

**PHOTOASSISTED DEGRADATION OF SOME ACID DYES
USING SEVERAL OXIDATION PROCESSES**

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ABSTRACT

The photodegradation of C.I. Acid Orange 8 (AO8) and C.I. Acid Orange 10 (AO10) in laboratory-scale experiments, using four advanced oxidation processes (AOPs): UV-Visible-air-equilibrated solutions, UV-Visible-H₂O₂, UV-Visible-TiO₂ and UV-Visible-TiO₂-H₂O₂ systems. The degradation was assessed spectrophotometrically at various irradiation time intervals (0-160 minutes for UV-Visible-air equilibrated and UV-Visible-H₂O₂ systems and 0-60 minutes for UV-Visible-TiO₂ and UV-Visible-TiO₂-H₂O₂ systems). The results show that the fading process follows pseudo-first-order kinetics. The effect of initial dye concentrations and also the effect of pH of the solution on the photodegradation rate constants are discussed. The relationship between photostability and chemical structure is also developed. Experimental results suggest that the species associated with the photodegradation of the titled compounds may be the semioxidized dye free radical cation, Dye^{o+}. Moreover, the results show that the values of the kinetic rate constants decrease with increasing dye concentration for both AO8 and AO10. In contrast, dye degradation rates increase reaching a maximum value at pH 3.50. The effect of sulphonic acid groups on decolorization rate was also discussed. Furthermore, the adsorption isotherms of AO8 and AO10 on TiO₂ were determined at room temperature and pH 5.5.

1. Introduction

Azo dyes are used as photothermal sensitizing agents in the photodynamic therapy (PDT) of some forms of cancer and other diseases [Isak *et al.*, (2000) and Ochsner (1997)]. Moreover, azo dyes still attract much attention because of their wide applications mostly in organic pigments and photographic technology [Tincher (1989); Viscardi *et al.*, (2002) and Hoffmann *et al.*, (1995)].

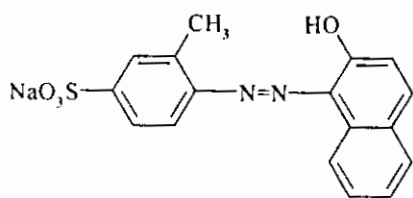
Moreover, the discharge of wastewater that contains high concentration of dyes is a well-known problem associated with dyestuff activities. Some of these dyes have documented health hazards [Hersey *et al.*, (1984)]. There are different physico-chemical and biological methods for the treatment of dyes in wastewater. However, these processes have operating cost and are of limited applicability. Hence, the necessity of investigating new alternatives for the adequate treatment of the dye present in wastewater is inevitable. The recent developments of chemical treatment of wastewaters gave birth to an improvement of the catalytic and oxidative degradation of organic compounds dissolved in aqueous media [Daneshvar *et al.*, (2002); Daneshvar *et al.* (2003), Daneshvar *et al.* (2004); Behnajady *et al.* (2004); Legrini *et al.* (1993) and Galindo *et al.*, (1998)]. These are generally referred to as "advanced oxidation processes" (AOPs), where highly oxidizing species, like hydroxyl radicals, are produced. Moreover, among these processes photocatalysis systems such as combination of a semiconductor (TiO_2 , ZnO, etc.) with UV/Vis light is a very promising technique. Due to a faster electron transfer to molecular oxygen, TiO_2 is found to be more efficient for photocatalytic degradation of pollutants [Daneshvar *et al.*, (2004)]. It has been demonstrated that in UV/ TiO_2 process, various parameters affect the degradation rate of compounds.

In the present study, photodegradation of C.I. Acid Orange 8 (AO8) and C.I. Acid Orange 10 (AO10), using four-advanced oxidation processes (AOPs): UV-Visible-air-equilibrated solutions, UV-Visible- H_2O_2 , UV-Visible- TiO_2 and combined action of UV-Visible- TiO_2 - H_2O_2 systems are discussed. The effect of substitution and different environments (pH and initial dyes concentrations) on the degradation rate of AO8 and AO10 have been undertaken. Furthermore, the adsorption isotherms of AO8 and AO10 on TiO_2 were obtained at room temperature and pH 5.5 by determining the amount of dye adsorbed on the catalyst surface at equilibrium.

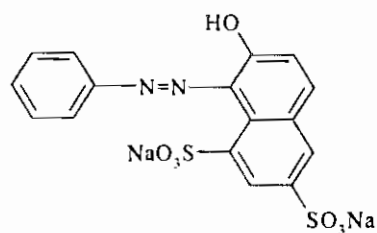
2. MATERIALS AND METHODS

C.I. Acid Orange 8 (AO8) and C.I. Acid Orange 10 (AO10) were commercial product (Aldrich) and was used without further purification. Bidistilled water was used throughout this study. The dye concentrations were in the range 0.04 –0.1 mM. A large excess of hydrogen peroxide from Prolabo (1.0 mM, 30% w/w) in comparison to the dye concentration was added, so that hydrogen peroxide concentration could be considered constant during the whole experiment. While the photocatalyst titanium dioxide (TiO₂, Degussa, P25) was used. The pH of the solution was adjusted using universal buffer measured with pH-meter WTW model 390.

Absorption spectra were recorded on a Spekol 11 spectrophotometer. Photodegradation of AO8 and AO10 were conducting at room temperature (27°C) in a batch microsol light tester equipped with a pre-settable timer and water-cooler jacket (BS 1006 UK-TN) fitted with 400W MB/U lamp.



C.I. Acid Orange 8 ($\lambda_{\max} = 488$ nm)



C.I. Acid Orange 10 ($\lambda_{\max} = 480$ nm)

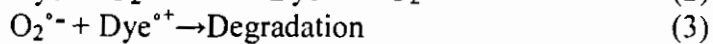
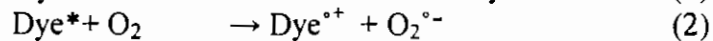
3. RESULTS AND DISCUSSION

3.1. Photodegradation of Aqueous AO8 and AO10 Solution:

The molar absorptivity of the two studied dyes are calculated at the maximum wavelength ($\epsilon_{\max} = 16.50 \times 10^3$ and 19.40×10^3 l mol⁻¹ cm⁻¹ at λ_{\max} at 488 and 480 nm and for dyes AO8 and AO10 respectively). These values are relatively high probably due to the π - π^* electronic transition [Monti *et al.*, (1982) and Naman *et al.*, (2002)]. It has been found previously that S_0 - S_1 transition for azo dyes is a weak n - π^*

transition, while the strong allowed transition ($\pi\text{-}\pi^*$) is an $S_0\text{-}S_2$ transition.

When these dyes are irradiated in air-equilibrated solutions, certain degree of degradation is observed. Since oxygen is a good electron acceptor, the reaction of AO8 and AO10 with the excited oxygen dissolved in the reaction media would normally characterize the primary process associated with photodegradation (Yang *et al.*, 2001). Therefore, the mechanism of photodegradation of AO8 and AO10 proceeds according to the following equations:



Based on an established mechanism for the oxidative photodegradation of AO8 and AO10, the rate equation can be given as:

$$-d[\text{Dye}]/dt = k[\text{Dye}][\text{O}_2] \quad (4)$$

Since the concentration of O_2 in air-saturated solution is constant (3.0×10^{-4} M) [Eggeling, *et al.*, (1999)], equation 4 is simplified into a pseudo -first order kinetic model:

$$-d[\text{Dye}]/dt = k_{\text{obs}}[\text{Dye}] \quad (5)$$

where k_{obs} represents the specific rate constant for pseudo-first order type for the degradation process.

A plot of $\ln[\text{Dye}]_0 / [\text{Dye}]_t$ against the reaction time should be a straight line of slope k_{obs} . The evaluation of the absorbance at λ_{max} at different time intervals for irradiation of AO8 and AO10 up to 160 minutes, exponential decay is observed (Figure 1a, b and c for 0.04 mM AO10 as an example. Similar behavior is observed for the other concentration and for AO8).

The values of photodegradation pseudo-first order rate constants for AO8 and AO10 in aqueous solutions calculated from the linear plots of $\ln [\text{Dye}]_0 / [\text{Dye}]_t$ against irradiation time (Figure 2a, b and c for AO8 as an example) are given in Table 1.

Moreover, the effect of pH is an important parameter in photodegradation, experiments are conducted for AO8 and AO10 at different initial pH values (3.5, 5.5 and 9.5). The calculated pseudo-first order rate constants are given in Table 1. The results show that the degradation rate constants of AO8 and AO10 are sensitive to light specially in acidic medium (pH 5.5). This can be explained by a change in the molecular structure [Khalil *et al.*, (1999)].

Furthermore, Figure 3 depicts a typical kinetic curve describing the photodegradation for different concentrations of AO8. It is observed that, the pseudo-first order rate constants increase with increasing initial dye concentrations up to 0.06 mM and then decrease for dye concentration of 0.08 and 0.10 mM. As the initial dye concentrations increase the color of the dye being irradiated become more and more intense, which prevents the penetration of light photons [Galindo *et al.*, (1998)]. Similar behavior is observed in case of AO10 (Table 1).

Table (1): Photodegradation kinetics of AO8 and AO10 at different initial dye concentrations (mM) and pH values.

Reagent	pH	$k_{obs} (\text{min}^{-1}) \times 10^3$							
		AO8				AO10			
		0.040	0.060	0.080	0.100	0.040	0.060	0.080	0.100
O ₂	9.5	0.437	0.835	0.238	0.158	0.534	0.835	0.411	0.237
	5.5	0.831	1.230	0.521	0.365	0.699	1.270	0.718	0.500
	3.5	1.350	1.800	0.958	0.774	1.600	1.800	1.180	0.964
H ₂ O ₂	9.5	2.070	2.710	1.560	1.270	2.600	2.710	1.940	1.600
	5.5	3.150	3.870	2.140	1.910	3.860	3.870	0.258	2.250
	3.5	4.160	4.690	3.100	2.670	5.430	4.690	3.810	3.170
TiO ₂	9.5	12.100	16.100	2.440	1.320	16.300	19.700	3.350	1.640
	5.5	15.900	20.200	4.000	2.520	18.900	23.800	4.490	3.630
	3.5	31.400	21.700	5.260	3.910	22.500	28.200	5.740	4.480
TiO ₂ + H ₂ O ₂	9.5	19.700	33.700	8.330	5.160	29.100	37.800	10.400	6.700
	5.5	26.000	41.000	10.900	6.850	34.000	49.700	13.800	8.970
	3.5	37.500	48.900	14.200	8.780	40.300	60.400	17.700	11.100

3.2. Photodegradation of AO8 and AO10 Solutions in Presence of H₂O₂:

The presence of hydrogen peroxide and the UV-Visible irradiation induces an increase of photodegradation of the studied dyes than in water (Figure 1d, e and f for AO10 as an example). Hydrogen peroxide may be dissociate into hydroxyl radicals due to the absorption of UV-Visible photons which then react rapidly and non-selectively with the organic dye [Galindo *et al.*, (1998)]. The main reaction that occurs in the dissociation of hydrogen peroxide in the presence of UV-Visible radiation is:



Thus, an expected increase of the rate constant results exclusively from the reaction between dye molecules and hydroxyl radicals, generated upon photolysis of H_2O_2 . The dosage of hydrogen peroxide is sufficient to maintain the concentration of hydroxyl radicals constant during the experiment (1.0 mM).

The major degradation rate of AO8 and AO10 can be expressed as follows [Wu *et al.*, (1999)].

$$-d [\text{Dye}] / dt = k_{\text{obs}} [\text{Dye}] [^{\circ}\text{OH}] \quad (7)$$

Where [Dye] represents dye concentration, t time and [$^{\circ}\text{OH}$] denotes the hydroxyl radical concentration. Assuming hydroxyl radical concentration [$^{\circ}\text{OH}$] reach equilibrium instantaneously with excess hydrogen peroxide. Thus the [$^{\circ}\text{OH}$] can be viewed as constant. Therefore, the rate equation is simplified into a pseudo-first order kinetic equation

$$\ln [\text{Dye}]_0 / [\text{Dye}]_t = k_{\text{obs}} t \quad (8)$$

Figure 2d, e and f depicts a typical kinetic curves describing the photodegradation for 0.04 mM AO8 in presences of 1.0 mM H_2O_2 . Same results are obtained for AO10.

The reactivity of hydrogen peroxide depends on the pH of the medium. The effect of pH on the degradation rate has been carried out at pH 9.5, 5.5 and 3.5. The results are shown in Table 1 and Figure 3. From the results, it is clear that the process is more efficient in acidic medium (pH 3.5). Increase of hydrogen ion concentration from pH 5.5 to 3.5 increases the degradation rate. The observed decrease in the rate constant at higher pH value (9.5) is due to the reduction of hydroxyl radical concentration. Under these condition H_2O_2 undergoes photodecomposition to water and oxygen rather than hydroxyl radical equation 7, [Galindo *et al.*, (1998)].

Furthermore, the effect of initial dye concentration $[\text{Dye}]_0$ on the degradation rate was shown in Figure 4 by plotting the calculated rate constants of AO8 and AO10 versus initial concentration $[\text{Dye}]_0$, ($[\text{Dye}]_0$ concentrations = 0.04, 0.06 0.08 and 0.1 mM for both dyes). It is interested to find that k_{obs} decline significantly by raising initial dye concentration. In every experiment, the concentration of hydrogen peroxide was high enough not to constitute a limiting factor (1.0 mM H_2O_2). On the other hand, the molar extinction coefficients (ϵ) of organic molecules are high, so that an increase in dye concentration induces a rise of the internal optical density. Taking into account that, the lifetime of hydroxyl radicals is very short [Galindo *et al.*, (2001)], they can only react where they are formed. Increasing the quantity of dye molecules per

unit volume logically enhance the probability of collision between organic matter and oxidizing agent, leading to an increase in the photodegradation rate. However, the molar absorptivity of AO8 and AO10 are high ($\epsilon_{\max} = 16.50 \times 10^3$ and $19.40 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ for AO8 and AO10, respectively), so that a rise in their concentrations induce an inner filter effect as the incident light would largely be wasted for dye excitation rather than for the oxidizing species precursor excitation. Consequently, the solution becomes more and more impermeable to UV-Visible radiations. As the rate of hydrogen peroxide photolysis directly depends on the fraction of incident light absorbed by H_2O_2 molecules and especially, in presence of organic matter [Galindo *et al.*, (1998)], the photodegradation rate slows down (Table 1) by increasing concentrations of dye (0.08 and 0.10 mM).

3.3. Photocatalytic Degradation of AO8 and AO10 Over TiO_2

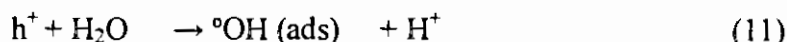
In the oxidation experiments with TiO_2 , photoexcitation with light of energy greater than the TiO_2 band gap ($h\nu \geq E_G = 3.2 \text{ eV}$) promotes electrons from the valence band to the conduction band, and leaves an electronic vacancy or hole (h^+) in the valence band. Thus the act of photoexcitation generates an electron-hole pair [De Heredia *et al.*, (2001)].



In order to achieve chemically productive photocatalysis, electron-hole pair recombination must be suppressed. This can be achieved by trapping these species with the surface adsorbates. The photo-excited electrons are trapped by molecular oxygen:



The principal hole traps are adsorbed water molecules and OH^- ions [Hofmann *et al.*, (1995) and Fox *et al.*, (1993)] producing $^{\circ}\text{OH}$ radicals.



As shown in Figure 1 (curves a, b and c), aqueous solution of 0.04 mM of AO10 was photolysed very slowly when irradiated alone. Addition of TiO_2 (0.5g/l. Figure 1(j, h and I)) significantly increased the rate of AO10 disappearance. The amount of AO10 adsorbed over the photocatalyst in the dark was evaluated as to be 6-10% Table I. It can be concluded that the loss of AO10 was almost exclusively due to photochemical processes. The same behavior is obtained for the other

concentrations (0.06, 0.08 0.1 mM) and in different pH's and also for the AO8.

Moreover, the concentration of AO8 and AO10 decreases exponentially in presence of TiO₂ with irradiation time (Figure 1 curves g, h and i). Figure 2 (curve g, h and i) shows the plot of $\ln [Dye]_0 / [Dye]_t$ versus time for all experiments of photocatalytic degradation where the pH of the solution was varied (pH 3.5, 5.5 and 9.5). The pH of the solution has a pronounced effect on the degradation rate.

The pH value strongly influences the surface charge properties of metal-oxide particles in the aqueous dispersion. Normally, surface of the net TiO₂ is positively charged in acid media, particularly when the pH of the aqueous dispersion is less than the pH_{pzc} (the point of zero charge, pH_{pzc} of TiO₂ is about 6.8) [Isak *et al.*, (2000) and Zhao *et al.*, (1993)]. Thus, adsorbate in the aqueous solution tends to adsorb on the surface of TiO₂ by the negatively charged or electron abundant group in acidic solution because of the electrostatic interaction. The acid dissociation exponent of the sulphonic groups of AO8 and AO10 were about 3.4 [Galindo *et al.*, (1998)]. Thus, at $pH \approx 3.5$ most of the sulphonic groups of AO8 and AO10 were dissociated and negatively charged at $-SO_3^-$ state. Therefore, AO8 and AO10 tend to adsorb on the surface of TiO₂ through the negatively charged sulphonic groups due to the electrostatic interaction.

Degradation experiments of AO8 and AO10 in presence of TiO₂ exhibited first order kinetics with respect to the concentration of Dye.

$$-d[Dye] / dt = k_{obs}[Dye] \quad (13)$$

Whose integration gives, for $[Dye] = [Dye]_0$ at $t = 0$

$$\ln[Dye]_0 / [Dye]_t = k_{obs} t \quad (14)$$

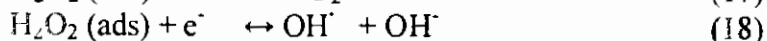
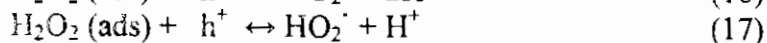
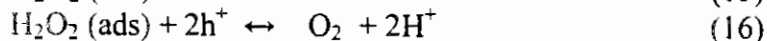
In which $[Dye]_t$ is the dye concentration at time t , $[Dye]_0$ is the Dye concentration at initial time, t the reaction time and k_{obs} the first order rate constant. On the basis of the previous consideration, a chemical kinetic model is proposed, able to explain the experimental results. The rate-determining step of the catalyzed reaction is considered to be the reaction between $^{\circ}OH$ radicals and dye molecules (AO8 or AO10) over the catalyst surface. The calculated rate constants for AO8 and AO10 at different pHs are given in Table 1. Data in Table 1 show that high photodegradation rate constants are obtained in acidic medium. Moreover, the results show that k_{obs} decreased with increasing initial concentration of AO8 or AO10 when other parameters are kept unchanged (Table 1). Therefore, the degradation rate was pseudo-first

order with respect to the initial concentration of AO8 and AO10 as cited previously [Daneshvar *et al.*, (2004)].

3.4. Photocatalytic Degradation of AO8 and AO10 Over TiO₂ in Presence of H₂O₂

Figure 1 ((g, h and i) ,(j, k and l)) shows the effect of addition of TiO₂ and mixture of TiO₂ and H₂O₂ on the photodegradation of AO10. The same results are obtained in case of AO8. It can be seen that degradation of both dyes occurred much more rapidly in presence of mixture of TiO₂ and H₂O₂ compared to that of TiO₂ alone.

The photodegradation mechanism using H₂O₂ as bleaching agent may be quite different from the proposed mechanisms with a solid catalyst as TiO₂. Using TiO₂ photocatalyst the electron/hole recombination (e⁻/h⁺) could represent a major energy-wasting step in order to achieve a high quantum yield. The use of H₂O₂ for inhibiting (e⁻/h⁺) recombination has been useful because they trap the photogenerated electrons more efficient than O₂ [Banda *et al.*, (2002)]. Moreover, hydrogen peroxide showed a beneficial effect on the photocatalytic degradation of model compounds as shown in Figure 4. The enhanced degradation rate in the presence of H₂O₂ can be explained by several reasons. Firstly, it increases the rate by removing the surface-trapped electrons, thereby lowering the electron-hole recombination rate and increasing the efficiency of hole utilization for reactions such as (OH[•] + h⁺ → OH⁺). Secondly, H₂O₂ may split photolytically to produce OH radicals directly, as cited in studies of homogeneous photooxidation using UV/(H₂O₂ + O₂) [Peyton *et al.* (1988)] Thirdly, the solution phase may at times be oxygen starved because of either oxygen consumption or slow oxygen mass transfer; peroxide addition thereby increases the rate towards what it would have been had an adequate oxygen supply been provided. The proposed mechanisms are shown in the reactions:



Although the presence of photocatalyst increases the photodegradation rate, yet the effect is more pronounced in case of mixture of TiO₂ and H₂O₂.

Furthermore, the photodegradation rates of AO8 and AO10 are calculated in presence of TiO₂ and H₂O₂ at different pHs (9.5, 5.5 and

3.5) and at different concentrations (0.04, 0.06, 0.08 and 0.1 mM for both dyes) and the calculated values are listed in Table 1. Data in Table 1 show that the photodegradation rate values increase in acidic medium and decrease with increasing the concentration. Figure 4 shows bar chart for the photodegradation of AO8 and AO10 with different oxidation processes.

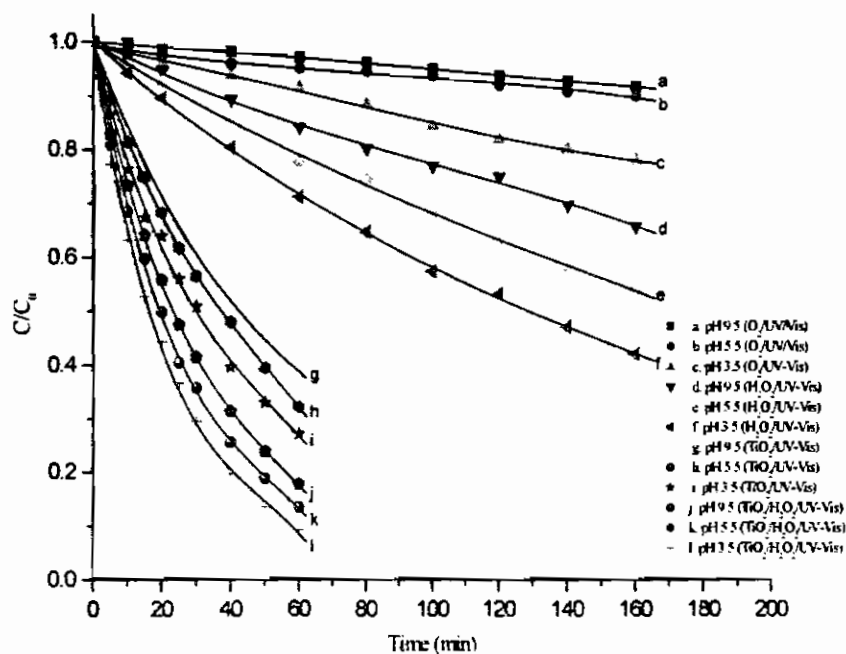


Fig. (1): Plot of absorbance vs. time for the photodegradation of 0.04 mM of AO10 at different pH values (9.5, 5.5 and 3.5) in aqueous solutions (curves a, b and c), in presence of 1.0 mM H_2O_2 (curves d, e and f), in presence of 0.5g TiO_2 (curves g, h and i) and in presence of 1.0 mM H_2O_2 and 0.5g TiO_2 (j, k and l), respectively as a function of irradiation time (same results are obtained in case of AO8).

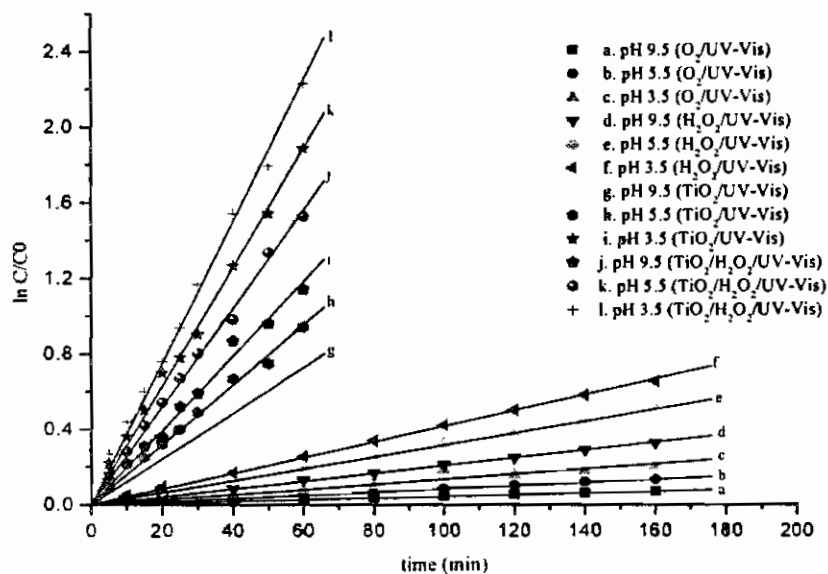


Fig. (2): Kinetics of photodegradation of 0.04 mM AO8 at different pH values (9.5, 5.5 and 3.5) in aqueous solutions (curves a, b and c), in presence of 1.0 mM H_2O_2 (curves d, e and f), in presence of 0.5g TiO_2 (curves g, h and i) and in presence of $1.0 \times 10^{-3} M H_2O_2$ and 0.5g TiO_2 (j, k and l), respectively (same results are obtained in case of AO10).

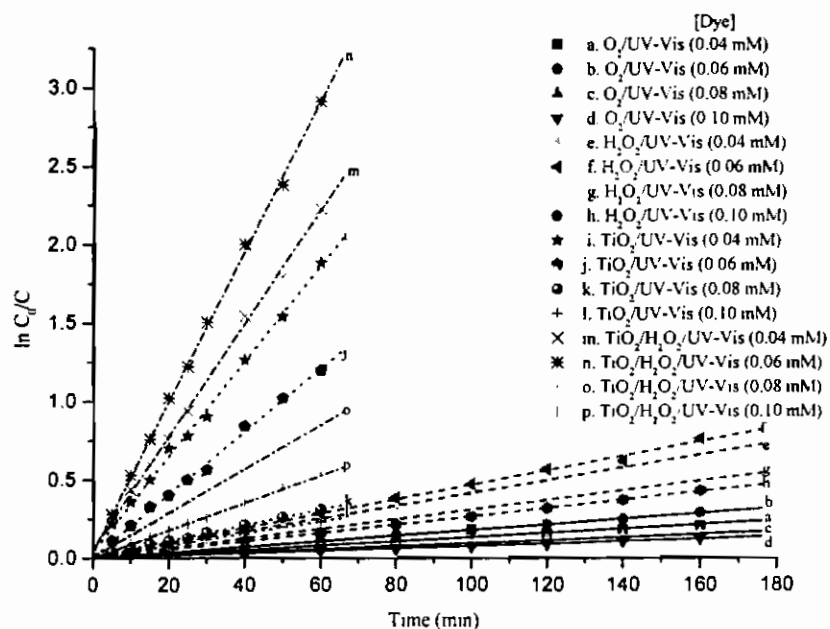


Fig. (3): Kinetics of photodegradation of different AO8 concentrations (0.04, 0.06, 0.08 and 0.1 mM) at pH 3.5 in aqueous solutions (curves a, b, c and d), in presence of 1.0 mM H_2O_2 (curves e, f, g and h), in presence of 0.5g/l TiO_2 (curves i, j, k. and l) and in presence of 1.0 mM H_2O_2 and 0.5g/l TiO_2 (m, n, o and p) respectively (same results are obtained in case of AO10).

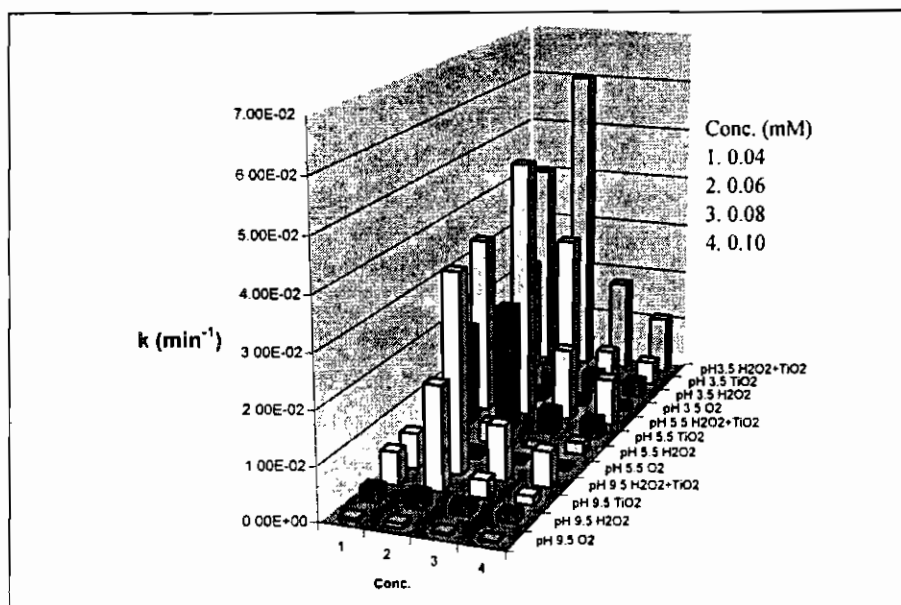


Fig. (4): The pseudo-first order rate constants of AO10 under O₂/UV-Vis, H₂O₂/UV-Vis, TiO₂/UV-Vis and TiO₂/H₂O₂/UV-Vis processes, at different initial dye concentrations and different pH values. Similar results are obtained in case of AO8.

The results show that the degradation rate of AO10 is more when compared with AO8 (Table 1). Hence, it can be said that the higher the number of sulphonic acid groups in the dye structure, the higher is the discoloration rate. This is because of the increased solubility rendered by the higher numbers of sulphonic acid groups, which in turn results in better interaction between the dye molecules with either O₂ or hydroxyl radicals produced in the reaction media. The results justify the belief that the rate of dye decomposition by advanced oxidation processes strongly depends upon the solubility of the dyes [Shu and Huang (1995)] reported such behavior in the treatment of effluents containing the dyes such as Acid Black 1, Direct Yellow 4, Acid Red 1 and Acid Orange 10 using ozone.

3.5. Equilibrium Adsorption Measurements

The adsorption isotherm of AO8 and AO10 on TiO₂ was obtained at room temperature and pH 5.5 by determining the amount of the dye adsorbed on the photocatalyst surface as a function of its concentration in

the solution, at equilibrium. For this, a fixed weight of TiO₂ (12.5 mg) was added in a series of 25 ml aliquots of aqueous solutions of A08 and A010 of variable concentration, in the range of 0.01-0.1mM. After sonication for 15 minutes, the suspensions were left overnight (12 hours) in the dark under continuous stirring. The samples were filtered using a 0.45 µm filter and the concentration of the dye in the filtrate was determined by measuring the absorbance at 488 and 480 nm for AO8 and AO10, respectively.

The amount of the dye molecules adsorbed on TiO₂, N_{ads} (mol/g), was calculated from the following equation [Stylidi *et al.*, (2003)].

$$N_{ads} = (V\Delta C)/w. \quad (19)$$

where $\Delta C = C_0 - C_{eq}$ (mol/l) is the decrease in the molarity of A08 or A010 after reaching equilibrium, with C_0 being the initial concentration, C_{eq} the A08 or A010 concentration at equilibrium, V (l) the volume of aqueous solution and w (g) the mass of the oxide. The concentration of the dye in the supernatant was determined spectrophotometrically and subtracted from the initial concentration to determine the adsorbed amount in each case.

3.5.1. The Adsorption Isotherm of AO8 and AO10 on TiO₂

The adsorption isotherm of A08 or A010 on TiO₂ is presented in Figure 5(A), in which the amount of dye adsorbed on the photocatalyst surface, N_{ads}, is plotted as a function of its concentration in the solution, at equilibrium, C_{eq}. It is observed that N_{ads} increases with increasing C_{eq}, and reaches a plateau at equilibrium concentrations above 0.08 mM. It may be assumed that this plateau corresponds to monolayer coverage of the dye on the titanium oxide surface. Increasing equilibrium concentrations above 0.1 mM results in the adsorption of additional amounts of A08 or A010, which may be attributed to the formation of additional layers.

Adsorption of A08 or A010 on TiO₂ at monolayer coverage can be expressed by the following equation [Stylidi *et al.*, (2003)]:

$$N_{ads} = (N_{max} K C_{eq}) / (1 + K C_{eq}) \quad (20)$$

where N_{max} is the total number of accessible adsorption sites, per gram of TiO₂, and K represents the equilibrium adsorption constant for the process of dye adsorption. The linearized form of equation 20 is the following:

$$C_{eq} / N_{ads} = (1/K N_{max}) + (C_{eq} / N_{max}) \quad (21)$$

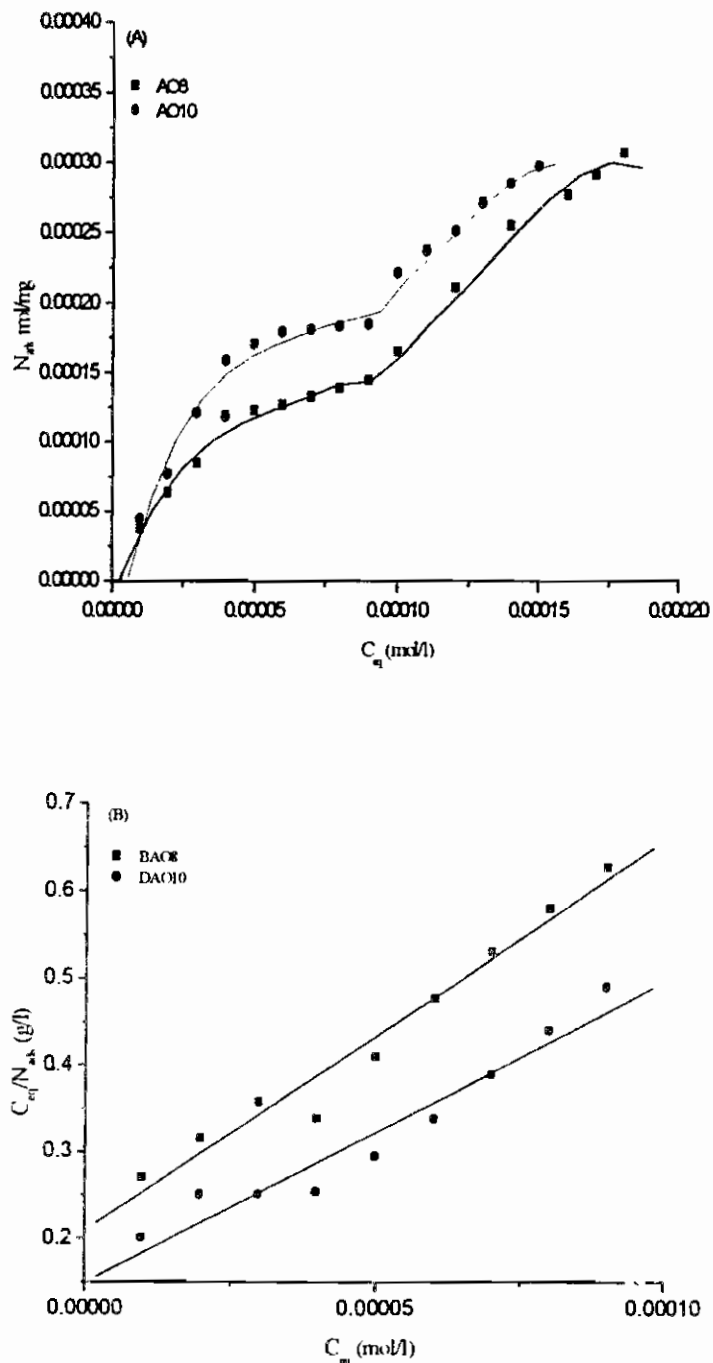


Fig. (5): A: Adsorption isotherm for AO8 and AO10 on TiO_2 (P25) at room temperature. B: Data plotted in the linearized form according to equation 24.

As observed in Figure 5(B), the plot of C_{eq}/N_{ads} versus C_{eq} results in a straight line, from the intercept and slope of which, the values of N_{max} and K are calculated (Table 2). Assuming that a complete monolayer is formed at total adsorption, N_{max} is equal to:

$$N_{max} A_{sp} / (N_A \sigma^0)$$

where A_{sp} is the adsorbent specific surface area. N_A is Avogadro's number and σ^0 is the area that each dye molecule occupies on the surface at monolayer coverage. The calculated values are listed in Table 2 for AO8 and AO10.

The high value of N_{max} for AO10 indicates that this dye occupied accessible adsorption sites greater than AO8. The presence of two sulphonic groups in the structure of AO10 leads to increment in the negative charge on the dye molecules and consequently increases the electrostatic interaction between dye molecules and TiO_2 surface leading to high value of equilibrium adsorption constant (Table 2). The obtained large value of σ^0 for AO8 may be due to the presence of sulphonic group in para position, which increases the area occupied by dye molecule.

Table (2): Equilibrium adsorption constants for AO8 and AO10.

Dye	K l mol ⁻¹	$N_{max} \times 10^4$ Mol. g ⁻¹	σ^0 Å ²
AO8	1969.24	2.307	36.00
AO10	16806.72	3.501	23.73

REFERENCES

Banda, E. R., Gelover, S., Leal, M.T., Arancibia-Bulnes, C., Jimenez, A. and Estrada, C.A., *Catal. Today*, **76**, 189, 2002.

Behnajady, M.A., Modirshahla, N. and Shokri, M., *Chemosphere*, **55**, 129, 2004.

Daneshvar, N., Salari, D. and Behnajady, M.A., *Iran. J. Chem. Chem. Eng.*, **21**, 55, 2002.

Daneshvar, N., Salari, D. and Khataee, A.R., *J. Photochem. Photobiol. A:Chem.*, **157**, 111, 2003.

Daneshvar, N., Salari, D. and Khataee, A.R., *J. Photochem. and Photobiol. A:Chem.*, **162**, 317, 2004.

Daneshvar, N., Rabbani, M., Modirshahla, N., Behnajady, M.A., *J. Photochem. and Photobiol. A: Chemistry* **168**, 39, 2004.

De Heredia, J. B., Torregrosa, J., Dominguez, J. R. and Peres, J. A., *J. Hazar. Mat.*, **B83**, 255, 2001.

Eggeling, C., Widengren, J., Rigler, R., Seidel, C. A. M., Relting, W., Strehmel, B., Strehmel, B. and Seifert, H., "Applied Fluorescence in Chemistry, Biology and medicine, Berlin, Springer", 315, 1999.

Fox, M. A. and Dulay, M. T., *Chem. Rev.*, **93**, 341, 1993.

Galindo, C. and Kalt, A., *Dyes and Pigments*, **40**, 27, 1998.

Galindo, C., Jacques, P. and Kalt, A., *J. Photochem. and Photobiol. A: Chem.*, **141**, 47, 2001.

Hersey, A. and Robinson, B. H., *J. Chem. Soc. Faraday Trans. I*, **80**, 2039, 1984.

Hoffmann, M. R. Martin, S. T., Choi, W. Y. and Bahnemann, D. W. *Chem. Rev.*, **95**, 69, 1995.

Isak, S., J. Eyring, E. M., Spoikes, J. D., and Meekins, P. A., *J. Photochem. and Photobiol. A: Chem.*, **134**, 77, 2000.

Khalil, M.M.H., Abdel-Shafi, A.A. and Abdel-Mottaleb, M.S.A., *International J. of Photoenergy*, **1**, 85, 1999.

Legrini, O., Oliveros, E. and Braun, A. M., *Chem. Rev*, **93**, 671, 1993.

Monti, S., Orlandi, G. and Palmieri, P., *Chem. Phys.*, **71**, 87, 1982.

Naman, A., Jassim, A. H. and Alias, M. F., *J. Photochem. and Photobiol. A: Chem.*, **150**, 41, 2002.

Ochsner, M., *J. Photochem and Photobiol B: Biol.*, **39**, 1, 1997.

Peyton, G. R. and Glaze, W. H., *Environ. Sci. & Technol.*, **22**, 761, 1988.

Shu, H. and Huang, C. R., *Chemosphere*, **31**, 3813, 1995.

Stylidi, M., Kondarides, D. I. and Verykios, X. E., *International J. of Photoenergy*, **5**, 59, 2003.

Tincher, M. R., *Text. Chem. Color.*, **21**, 23, 1989.

Viscardi, G., Quagliotto, P., Barolo, C., Diulgheroff, N., Caputo, G. and Barni, E., *Dyes and Pigments*, **54**, 131, 2002.

Wu, T., Liu, G., Zhao, J., Hidaka, H. and Serpone, N., *J. Phys. Chem. B*: **103**, 4862, 1999.

Yang, S., Tian, H., Xiao, H., Shang, X., Gong, X., Yao, S. and Chen, K., *Dyes and Pigments*, **49**, 93, 2001.

Zhao, J., Hidaka, H., Takamura, A., Pelizzetti, E. and Serpone, N., *Langmuir*, **9**, 1646, 1993.

التكسير الضوئى الحفزى لبعض الصبغات الحامضية
باستخدام طرق أكسدة متعددة

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يتضمن هذا البحث دراسة التكسير الضوئى للصبغة الحامضية البرتقالية ٨، والصبغة الحامضية البرتقالية ١٠ باستخدام طرق الأكسدة المتطورة فى وجود فوق أكسيد الهيدروجين وأكسيد التيتانيوم وقيس معدل التكسير بالطريقة الاسبكتروفوتومترية عند أزمنة مختلفة من التعرض للأشعة المرئية وفوق البنفسجية. وأظهرت النتائج أن التدرج فى اختفاء اللون يتبع التفاعل الحركى من الدرجة الأولى. كما نوقش تأثير كل من التركيز الابتدائى للصبغة، الأس الهيدروجينى للمحلول على قيمة ثابت معدل التكسير وتم مقارنة الثبات الضوئى مع التركيب الجزيئى للصبغات المستخدمة.

بالإضافة إلى الدراسة الحركية للتكسير فقد تم دراسة منحنى الادمصاص للصبغتين قيد الدراسة عند درجة حرارة الغرفة وعند اس هيدروجينى 5.5 وذلك بإيجاد كمية الصبغة المدمصة على سطح عامل الحفز (أكسيد التيتانيوم) عند الاتزان.