

Effects of gap size and UV dosage on decolorization of C.I. Acid Orange 7 by UV/H₂O₂ process

Aleboye Azam*, Aleboye Hamid

Laboratoire Génie des Procédés de Traitement des Effluents, Ecole Nationale Supérieure de Chimie de Mulhouse,
Université de Haute Alsace, 3, rue Alfred Werner, 68093 Mulhouse, France

Received 8 June 2005; received in revised form 29 September 2005; accepted 4 October 2005
Available online 17 November 2005

Abstract

Wastewater from textile processing plants can be highly colored and difficult to decolorize. During the past few years attention has been drawn to chemical techniques that could be used to textile wastewater decolorization. A crucial feature in designing such systems is the optimization of operating conditions. In the present study, advanced oxidation treatment, the UV/H₂O₂ process has been applied to decolorization of the azo dye C.I. Acid Orange 7 (AO7) in aqueous solution in a batch photo reactor. The effects of the reactor gap size and UV dosage on decolorization of dye have been investigated. The method of study involved monitoring the rate of dye solution decolorization during irradiation by a low-pressure mercury lamp and varying gap size and volume of the reactor. The rate of color removal was studied by measuring of the absorbance at characteristic wavelength. The gap size of the reactor was adjusted by different depths of the reactor. The results of this study showed that the removal efficiency of AO7 is optimal with 0.3 cm gap size and 83.33 W l⁻¹ of UV dosage.

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Keywords: AOP; C.I. Acid Orange 7; Decolorization; UV/H₂O₂; Reactor gap size

1. Introduction

Colored wastewater from textile processing plants can be highly colored and difficult to decolorize. This is an environmental problem for the dyestuff manufacturing and textile industries. Azo dyes represent the largest class of textile dyes in industrial use, accounting for 50% of all commercial dyes [1]. They are characterized by nitrogen-to-nitrogen double bonds (N=N). However, large amounts of azo dyes remain in the effluent after the completion of dyeing process. Consequently, the textile wastewaters are heavily colored with large variation in chemical composition.

Due to the large number of aromatics present in these molecules and the stability of dyes, most azo dyes are non-biodegradable [2,3] and conventional treatment methods are ineffective for decolorization and degradation. 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 ($\cdot\text{OH}$), have emerged [4] as an important class of technologies for accelerating the oxidation of a wide range of organic contaminants in polluted water. A partial list of these technologies includes: homogeneous ultraviolet irradiation, either direct irradiation of the contaminant or photolytic oxidation mediated by hydrogen peroxide (UV/H₂O₂) and/or ozone (UV/H₂O₂/O₃ or UV/O₃), heterogeneous photo catalysis using semiconductor catalysts (UV/TiO₂) [5].

Combining UV radiation and hydrogen peroxide oxidation has been applied successfully in advanced oxidation processes to treat different pollutants in water [6–11]. The mechanism of dye destruction in UV/H₂O₂ process is based on the formation of a very reactive hydroxyl radical ($\cdot\text{OH}$), that, with an oxidation potential of 2.80 V [5], can oxidize a broad range of organic compounds. In comparison with other AOP's, such as Fenton, ozone, UV/O₃, UV/TiO₂, etc., the photolysis of hydrogen peroxide shows some advantages, such as the complete miscibility of H₂O₂ with water, the stability and commercial availability of hydrogen peroxide, no phase transfer problems and lower

* Corresponding author. Tel.: +33 3 89 33 68 24; fax: +33 3 89 33 68 15.
E-mail address: A.Aleboye@uha.fr (A. Azam).

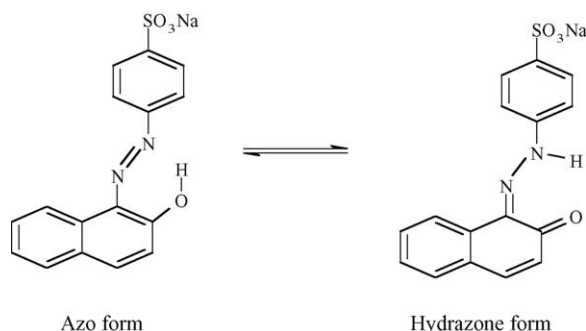
investment costs. It can be carried out under ambient conditions and may lead to complete mineralization of organic carbon into CO₂ [12]. Several studies have been reported about the successful application of the UV/H₂O₂ process on the Acid Orange 7 dye removal [12,13]. However, studies on reactor configuration effect are scarce.

We have already reported the kinetics of oxidative decolorization of C.I. Acid Orange 7 dye by UV/H₂O₂ process. The effects of initial dye concentration, H₂O₂ dosage and pH on the decolorization reaction rate have been studied [14]. The rate of color degradation increases with increasing concentrations of H₂O₂ up to a threshold value, above which it declines exhibiting typical inhibition. The purpose of this study is to conduct experimental investigation concerning the decolorization of C.I. Acid Orange 7 (AO7) azo dye solutions in a batch photochemical reactor. We have evaluated the effect of the reactor gap size and the unit UV dosage on the rate of the dye decolorization reaction. The calculated pseudo-first order reaction rates were used for the comparison of the decolorization efficiency between different reactors.

2. Materials and experimental methods

The 4-(2-hydroxy-1-naphthylazo) benzene sulfonic acid sodium salt, commonly named C.I. Acid Orange 7 (90%) was obtained from Aldrich chemical. The dye solutions were prepared by dissolving a defined quantity of the dye in deionised water. The characteristics of the dye are as follows:

$M_w = 350 \text{ g mol}^{-1}$, $\lambda_{\text{max}} = 483 \text{ nm}$, $\varepsilon_{\lambda_{\text{max}}} = 19.43 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$, $\varepsilon_{253.7} = 11.96 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ and structure:



In solution, AO7 exists as an azo (A)–hydrazone (H) mixture. Factors such as solvent play a significant part in determining the tautomeric equilibrium. The hydrazone form is usually more stable [15].

Hydrogen peroxide (30%, w/w) was obtained from Prolabo. The optical absorption spectrum of each dye concentration was determined by a UV–vis spectrophotometer model V-530. Irradiation was performed by using a 15 W low-pressure mercury lamp (emission at 253.7 nm), which was put 5 cm above a batch photo reactor. The radiant flux of this lamp was determined by means of the chemical actinometer hydrogen peroxide [16]. The incident photon flux was $6.1 \times 10^{-6} \text{ Einstein s}^{-1}$. In order to study the effects of reactor gap size and UV dosage on the rate of the decolorization reaction, the liquid film thickness exposed on the UV irradiation was varied from 0.3 up to 4.6 cm. The

Table 1
Characteristics of the reactors used

Reactor	Gap size (cm)	Volume (l)	Average light intensity (W l^{-1})
R1	0.3	0.18	83.33
R2	1	0.44	34.09
R3	1.80	0.62	24.19
R4	2.60	1.10	13.64
R5	3.50	1.52	9.82
R6	4.60	2.08	7.21

reactor volume changed between 0.18 and 2.08 l (Table 1). The concentration of the residual dye in solution 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.

3. Results and discussion

Absorption spectra of the dye solutions irradiated by UV light were recorded. The maximum absorption wavelength (λ_{max}) for C.I. Acid Orange 7 dye was determined to be 483 nm. This peak accounts for the orange color of solutions and can be attributed to the $n-\pi^*$ transition of the non-bonding nitrogen electrons to the anti bonding π^* group orbital of the double bond system and it is used to monitor the decolorization 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 (Fig. 1). As a result, we can conclude that the absorption bands are not disturbed by intermediate oxidation products.

We have set the initial dye concentration to $5 \times 10^{-5} \text{ mol l}^{-1}$. A selected quantity of AO7 was dissolved in deionised water prior to use. The initial H₂O₂ dosages of the $4.89 \times 10^{-2} \text{ mol l}^{-1}$ (optimum value) were added to each dye solution to prepare the reaction mixtures. The initial pH was measured by a SCHOTT GERATE pH meter CG817T in the solution (≈ 5.5). At regular time intervals samples were collected and analyzed by UV–vis spectrophotometer to determine the decolorization rate.

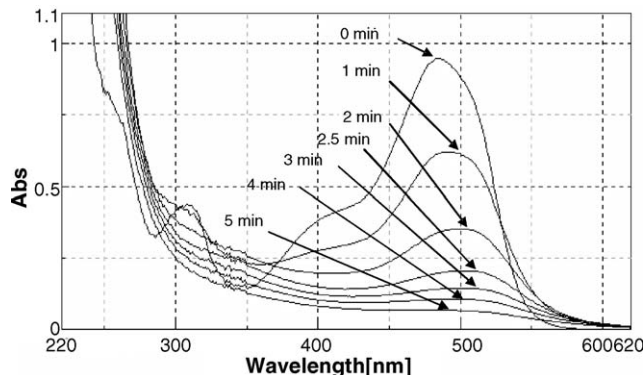


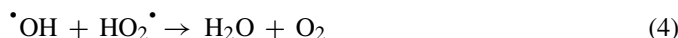
Fig. 1. Spectral evolution upon photo irradiation for different time of radiation in reactor R2.

3.1. The effect of initial hydrogen peroxide concentration

The action of UV alone or H_2O_2 in the absence of UV irradiation was negligible after three days of treatment. When hydrogen peroxide is applied simultaneously with UV irradiation there is a drastic increase in the decolorization reaction rate. In our recent work we have reported the effect of initial H_2O_2 dosage on the decolorization of the C.I. AO7 dye. The rate of dye degradation increases with increasing concentrations of H_2O_2 up to a threshold value, above which it declines, exhibiting typical inhibition. This phenomenon could be explained by considering the two opposing effects of H_2O_2 in the photo oxidation reaction. 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. More hydroxyl radicals are available for dye oxidation (reactions (1) and (2)).



If additional of H_2O_2 is used, H_2O_2 acts as a scavenger of highly reactive $\cdot OH$ free radicals to form peroxy radicals and oxygen (reactions (3) and (4)), which are much less reactive. In addition, $\cdot OH$ radicals, generated at high local concentration, will readily dimerize to H_2O_2 (reaction (5)).



So that H_2O_2 in excess contributes to the $\cdot OH$ scavenging capacity and reduces the efficiency of the color degradation. When the relative quantity of H_2O_2 to that of the dye in the mixture is higher than the “most effective level”, which yields maximum dye degradation, a competition for $\cdot OH$ is anticipated [14].

3.2. The effect of the reactor gap size

In order to describe the experimental results, we have calculated the decolorization percentage as follow:

$$D\% = (1 - (C/C_0)) \times 100$$

where C and C_0 are dye concentrations at time t and zero.

In this set of experiments, six different gap sizes were applied to the decolorization of C.I. AO7 dye. The average light intensity, which was varied by gap size, was calculated by dividing the UV intensity by various reactor volumes (Table 1).

In Fig. 2, the decolorization percentage as a function of the UV irradiation time is illustrated for each reactor. The highest removal percentage was obtained with the smallest gap size (0.3 cm). As we can observe, 95% color removal was obtained in about 3 min for an irradiation film of 0.3 cm against 15 min to reach 90% color removal for 4.6 cm of the solution depth. Fig. 3 shows the retention time needed for 90% color removal of the C.I. AO7 dye for different reactors gap sizes. When reactor gap

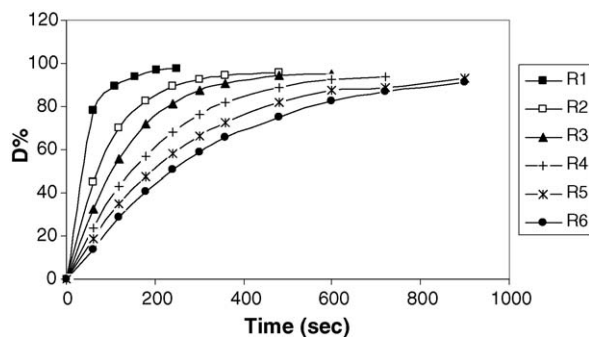


Fig. 2. Color removal percentage ($D\%$) of C.I. AO7 vs. time in different reactors used.

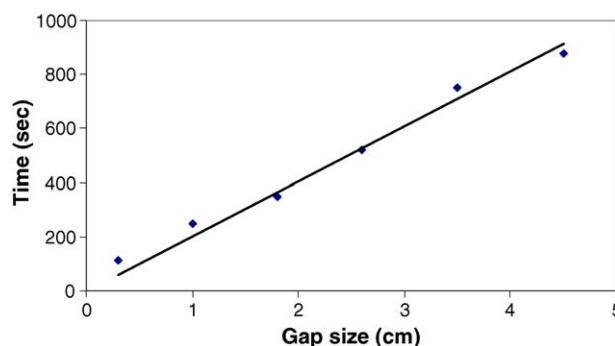


Fig. 3. Retention time needed for 90% color degradation as a function of gap size.

size is increased from 0.3 up to 4.6 cm, retention time increases from 3 up to 15 min.

The semi-logarithmic graphs of the C.I. AO7 concentration in the different reactor versus UV irradiation time (Fig. 4) yield straight lines for reaction time $t < 10$ min, an indication of pseudo-first order reaction with respect to C.I. AO7 concentration. For each dye solution, color removal apparent rate constants (k) were evaluated using a linear regression of the plot of color degradation with time ($\ln C/C_0 = -kt$). The values of the correlation coefficients (R^2) confirm the goodness of the assumed kinetics for the UV/ H_2O_2 photo catalytic decolorization reactions of this dye (in all cases $R^2 > 0.99$).

As we can see from Fig. 5, the apparent rate constants decrease by increasing the depth of the film irradiated by UV.

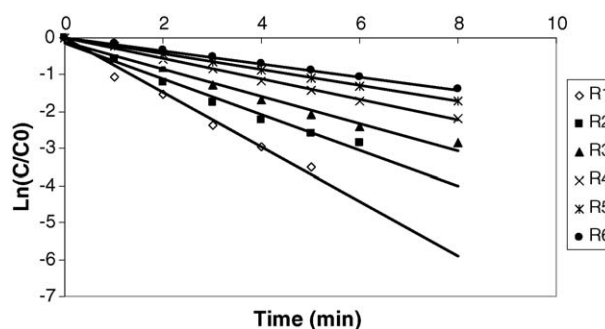


Fig. 4. First order plot of C.I. AO7 color degradation with time under various gap sizes.

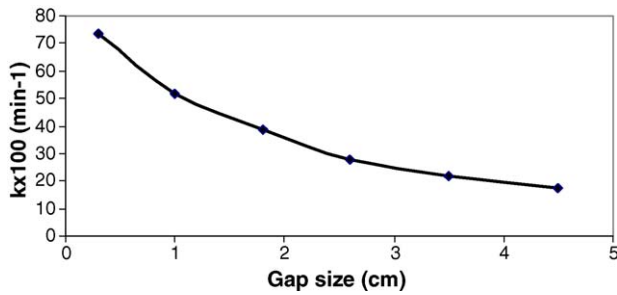


Fig. 5. Pseudo-first order rate constant as a function of gap sizes.

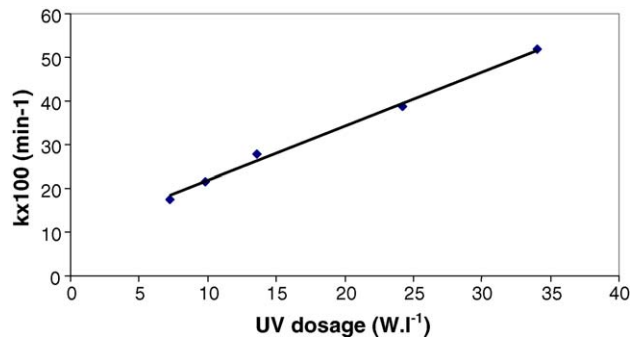


Fig. 7. Pseudo-first order rate constant as a function of volumetric UV dosage.

The decolorization reaction in reactor R1 is 4.18 times faster than in reactor R6. These results can be explained as follows:

1. The mechanism of dye destruction in the UV/H₂O₂ system is based on the formation of a very reactive hydroxyl radical produced by H₂O₂ photolysis (reaction (1)), which, with an oxidation potential of 2.80 V can oxidize C.I. AO7 dye molecules (reaction (2)). The result of this reaction is the destruction of color.
2. UV light absorbed by H₂O₂ molecules is an important parameter, which can affect the azo dye decolorization in the UV/H₂O₂ process. UV irradiates H₂O₂ molecules while the wastewater absorbs UV light at the same time. The extinction coefficients (ϵ) of the dye at 253.7 nm is high ($11.96 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$), so that an increase in the reactor gap size induces a rise of the internal optical density. Consequently, as more UV light absorbed by wastewater, the solution becomes more and more impermeable to UV radiation. The hydrogen peroxide molecules on the outer layer of the lamp receive less intensity of UV irradiation. This has been verified by studying of the photolysis of H₂O₂. Hydrogen peroxide residual concentration was determined by absorption spectrophotometry method. As we can see from Fig. 6 the rate of H₂O₂ photolysis decreases by increasing reactor gap size so less free radicals can be formed and the color degradation rate decreases.
3. On the other hand, at a fixed hydrogen peroxide dosage, the decolorization rate is significantly affected by UV dosage. The unit UV dosage, which applied a UV power input per certain reaction volume, was calculated in W l⁻¹ and presented in Table 1. An approximately linear relationship between observed pseudo-first order reaction constants (k) and unit

UV dosage is shown in Fig. 7. Similar results have been reported by Shu et al. [17]. The k values increase with unit UV dosage. By increasing UV dosage from 7.21 up to 83.33 W l⁻¹, the k values increase from 17.52×10^{-2} up to $73.37 \times 10^{-2} \text{ min}^{-1}$, respectively. Theoretically, the higher C.I. AO7 dye decolorization rate in higher UV dosage is in the result of faster formation of OH free radicals (reactions (1) and (2)). Therefore, the smaller gap size batch reactor has better decolorization capability and efficiency.

4. Conclusion

It can be concluded that the UV/H₂O₂ process using a batch reactor provides good performance in the decolorization treatment of C.I. Acid Orange 7 dye in water. The observations of these investigations clearly demonstrated the importance of choosing the optimum photo catalytic reactor configuration to obtain a high reaction rate. The reactor gap size plays an important role on the kinetics of the dye decolorization reaction. A thin gap was the optimum design to decolorize C.I. Acid Orange 7. The higher pseudo-first order rate constant of $73.37 \times 10^{-2} \text{ min}^{-1}$ was obtained for R1 with an 0.3 cm gap size and 83.33 W l⁻¹ of UV dosage.

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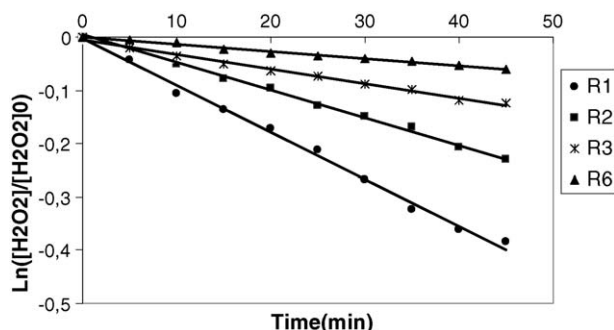


Fig. 6. Plot of $\ln([H_2O_2]/[H_2O_2]_0)$ vs. UV irradiation time in different reactors.

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