

Full Paper

Photochemical oxidation of an azo dye in aqueous solutions by UV/H₂O₂ process

Ahmed H. Osman* and Gamal A-W. Ahmed

Chemistry Department, Faculty of Science, Assiut University, 71516 Assiut, Egypt

Email: ahosman@aun.edu.eg

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Abstract

Advanced oxidation process (AOP) employing hydrogen peroxide with UV light has been found to be very effective method that is capable of transformation refractory non biodegradable and/or toxic organic compounds into harmless end products such as carbon dioxide and water. The UV/H₂O₂ oxidation process is characterized by generation of a very powerful oxidizing species, namely hydroxyl radicals. The aim of the present work is to study of the kinetics and mechanism of the photochemical oxidation of a synthetic dye with UV/H₂O₂ process. Choice of the present model based on its similarity of chemical structure with commercial importance dyes. The primary analysis was performed by recording the spectral changes of aqueous solutions of the dye under the following conditions (i) direct photolysis of the dye solution with light of wave length of 298 nm., (ii) thermal reaction between the dye and H₂O₂ in dark, and (iii) photolysis of the dye solution containing H₂O₂. The results demonstrate that, direct photolysis of the dye is not negligible but is very slow; the thermal reaction of the dye and H₂O₂ in dark is negligible. However the combination of both H₂O₂ and UV light enhanced both decolourisation and degradation processes. The effect of reaction pH, applied H₂O₂ dose and irradiation wavelength has been studied. The results indicate that the reaction is more efficient in alkaline medium. Also, the rate of photoreaction is inversely proportional with irradiation wavelength. Moreover the addition of potassium ferrioxalate generally enhanced the photochemical conversion. The kinetics and mechanism of investigated reaction have been postulated.

Keywords: Azo dye. UV/H₂O₂. Decolourisation. Photodegradation.

1. Introduction

Reactive dyes constitute a significant portion of colorants used in industries ranging from the textile industry to the paper industry. Due to their complex structures, most of the dyes

are resistant to biodegradation [1]. Some physical and chemical techniques are currently available for the treatment of the dye effluent, but these processes have only limited success. Thus there is an urgent need

for textile industries to develop effective methods for water processing. Recently attention has been focused on the chemical techniques that could be used to discolor of textile wastewaters [2, 3]. Advanced oxidation process (AOP) employing hydrogen peroxide with UV- Light has been found to be very effective method that is capable of transforming refractory non-biodegradable and/or toxic organic compounds into harmless end products such as carbon dioxide and water [4-7]. The UV/H₂O₂ oxidation process is characterized by generation of a very powerful oxidizing species namely hydroxyl radicals [8, 9]. The general patterns of the reactions of these radicals with saturated aliphatic compounds involve abstraction of hydrogen atom in the rate-determining step [10, 11]. On the other hand, when the organic molecule contains a double bond, the abstraction of hydrogen atom is completed by addition of hydroxyl radical on such unsaturated bond [12]. With monosubstituted benzene ring, the main reaction is electrophilic addition [13, 14]. However, the mechanism of the hydroxyl radical induced degradation of more complex molecules for instance water soluble dyes has not been extensively studied. Thus, one of the objectives of the present study is to investigate the kinetics and mechanism of photochemical oxidation of a synthetic azo dye with UV/H₂O₂ process. A choice of the present molecule was made based on similarity with azo dyes of commercial importance.

2. Materials and methods

The heterocyclic azo dye under investigation was synthesized by coupling freshly prepared

diazonium salt of 2-(p-amino phenyl) oxazolophen oxazine with sodium salt of j-acid (6-Amino-1-naphthol-3-sulphate) as reported in published procedure [15], and its structure is presented in Fig.1. The dye stock solution was prepared in double distilled water and was diluted to the desired concentrations. All dye solutions were found to follow Beer-Lambert law in the concentration range from 1×10^{-5} mol/L to 1×10^{-3} mol/L. Hydrogen peroxide (30% volume) was purchased from Sigma- Aldrich and used without any further purification. The exact concentration of a freshly prepared hydrogen peroxide solution was determined with standard potassium permanganate solution.

2.1 Apparatus

The photolysis was achieved using an Osram HBO 200 w / 2 lamp as a light source. Cut – on filters of wavelengths 365, 333, and 298 nm were used. Irradiations were carried out in 1-cm spectrophotometer cell at room temperature. Progress of the photolysis was monitored by UV- 2101 PC Shimadzu spectrophotometer. pH measurements were made with Jenway 3040 ion analyzer pH meter. All kinetic experiments were carried out under pseudo first-order conditions, with $[Dye]_0 \geq 10 [H_2O_2]_0$ at a constant ionic strength. The course of reaction was followed by recording the decrease in absorbance of the investigated dye at its absorption maximum, 563 nm and 411 nm, as a function of time. k_{obs} values were evaluated from plotting $\ln(A_t)$ vs. time, where A_t is the absorbance of dye at time (t). A short computer program was used to perform a least square analysis of obtained rate data and calculate rate constants.

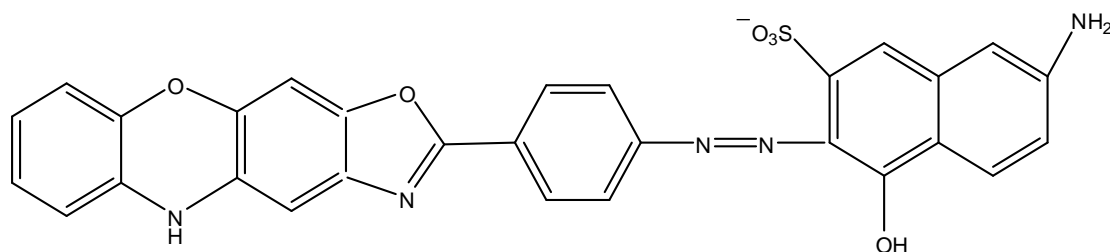


Fig. 1: Chemical structure of investigated dye.

3. Results and discussion

The UV spectrum of the investigated dye in double distilled water exhibits two bands at $\lambda_{\max} = 563$ nm and 411 nm, which are assigned $n \rightarrow \pi^*$ transition of N = N group and $\pi \rightarrow \pi^*$ transition in naphthalene ring respectively. The former absorbance is responsible for color of the dye and the decrease in its intensity is used to monitor the decolourisation of the dye, while the decrease in the second band absorbance represents the degradation of the aromatic part of the dye. The progress in the absorbance spectra of the dye solution during the reaction was monitored at 0.5% dose of H_2O_2 of reaction sample and at pH 7. Typical obtained results are shown in Fig. 2. This figure demonstrates the changes of absorption spectra of the dye upon irradiation with UV at different irradiating time in the presence of H_2O_2 .

The first analytic picture was obtained by recording the spectral changes of absorbance of aqueous solutions of the investigated dye with time under the following conditions:

- i) Direct photolysis of the dye solution with light of wavelength of 298 nm.
- ii) Thermal reaction between the dye and hydrogen in the dark.
- iii) Photolysis of the dye solution containing hydrogen peroxide.

The obtained results which are shown in Fig. 3, demonstrate that direct photolysis of the dye is not negligible, but it is very slow, while the thermal reaction of dye with hydrogen peroxide is negligible. However, the combination of both hydrogen peroxide and ultraviolet light radiation enhanced both decolorization and degradation processes. Photoactivity of the dye in the absence of hydrogen peroxide can be attributed to the stability of photoelimination products dinitrogen [16].

In UV/ H_2O_2 process, the hydroxyl radicals generated upon photolysis of H_2O_2 , which are very oxidizing agent with oxidation potential 2.8 V [17], attack the dye and transfer it to mineralization products (eqs.1-3).

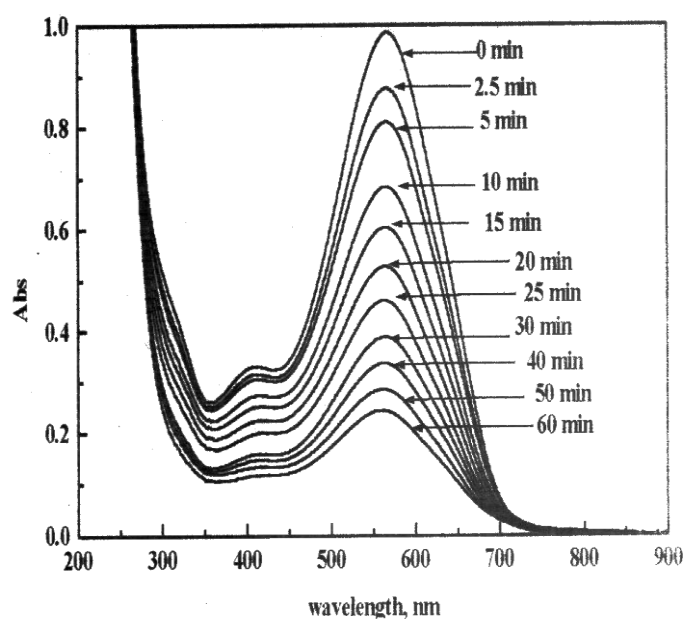


Fig. 2: The absorption spectra of the investigated dye upon irradiation with UV in the presence of H_2O_2 , $[Dye] = 2.4 \times 10^{-4}$ mol/L, $[H_2O_2] = 0.01$ mol/L; $\lambda_{irr} = 298$ nm; irradiating time = 0- 60 min.

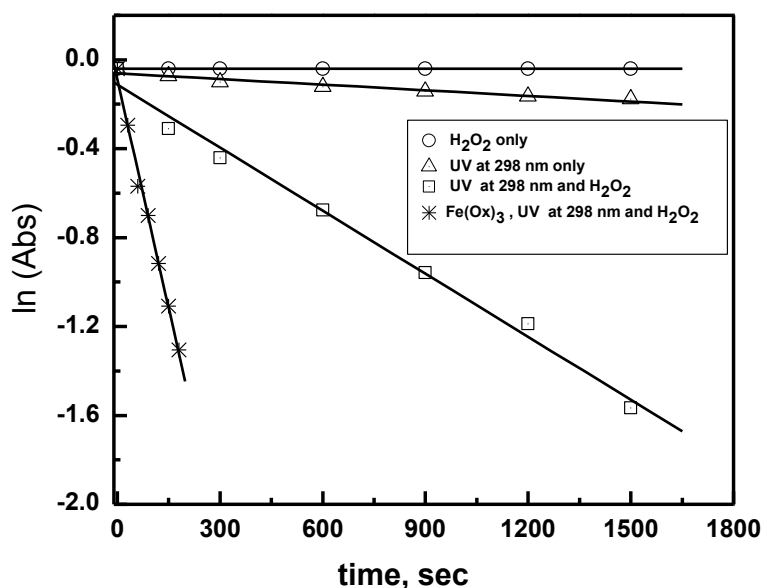
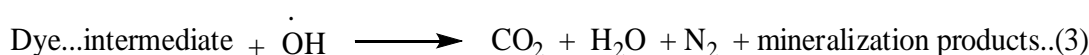
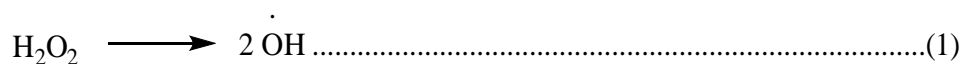


Fig. 3: Dependence of absorbance of the dye on time of radiation at $\lambda_{\max}=563\text{ nm}$, $[\text{Dye}] = 2.4 \times 10^{-4}\text{ mol/L}$ and $[\text{H}_2\text{O}_2]=0.01\text{ mol/L}$, $\lambda_{\text{irr}}=298\text{ nm}$.



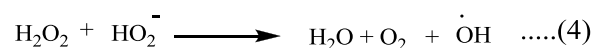
3.1 Effect of irradiating wavelength

The generation of hydroxyl radicals depends on the irradiation wavelength, since upon shift of λ_{irr} in the UV region, the production of hydroxyl radical increases. It was observed that, upon decreasing irradiating wavelength, The efficiency of photo- decolorization increases. Three irradiating wavelengths, namely 298, 333 and 365 nm have been investigated and obtained results are presented in Fig. 4.

3.2 Effect of pH

The reactivity of hydrogen peroxide depends on the pH of the reaction medium. To study

the effect of pH on decolourisation of investigated dye, experiments were conducted at different pH values ranging from 2.0 to 12.0. It is clear from Fig. 5 that increasing the pH of dye solution led to enhance the dye decolourisation efficiency. In alkaline medium, the oxidizing species, hydroxyperoxy anion (HO_2^-), which is conjugated base of hydrogen peroxide is formed. This anion reacts with hydrogen peroxide which consequently increases the hydroxyl radical concentrations as represented by the following equation:



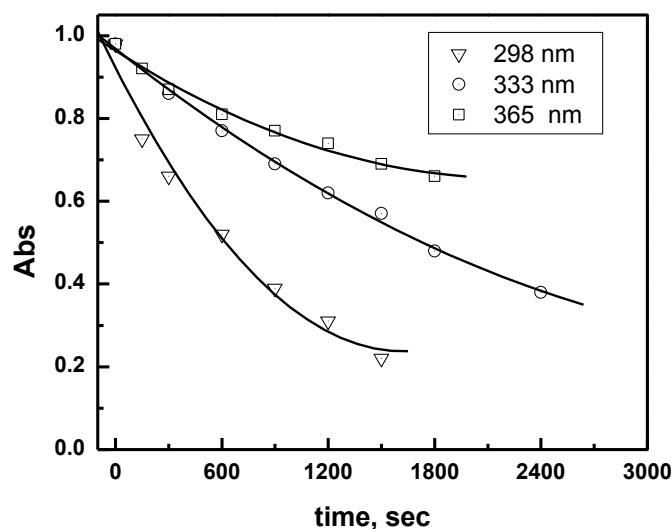


Fig. 4: Effect of irradiating wavelength on the decolorization of the dye, $[\text{Dye}] = 2.4 \times 10^{-4} \text{ mol/L}$, $[\text{H}_2\text{O}_2] = 0.01 \text{ mol/L}$.

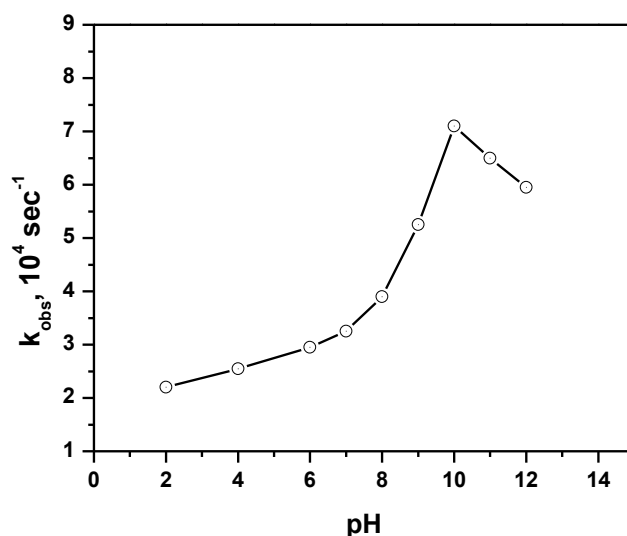


Fig.5: Effect of pH on the pseudo-first-order rate constant for decolorization of dye, $[\text{Dye}] = 2.4 \times 10^{-4} \text{ mol/L}$ and $[\text{H}_2\text{O}_2] = 0.01 \text{ mol/L}$, $\lambda_{\text{irr}} = 298 \text{ nm}$.

3.3 Dependence of reaction rates on dye concentrations

Series of experiments were conducted at different initial concentrations of dye in the range of $5.0 \times 10^{-5} - 15.0 \times 10^{-5} \text{ mol/L}$, constant concentration of the hydrogen peroxide and same wavelength of irradiation. The results indicated that the changing of the initial concentration of the investigated dye has no significant effect on the value of

pseudo-first-order rate constant indicating to first-order dependence on dye concentration as presented in Table 1. Also, plots of $\ln(A_t)$ versus time, where A_t denotes the absorbance of the dye at any time of irradiation (t). Such plots were found to be linear for over 70% of the reaction complete indicating also a first-order dependence on initial concentrations of dye.

Table 1: Influence of [Dye] on the pseudo-first-order rate constants for decolorization and degradation of dye with UV/ H₂O₂. [H₂O₂] = 0.01 mol/L and λ_{irr}= 298 nm.

[H ₂ O ₂]. mol/L	Decolorization rate, 10 ⁴ k _{obs} , s ⁻¹	Degradation rate, 10 ⁴ k _{obs} , s ⁻¹
0.50	8.62	7.10
0.70	8.47	6.54
1.00	8.21	6.48
1.50	7.32	6.32

3.4 Dependence of reaction rates on hydrogen peroxide concentrations

The rates of decolourisation and degradation of dye were determined at different initial concentration of hydrogen peroxide to elucidate the order with respect to H₂O₂. Kinetic measurements were performed at constant concentration of dye and the same wavelength of irradiation. The obtained results indicate that the rate of decolourisation and degradation of dye increased with increase in H₂O₂ concentration. The results are summarized in Table 2.

The major kinetic pathway of azo dye degradation could be expressed by the following equation

$$\frac{-dC_A}{dt} = k_2 C_A C_{OH} \dots\dots\dots(5)$$

where C_A represents azo dye concentration and C_{OH} denotes hydroxyl radical concentration. By the pseudo-stationary hypothesis (i.e. the C_{OH} can be considered as constant in presence of excess concentration of hydrogen peroxide with respect to dye concentration. Therefore, the rate expression

in Eq. 5 can be simplified into a pseudo-first-order kinetic model (Eq. 6)

$$\frac{-dC_A}{dt} = k_{obs} C_A \dots\dots\dots(6)$$

3.5 Effect of addition of ferrioxalate complex

One common problem of the advanced oxidation process is the high demand of electric energy for ultraviolet lamps, which needs high operation costs. In order to minimize the required irradiation time and energy consumed through reaction optimization of use ferrioxalate complex has been investigated. As shown in Fig (3), it clear that the photodecolorization of the dye increased sharply upon adding the Ferrioxalate complex.

4. Conclusion

The dye under investigation underwent both delocalization and degradation upon irradiation with U.V light in presence of H₂O₂, which is attributed to generation of a very powerful oxidizing species namely

hydroxyl radicals $\dot{O}H$. These process enhanced by decreasing the wavelength of

Table 2. Influence of [H₂O₂] on the pseudo-first-order rate constants for decolorization and degradation of dye with UV/ H₂O₂. [Dye] = 2.4 × 10⁻⁴ mol/L and λ_{irr}= 298 nm.

[H ₂ O ₂]. mol/L	Decolorization rate, 10 ⁴ k _{obs} , s ⁻¹	Degradation rate, 10 ⁴ k _{obs} , s ⁻¹
0.02	3.44	1.72
0.05	4.96	2.88
0.10	6.3	4.94
0.20	6.64	5.77
0.50	7.92	6.09
1.00	8.21	6.48

irradiation light as well as increasing the alkalinity of the solution. Also the rate of decolorization and degradation of the dye increased with increasing H₂O₂ concentration in consistent with pseudo-first order kinetics.

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