase the decolourisation rate of the dye, but there is an optimal hydrogen peroxide dosage at which the rate of the reacton is maximum.

Keywords: Acid Orange 8; kinetic; AOP; color removal; UV/H_2O_2

INTRODUCTION

The textile industry consumes considerable amounts of water during the dyeing printing and finishing operations. These effluents streams can be highly coloured and difficult to decolorize. Azo dyes represent the largest class of textile dyes in industrial use. Common treatment processes like adsorption and flocculation, are not efficient methods because they result in solid waste, thus creating other environmental problems requiring further treatment. Advanced Oxidation Processes (AOPs) ,which involve the in situ generation of highly potent chemical oxidants, such as the hydroxyl radical (ˑOH), have emerged [1] as an important class of technologies for accelerating the oxidation of a wide range of organic contaminants in polluted water and air. A partial list of these technologies includes: Homogeneous ultraviolet irradiation [2], either direct irradiation of the contaminant or photolytic oxidation mediated by hydrogen peroxide (UV/H2O2) and/or ozone (UV/H_2O_2/O_3 or UV/O_3), Heterogeneous photo catalysis using semiconductor catalysts (UV/Ti O_2) [3].

Combined UV and hydrogen peroxide oxidation, has been successfully applied to the treatment of the various water pollutants [4-7]. Mercury lamps emitting at 254 nm being the most commonly used in order to dissociate H_2O_2 into hydroxyl radicals which are very powerful oxidizing species. These reactive radicals can decompose and even mineralize the organic contaminates with high efficiency [8, 9]. The main advantages of this process are that no additional disposal problems are generated after the completion of the above treatment and they are non-selective to a very broad range of chemicals.

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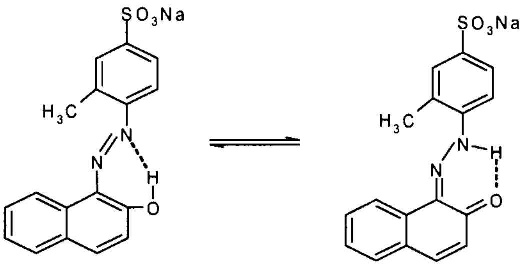
[*] Corresponding author: E-mail: A.Aleboyeh@uha.fr

The aim of this study was to propose a kinetics model for the decolourisation of AO8 by UV/H_2O_2 process. We have applied the steady state approximation, for highly reactive intermediates such as $^\bullet OH$ and $HO_2^\bullet$ radicals. A kinetic model for the decolourisation of dye was developed, which is based on experimental results as well as on a reaction kinetic mechanism of photolysis of H_2O_2 The results obtained by this model are in good agreement with the experimental data.

MATERIALS AND EXPERIMENTAL METHODS

Acid Orange 8 (65%), was obtained from Aldrich Chemical and used without further purification. The characteristics of the dye are as following:
$M_w = 364$ (g.mol^{-1}); $\lambda_{max} = 488$ (nm); $\varepsilon = 28.12 x 10^3$ (l.mol^{-1}.cm^{-1}) and structure:



Azo form Hydrazone form

Hydrogen peroxide (30% w/w) was obtained from Prolabo. The optical absorption spectra of dye were determined by a V-530 UV/VIS spectrophotometer. The reactor used in this study is a continuous column circulation photo reactor fitted with a 15 Watt electric power, low-pressure mercury lamp (Philips emission at 253.7 nm) reported in our recent work [10] (Figure 1).

The radiant flux of this lamp was determined by means of the chemical actinometer hydrogen peroxide [11]. The incident photon flux was $6.1x10^{-6}$ 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[12-13].

Absorption spectra of the dye solutions irradiated by UV light were recorded. We have determined the following maximum absorption wavelength (λ_{max}): 488 nm for AO8 dye. This peak accounts for the orange colour of solutions and can be attributed to the n-π* transition of the non-bonding nitrogen electrons to the anti banding π* group orbital of the double bond system and it is used to monitor the decolourisation of dye. In the UV region, there is a second group of bonds, with an increasing absorbency towards lower wavelengths, characteristic of aromatic rings. We have observed that the position of the maximum absorption wavelengths varied, depending on the solution concentration. In addition, no new absorption peaks occurred near the original maximum (Figure 2). As a result, we can conclude that the absorption bands are not disturbed by intermediate oxidation products.

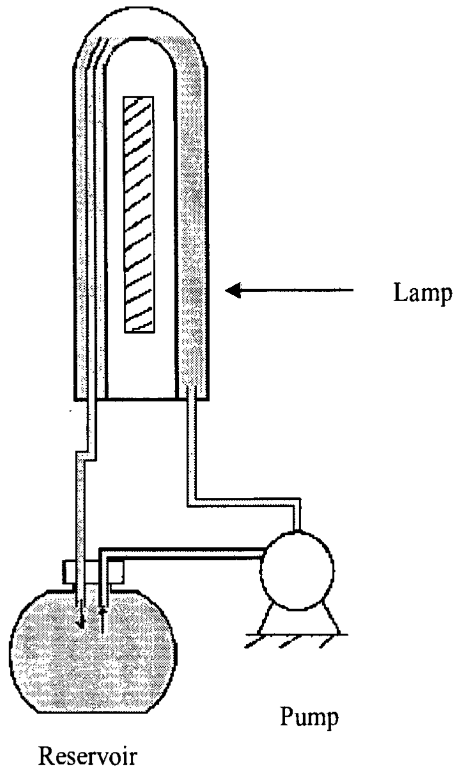


Figure 1. Continuous circulation photochemical reactor.

The concentration of the residual dye in solution were calculated by Beer Lambert law using the optical density and molar extinction observed at the characteristic wavelength (λ= 483 nm).

$$A = l.\varepsilon.C$$

A: Absorbency, *l*: Path length (cm).
ε: Molar extinction coefficient. (l.mol^{-1}.cm^{-1}), C: Dye concentration at time t. (mol.l^{-1}).

A total of 2500 ml of dye solution was treated while the liquid level in the radiation column was kept constant at 1600 ml. 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}.

Selected dye quantity was dissolved in deionised water prior to use. A large excess of hydrogen peroxide in comparison to the dye was added to this solution so that [H_2O_2] could be considered as constant during the whole experiment. The pH was measured by a Swott Gerate pH meter CG817T.

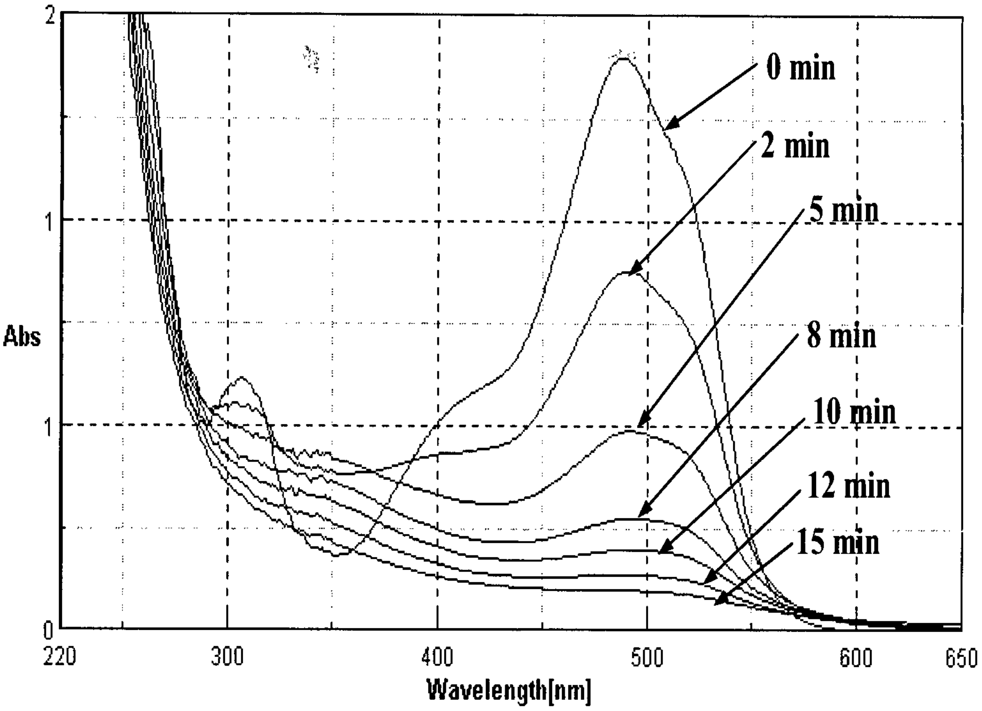


Figure 2. Spectral evolution upon photo irradiation for the dye Acid Orange8.

RESULTS AND DISCUSSION

At regular time intervals samples were collected and analyzed by UV/VIS spectrophotometer to determine the decolourisation rate. The action of UV alone or H_2O_2 in the absence of UV irradiation was negligible after three days of treatment. Decolourisation rate follows pseudo-first order kinetics with respect to dye concentration up to 95% of the colour removal. After this value, the data points deviate from linearity (Figure3). The second order rate constant has been calculated (1.32×10^9 $l.mol^{-1}.sec^{-1}$).

The removal and eventual mineralization of organic contaminants through advanced oxidation processes can be complex and involves a number of elementary chemical steps. The overall kinetics or rate of removal of a specific component and even the reduction of the total organic carbon (TOC) content can often be described by simple rate expression.

The catalytic effect of hydrogen peroxide can be explained by the chain reaction mechanism proposed by Baxendale and Wilson [14]. The kinetic model for decolourisation of AO8 was modelled by the following simple mechanism:

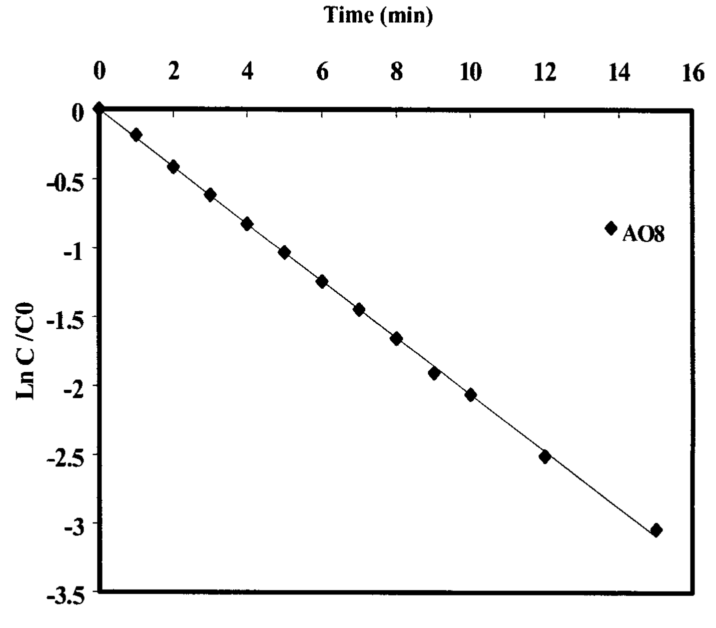


Figure 3. First-order plot of colour degradation with time under the following experimental conditions: [AO8] =18.2 mg.l-1, [H2O2] =2665.6 mg.l-1, 2500 ml treated.

$H_2O_2 + h\upsilon$	$2^{\bullet}OH$	$r_1=k_1\,[H_2O_2]$
$^{\bullet}OH + H_2O_2$	$HO_2^{\bullet} + H_2O$	$r_2=K\ [H_2O_2]\,[^{\bullet}OH]$
$2^{\bullet}OH$	H_2O_2	$r_3=k_3\,[^{\bullet}OH]^2$
$^{\bullet}OH + HO_2^{\bullet}$	$O_2 + H_2O$	$r_4=k_4\,[^{\bullet}OH]\,[HO2^{\bullet}]$
$^{\bullet}OH$ + dye	P	$r_5=k_5\,[^{\bullet}OH]$ [Dye]
$HO_2^{\bullet}$ + dye	P	$r_6=k_6\,[HO_2^{\bullet}]$ [dye]
$HO_2^{\bullet} + H_2O_2$	$^{\bullet}OH + H_2O + O_2$	$r_7=k_7\,[HO_2^{\bullet}]\,[H_2O_2]$
Overall reaction		
H2O2 + dye +hv	P	r= k [H2O2] [dye] = k_{ap}[dye] r= r5+r_6

We can suppose: *[dye] = C, [H_2O_2] = C'* and $H = \frac{C'}{C}$

A steady-state analysis of this general mechanism yields the following expressions:

For $^{\bullet}OH$; $2r_1 + r_7 = r_2 + 2r_3 + r_4 + r_5$

For $HO_2^{\bullet}$; $r_2 = r_4 + r_6 + r_7$

$$[^{\bullet}OH] = \frac{2k_1H}{k_2H + k_5}$$

$$[^{\bullet}HO_2] = \frac{2k_1k_2H^2}{(k_2H + k_5)(k_6 + k_7H)}$$

For the dye decolourisation reaction; $k_{ap}C$= k5C[•OH] +k6C[HO2•]

k_{ap}= k5[•OH] +k6[HO2•]

$$k_{ap} = k5 \times \left(\frac{2k_1H}{k_2H + k_5}\right) + k6 \times \left(\frac{2k_1k_2H^2}{(k_2H + k_5)(k_6 + k_7H)}\right)$$

$$k_{ap} = a + \frac{b.H}{1 + cH + dH^2}$$

Where: $a = 2k_1\left(\frac{k_2k_6 + k_7k_5}{k_2k_7}\right)$

$$b = 2k_1 - \frac{2.k_1(k_5k_7 + k_2k_6)^2}{k_2k_5k_6k_7}$$

$$c = \frac{k_2k_6 + k_5k_7}{k_5k_6} \quad \textit{and} \quad d = \frac{k_7k_2}{k_5k_6}$$

Our experimental results show that the rate constant increases with increasing H_2O_2 concentration up to a critical value. Beyond this point, degradation of colour is inhibited. The increased photolysis of H_2O_2 at higher concentrations may be counterbalanced by $^{\bullet}OH$ scavenging by H_2O_2.

Comparison between model prediction and observed data appears that the model closely predicts the experimental data for k_{ap} values (table1 and Figure 4).

Table 1. Apparant and calculated Kinetic constants of dye ; [AO8] = 5×10^{-5} mol.l^{-1}.

H=H_2O_2/AO8 (mol.l^{-1}/mol.l^{-1})	k $_{ap}$ (min^{-1})	k $_{cal}$ (min^{-1})
0.00	0.0012	0.0017
9.74	0.0217	0.0209
49.04	0.0581	0.0578
98	0.1311	0.1305
150.37	0.1642	0.1598
195.89	0.2029	0.2019
299.34	0.2251	0.2195
392.20	0.2305	0.2315
588.19	0.2342	0.2349
784.29	0.2300	0.2295
978.36	0.2200	0.2205
1176.49	0.2191	0.2188
1372.49	0.2131	0.2102
1568.59	0.2060	0.1959
1765.01	0.2020	0.2005

CONCLUSION

The impact of H_2O_2 in colour removal of Acid Orange8 by UV/H_2O_2 process was investigated. It was found that the rate of decolourisation increases with increasing the initial concentration of H_2O_2 up to 0.04 mol.l^{-1} at which it reaches a maximum and beyond which it is inhibited. A kinetic model for the decolourisation of dye was developed, which is based on experimental results as well as on a reaction kinetic mechanism of photolysis of H_2O_2 The model is able to predict the decolourisation rate as a function of the relative concentration of H_2O_2 to that of dye in good agreement.

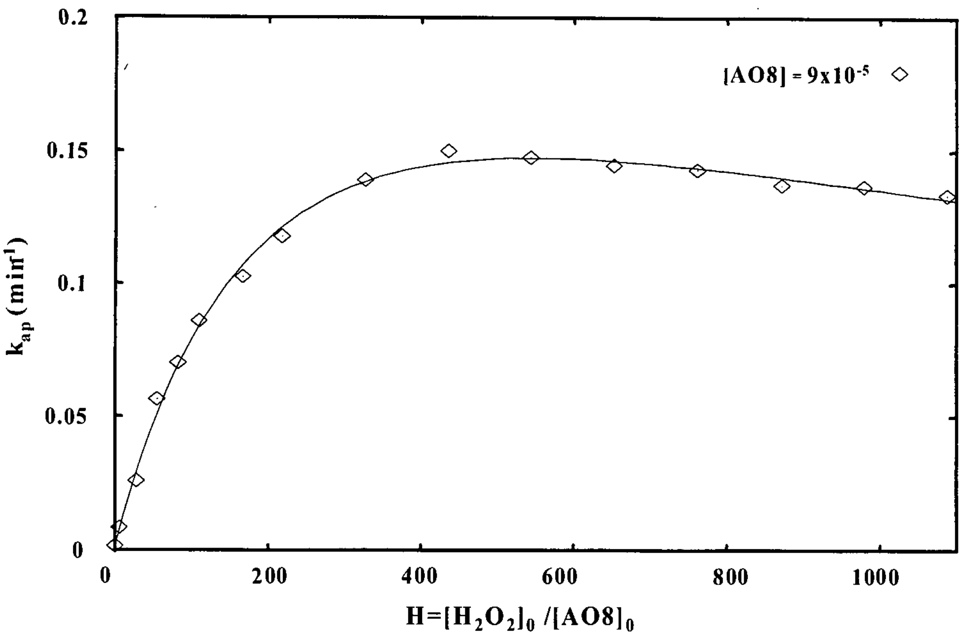


Figure 4. First order decolourisation rate constant of the dye AO8 as a function ofrelative concentration of H2O2 to that of dye. The solid line represents a nonlinear regression fit to the data.

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