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Kinetic Modeling on Photooxidative Degradation of C.I. Acid Yellow 23 by UV/H_2O_2 Process

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ABSTRACT

The kinetics of photooxidative decolorization of C.I. Acid Yellow 23 (AY23) was investigated in UV/H_2O_2 process. The semi-logarithmic graphs of the concentrations of AY23 versus irradiation time were linear, suggesting pseudo-first order reaction. A simple kinetic model is proposed which confirms pseudo-first order reaction. The results indicate that the apparent reaction rate constant is a function of light intensity, H_2O_2 and AY23 initial concentrations. These results are in good agreement with proposed kinetic model.

Keywords: Advanced oxidation processes (AOPs); Photooxidation; UV/H_2O_2; C.I. Acid Yellow23; Kinetic model .

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INTRODUCTION

Wastewater from textile, paper, and some other industries contain residual dyes, which are not readily biodegradable. One of them is tartrazine or C.I. Acid Yellow 23 (AY23) which is an azo dye present in thousands of foods and drugs and has been reported as a possible cause of asthma, urticaria and angioedema [1]. It also has phototoxic potentials. Due to their toxicity and slow degradation, these dyes are classified as environmentally hazardous materials.

Adsorption and chemical coagulation are two common techniques of treatment of such wastewater. However, these methods merely transfer dyes from the liquid to the solid phase causing secondary pollution and requiring further treatment [2]. Recent developments of chemical treatment of wastewater resulted in a considerable improvement in the oxidative degradation of organic compounds dissolved in aqueous media [3-6]. Among these methods called advanced oxidation processes (AOPs), homogeneous chemical oxidation using ultraviolet radiation (UV) in the presence of H_2O_2 seems to be a very promising technique [7-9]. AOPs although making use of different reacting systems, the reactive species in all of them are hydroxyl radicals. Hydroxyl radicals have a little selectivity of attacking to organic molecules, which is a useful attribute for an oxidant used in wastewater treatment in order to solve pollution problems.

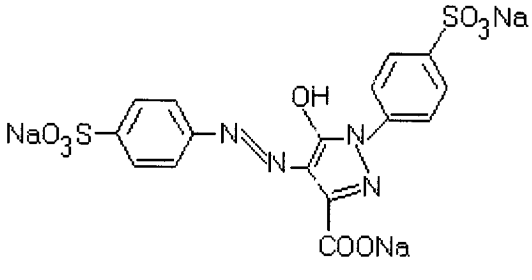
The aim of the present work is to investigate the influence of operational parameters on the decolorization kinetics of AY23 in the UV/H_2O_2 process and also kinetic modeling.

EXPERIMENTAL

Materials

C.I. Acid Yellow 23 (AY23), a mono azo anionic dye was obtained from ACROS organics (USA). Its chemical structure and other characteristics are listed in Table 1. H_2O_2 was purchased from Merck (Germany). Solutions were prepared by dissolving appropriate amount of the dye in double distilled water before each experiment.

Table 1. Structure and characteristics of C.I. Acid Yellow 23

structure	Other name	C.I. number	λ_{max} (nm)	M_w (g mol^{-1})
	Tartazine	19140	428	534.385

PROCEDURES

All experiments were carried out in a batch photoreactor. The radiation source was a mercury UV lamp emitting at 254 nm (30 W, UV-C, manufactured by Philips, Holland) which was placed above a bath photoreactor of 0.5 l volume [9]. The light intensity was measured by a Lux-UV-IR meter (Leybold Co.). In each experiment, 200 ml of the dye solution of nearly constant concentration (40 mg l^{-1}) and variable concentration of hydrogen peroxide was transferred to the reactor. Then the lamp was switched on to initiate the reaction. During irradiation, the solution was agitated in a constant rate. At certain reaction intervals, 2 ml of sample was withdrawn and the concentration of the dye was determined by means of a spectrophotometer. The decolorization of AY23 was measured with UV-Vis spectrophotometer (Ultrospec 2000, Biotech Pharmacia, England) at 428 nm. A calibration plot based on Beer-Lambert's law was established by relating the absorbance to the concentration.

RESULTS AND DISCUSSION

The following simplified mechanism may interpret the decolorization process of AY23 with $^{\circ}OH$ in the presence of radical scavengers (S).

$$AY23 + {}^{\circ}OH \xrightarrow{k_1} P \quad (1)$$

$$S_i + {}^{\circ}OH \xrightarrow{k_i} P_i \quad (2)$$

In the above equation S_i is the scavenger molecules such as intermediates, excess H_2O_2 and $^{\circ}OH$ or HO_2° [10].

The corresponding kinetic equation for AY23 and $^{\circ}OH$ are:

$$\frac{d[\mathrm{AY23}]}{dt} = -k_1[{}^{\circ}OH][\mathrm{AY23}] \quad (3)$$

$$\frac{d[{}^{\circ}\mathrm{OH}]}{dt} = \phi I_a - k_1[{}^{\circ}\mathrm{OH}][\mathrm{AY23}] - \sum_i k_i[{}^{\circ}\mathrm{OH}][S_i] \quad (4)$$

As a consequence the steady state concentration of hydroxyl radicals can be described by Eq. (5), which is obtained by solving Eq. 4 for $[{}^{\circ}OH]_{ss}$.

$$[{}^{\circ}OH]_{ss} = \frac{\phi I_a}{k_1[\mathrm{AY23}] + \sum_i k_i[S_i]} \quad (5)$$

also:

$$I_a = I_0 f_{H_2O_2}[1 - \exp(-2.3l(\varepsilon_{H_2O_2}[H_2O_2] + \varepsilon_{AY23}[\mathrm{AY23}]))] \quad (6)$$

$$f_{H_2O_2} = \frac{\varepsilon_{H_2O_2}[H_2O_2]}{\varepsilon_{H_2O_2}[H_2O_2] + \varepsilon_{AY23}[\mathrm{AY23}]} \quad (7)$$

In Eq. 6, I_o is the incident UV-light intensity, *l* is the optical path length of the system, $\varepsilon_{H_2O_2}$ and ε_{AY23} are the molar extinction coefficients for H_2O_2 and AY23, respectively. Since AY23 and H_2O_2 have a high absorbance in the early stages of the process, it can be written as:

$$1 - \exp(-2.3l(\varepsilon_{H_2O_2}[H_2O_2] + \varepsilon_{AY23}[\mathrm{AY23}])) \approx 1 \quad (8)$$

$$[{}^{\circ}OH]_{ss} = \frac{\phi I_0 f_{H_2O_2}}{k_1[\mathrm{AY23}] + \sum_i k_i[S_i]} \quad (9)$$

By inserting the above expression in to Eq. 3 the following overall rate law is deduced:

$$-\frac{d[\mathrm{AY23}]}{dt} = \frac{k_1 \phi I_0 f_{H_2O_2}}{k_1[\mathrm{AY23}] + \sum_i k_i[S_i]}[\mathrm{AY23}] \quad (10)$$

If the concentration of the substrate is to be high, so that $k_1[\mathrm{AY23}] \rangle\rangle \sum_i k_i[S_i]$, and the overall rate expression simplifies to a zero order reaction rate:

$$-\frac{d[\mathrm{AY23}]}{dt} = \phi I_0 f_{H_2O_2} \quad (11)$$

But in the present study the concentration of AY23 is lower than that of H_2O_2, hence $k_1[\mathrm{AY23}] \langle\langle \sum_i k_i[S_i]$, and the overall rate expression simplifies to a pseudo – first order reaction rate:

$$-\frac{d[\mathrm{AY23}]}{dt} = \frac{k_1 \phi I_0 f_{H_2O_2}}{\sum_i k_i[S_i]}[\mathrm{AY23}] \quad (12)$$

or:

$$-\frac{d[\mathrm{AY23}]}{dt} = k_{ap}[\mathrm{AY23}] \quad (13)$$

The above equation corresponds to a first order reaction. The semi-logarithmic graphs of the concentration of AY23 versus time yield straight lines, indicating reaction of pseudo-first order. The apparent reaction rate constants (k_{ap}) for photooxidation of AY23 in the different light intensities were evaluated from experimental data (Fig. 1) using linear regression. In all cases R^2 (correlation coefficient) values are higher than 0.99 which confirm the proposed kinetics for decolorization of AY23 in this process. The results show that the UV light intensity plays an important role in degradation of AY23. This is due to effective role of light intensity in the formation of high amounts of $^{\cdot}OH$ from H_2O_2 in the solution, which can be used for decolorization and degradation of AY23. On the basis of kinetic modeling and Eq. (14), k_{ap} has a linear relation with light intensity.

$$k_{ap} = \frac{k_1 \phi f_{H_2O_2}}{\sum_i k_i [S_i]} I_0 \quad (14)$$

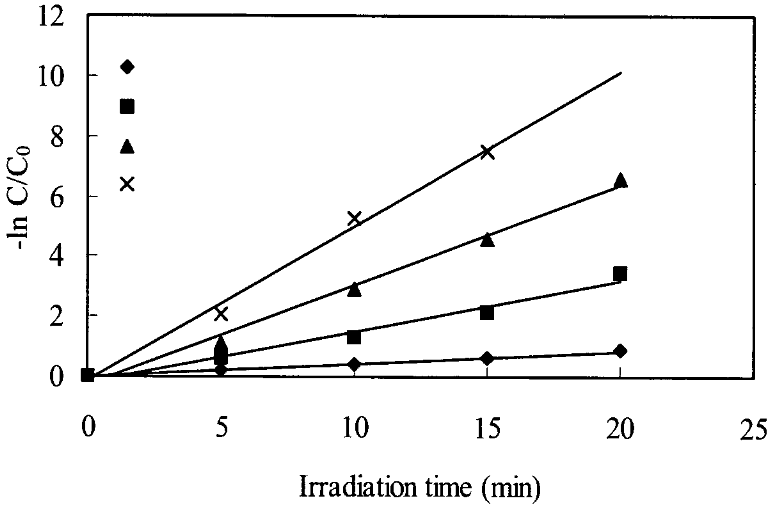


Fig. 1. Derivation of the pseudo-first order rate constants of AY23 in the UV/H_2O_2 process by linear regression. $[AY23]_o = 40\ mgl^{-1}$, $[H_2O_2]_o = 700\ mg\ l^{-1}$.

A plot of the k_{ap} against light intensity was shown in the Fig. 2. From this plot, it can be seen; results obtained from the kinetic modeling are in good agreement with the experimental data.

Eqs. 7 and 13 indicate that k_{ap} is a function of H_2O_2 concentration. The results in Fig. 3 reveal that k_{ap} increases with increasing the amount of H_2O_2 and reaches to an almost constant value above optimum concentration. Since increasing H_2O_2 concentration has two opposing effects: 1. As the concentration of H_2O_2 is increased, more hydroxyl radicals are available to attack the aromatic rings and the rate of reaction increases (Eq. (15)). 2. Above optimum value hydroxyl radical efficiently reacts with H_2O_2 and produces $HO_2^{\cdot}$ (Eq. (16)). Note that $HO_2^{\cdot}$ radicals are less reactive than $OH^{\cdot}$, leading therefore to negligible contribution in the dye destruction [10].

$$H_2O_2 + h\upsilon \rightarrow 2^{\bullet}OH \quad (15)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet} \quad (16)$$

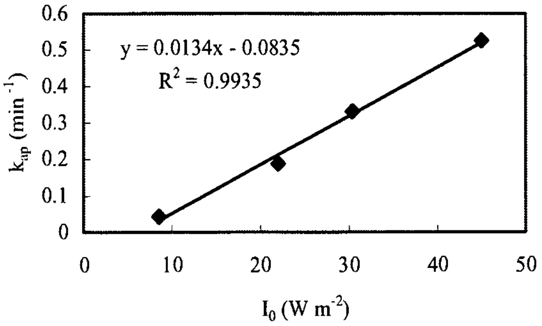


Fig. 2. Relation between pseudo-first order rate constants and light intensity.

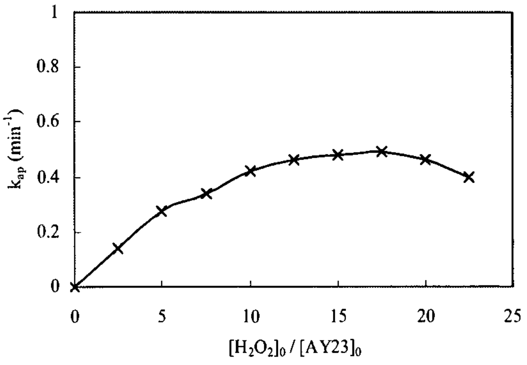


Fig. 3. The pseudo-first order rate constants of AY23 as a function of ratio of H_2O_2 to AY23. $[AY23]_o$= 40 mg l^{-1}, I_o = 45 W m^{-2}.

The influence of initial concentration of the dye solution on the photooxidative degradation is an important aspect of the study. Initial concentrations of AY23 were varied in the range of 20 - 50 mg l^{-1} and the photodegradation percent decreased with increasing initial concentration of the dye solution. On the basis of Eq. (14), k_{ap} is a function of concentration of intermediates products produced from parent compound (AY23). With increasing of initial concentrations of AY23, concentration of intermediates products were increased therefore k_{ap} decreases with increasing of AY23 concentration. The Eq. (14) shows k_{ap} has a linear relation with reverse of initial concentration of the dye. This relation can be tested using experimental data by varying initial concentration of AY23. The plot of k_{ap} versus $1/[AY23]_0$ has been presented in Fig. 4, and shows experimental data are in good agreement with kinetic model.

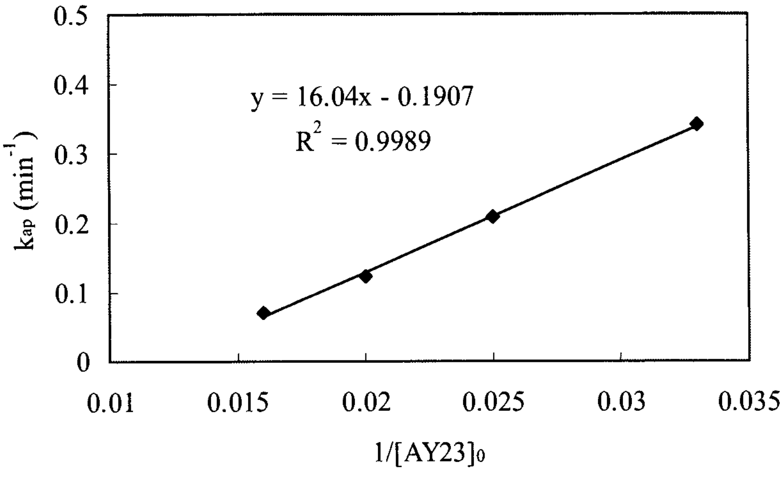


Fig. 4. Relation between pseudo-first order rate constants and initial concentration of the dye. $[H_2O_2]_o$ = 700 mg l^{-1}, I_o = 30.3 W m^{-2}.

5. Conclusions

The results of this study have shown that the kinetics of decolorization of AY23 in the UV/H_2O_2 process is pseudo-first order. On the basis of proposed kinetic model pseudo-rate constant (k_{ap}) is affected with varying light intensity and initial concentrations of AY23 and H_2O_2. Pseudo-rate constant (k_{ap}) decreases as the initial concentration of AY23 increases but it increases with increasing the amount of H_2O_2 and remains almost constant above an optimum value. Between k_{ap} and light intensity is also a linear relation. These findings are in a very good agreement with kinetic model.

Acknowledgements

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