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# Development of a rate expression for predicting decolorization of C.I. Acid Black 1 in a UV/$H_2O_2$ process

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## Abstract

A kinetic rate expression was developed by the experimental results of photochemical reactions that decolorize model azo dye, C.I. Acid Black 1. The decolorization was efficient by UV irradiation with hydrogen peroxide addition. The observed reaction rate constants were determined and correlated as a function of volumetric UV dosage and initial hydrogen peroxide concentration. The decolorization rate follows pseudo-first order kinetic with respect to dye concentration. The rate increases linearly by volumetric UV dosage, yet nonlinearly by hydrogen peroxide concentration. The proposed rate expression model, which considers both the kinetic mechanism and operation parameters, can predict the experimental results well. The prediction and experimental data are in a very good agreement. Besides, this model also integrates the correlation of pH and initial dye concentration in order to enlarge more versatile applications while various dye concentrations and pH range in the real case.

*Keywords:* Rate expression equation; Azo dye; Decolorization; UV/$H_2O_2$; AOPs; Oxidation

## 1. Introduction

Textile industry is one of the most important industries among Taiwan's economics since last few decades. There are about 10,000 dyes used in textile industry. Among these dyes, azo dyes constitute the largest and the most important class of commercial dyes. Effluents of textile dyeing and finishing industries often contain high intensity of color and high chemical oxygen demand (COD), which are objectionable if they were discharged without proper treatment. Therefore, the efficient treatment of dyeing and finishing wastewater becomes the major environmental concern of textile industries.

The Taiwan EPA issues stricter effluent standards to enforce textile industries decolorize and eliminate pollutants in wastewater before discharge to surface water. Because of the regulatory enforcement, technologies of dye wastewater decolorization become more and more important. The textile dyeing and finishing wastewater contaminated with azo dyes was typically treated in a conventional wastewater treatment system. Textile dyestuffs have complicated aromatic structures which resist degradation in biological system. It was first reported by U.S. Water Engineering Research Laboratory of EPA that 11 out of 18 studied azo dyes were substantially unaffected by the activated sludge process [1]. Further studies on biodegradability showed that azo dyes were very difficult to biodegrade under aerobic conditions [2,3]. Consequently, alternative technologies to treat these refractory azo dyes have to be explored. Advanced oxidation processes (AOPs) are widely used to decompose various hazardous organics in industrial

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**Nomenclature**

| | |
|---|---|
| $C_d$ | AB1 concentration, mM; |
| $C_{OH\cdot}$ | the hydroxyl radical concentration, mM; |
| $k$ | the second order rate constant, $min^{-1} mM^{-1}$; |
| $k_{obs}$ | the observed first order rate constant, $min^{-1}$; |
| $D$ | volumetric UV dosage, W/l; |
| $k_I$ | the slope of each line (in Eq. (3)), $min^{-1} W^{-1} l$; |
| $C_{h0}$ | the initial concentration of hydrogen peroxide, mM; |
| $\varphi_{pH}$ | the pH correlation index; |
| $C_{d0}$ | the initial dye concentration, mM; |
| $\varphi_c$ | the initial dye concentration correlation index. |

wastewater and groundwater. The extensive literature in this field that contains $O_3$, UV/$H_2O_2$, UV/$O_3$, $O_3$/$H_2O_2$, etc., has been reviewed by Venkatadri and Peters [4]. When dealing with refractory organic in wastewater, AOPs appear to possess distinct advantages such as powerful oxidation ability, high decomposition efficiency of hazardous organics, small requirements of reactor volume, no sludge production, and low toxic intermediates. During the last decade, some investigations have reported about the successful application of the UV/$H_2O_2$ process, one of the AOPs, for dye wastewater treatment. Our previous study demonstrated that the UV/$H_2O_2$ process was able to decolorize Acid Red 1 and Acid Yellow 23 [5]. Meanwhile, initial hydrogen peroxide concentration was found to be a very important operating parameter, which can affect the pseudo-first order reaction rate. There was an optimum molar concentration ratio of about 416 of hydrogen peroxide to dye ($C_{h0}/C_{d0}$) for Acid Red 1. Similarly, Galindo and Kalt found an optimum ratio of $C_{h0}/C_{d0}$ of about 1754 for Acid Orange 7 [6]. Colonna et al. demonstrated that there was an optimum ratio of $C_{h0}/C_{d0}$ of about 500 for Acid Red 1 [7]. Neamtu et al. and Cisneros et al. also reported the same observation of optimum ratio of $C_{h0}/C_{d0}$ for Reactive Black 5 and Hispamin Black CA, respectively [8,9]. Ince reported [10] an optimum ratio of $C_{h0}/C_{d0}$ of about 826 for Remazol Black-B. The author also established a useful mathematical relation between decolorization rate and initial $H_2O_2$ concentration in a UV/$H_2O_2$ process. In addition, Mohey El-Dein et al. developed a kinetic model for decolorization of Reactive Black 5 that described $H_2O_2$ concentration and UV intensity affected the experimental observed rate coefficients [11]. Most of the previous kinetic models of UV/$H_2O_2$ reactor were developed only considering certain UV light source and dye species. They can be limited to be applied by other researchers or industries.

The objective of our study was to evaluate the feasibility of alternative wastewater treatment of azo dye, C.I. Acid Black 1 (AB1), by UV/$H_2O_2$ process. The optimization of operating parameters was reported in our previous paper [12], in this work, we aim to develop a kinetic model, rate expression equation, which describes the scenario of AB1 decolorization using UV/$H_2O_2$ reactor. A decolorization model was developed not only in consideration of well-known theory of chemical reaction mechanism, and the operating parameters such as volumetric UV intensity (UV energy input per reactor volume), initial $H_2O_2$ concentration, but also integrating effects of initial dye concentration and pH to make our model applications for all situations. On the other hand, we also adjusted the UV light intensity to a volumetric UV dosage in order to gain the model versatile applications.

## 2. Experimental

### 2.1. Materials

Hydrogen peroxide was obtained from Fluka Chemical (30% w/w). The C.I. Acid Black 1 (AB1, $C_{22}H_{14}N_6Na_2O_9S_2$, M.W. 616.50, $\lambda_{max} = 618$ nm, dye content 85%) was obtained from Aldrich Chemical Co. without further purification. The chemical structure of C.I. Acid Black 1 is shown in Fig. 1.

### 2.2. Apparatus and procedure

The reactor used in this study was New England Photochemical Co. Model RPR-100 photochemical reactor fitted with 16 low pressure mercury arc UV lamps (wavelength 253.7 nm, 35 W/lamp) along the inner wall of reactor. This allowed a total of 560 W that may be applied in a 500 ml quartz stirred vessel. The details of this reactor and its operation were given in our previous paper [12].

### 2.3. Analyses

Optical absorption spectra on AB1 were determined by a Cray DMS-300 spectrophotometer. The characterized wavelength of 618 nm for AB1 was selected for

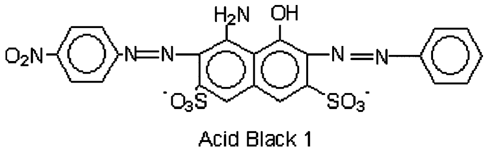

Fig. 1. The molecular structure of C.I. Acid Black 1 studied in this work.

quantitative analysis. Hydrogen peroxide concentration was determined by spectrophotometer method proposed by Masschelein et al. [13].

## 3. Results and discussion

### 3.1. Observed first order rate constants

The decolorization kinetics of azo dye, AB1, in aqueous solution by UV/$H_2O_2$ process was investigated in order to determine a rate expression. The decolorization rate was measured by operating parameter study considering the volumetric UV light intensity ($D$), initial hydrogen peroxide concentration ($C_{h0}$), initial dye concentration ($C_{d0}$) and pH. The reason why we chose AB1 as a target dye in this work was its property on the non-biodegradable list of USEPA [1]. From our previous study, AB1 was also identified as a di-azo dye of fairly difficult treatment among eight azo dyes by either ozonation or UV induced ozonation process [14]. In order to study the reaction kinetics of AB1 decolorization, the pseudo-first order kinetic model derived straight lines by plotting a semi-log scale of dye concentration versus time. Besides, the photo-oxidation of UV/$H_2O_2$ process was conducted in order to verify not only the treatment effectiveness, but also to observe the decolorization rate. Thus, the experiment was designed to run by UV light or hydrogen peroxide alone without using the other. The decolorization was negligible in both cases, that is, neither hydrogen peroxide nor UV radiation alone decolorizes AB1 significantly. However, it was decolorized by a relatively high reaction rate once UV was mixed with $H_2O_2$ because of hydroxyl radical ($OH^{\bullet}$) generation by UV irradiating hydrogen peroxide. Thus, the more reactive hydroxyl radicals irradiated by UV/$H_2O_2$ process definitely created the greater decolonization rates of AB1.

The major decolorization rate expression of AB1 can be described as follows (Eq. (1)):

$$-\frac{dC_d}{dt}=kC_dC_{OH^{\bullet}} \quad (1)$$

where, $C_d$ represents AB1 concentration; $C_{OH^{\bullet}}$ denotes the hydroxyl radical concentration; $k$ is the second order rate constant. Assuming hydroxyl radical concentration reaches equilibrium instantaneously, once the reaction starts under excess concentration of hydrogen peroxide, $C_{OH^{\bullet}}$ can be viewed as a constant. The rate equation is then simplified into a pseudo-first order kinetic model (Eq. (2)).

$$-\frac{dC_d}{dt}=k_{obs}C_d \quad (2)$$

where, $k_{obs}$ represents the observed first order rate constant. Experiments were conducted in a 400 ml bench scale photochemical reactor, while from 175 to 1400 W/l of volumetric UV dosage, 3.54–42.48 mM of initial hydrogen peroxide concentration and $2.758 \times 10^{-2}$ mM of AB1 concentration. Fig. 2 shows the logarithmic changes of AB1 concentration versus time while hydrogen peroxide concentration is 7.08 mM. The observed pseudo-first order rate constants ($k_{obs}$) of photo-oxidation were calculated by linear regression: 0.9677 $min^{-1}$ by 1050 W/l and 1.3180 $min^{-1}$ by 1400 W/l. Consequently, the values of square of relative correlation coefficients ($R^2$) were 0.996 and 0.984, respectively. Table 1 presents the observed pseudo-first order rate constants ($k_{obs}$) of various experimental runs. The $k_{obs}$ values increased by increasing UV dosage with same initial $H_2O_2$ concentration. In addition, the amount of UV irradiated photolysis of $H_2O_2$ affects importantly the formation of a large amount of $OH^{\bullet}$ in solution which enhances the decolorization of AB1. The decolorization rate increases by increasing UV dosage. Also, the more UV energy consumed per unit volume, the faster the decolorization rates of the AB1 performed.

### 3.2. Kinetic modeling

The kinetic model for decolorization of AB1 was derived using the reaction mechanism reported in previous study [15]. In this model, mainly two dependable steps were proposed for decolorization: (1) the

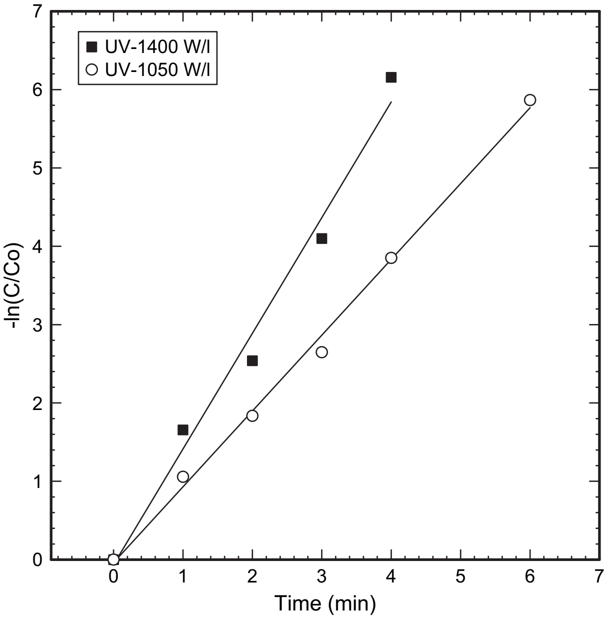

Fig. 2. The first order rate constants versus time while initial dye concentration of $2.758 \times 10^{-2}$ mM and hydrogen peroxide concentration of 7.08 mM. The constants are as function of volumetric UV dosage.

Table 1
Observed pseudo-first order rate constants ($k_{obs}$) of experimental runs

| $C_{h0}$ (mM) | Volumetric UV dosage (W/l) | | | | | |
|---|---|---|---|---|---|---|
| | 175 | 350 | 525 | 700 | 1050 | 1400 |
| 3.54 | 0.1077 | 0.1772 | 0.3416 | 0.4771 | 0.6930 | 0.9620 |
| 7.08 | 0.1669 | 0.2862 | 0.4475 | 0.6755 | 0.9677 | 1.3180 |
| 14.06 | 0.1585 | 0.3664 | 0.6434 | 0.8802 | 1.3229 | 1.9110 |
| 21.24 | 0.1793 | 0.4804 | 0.7753 | 1.0979 | 1.6655 | 2.1526 |
| 28.56 | 0.1808 | 0.4967 | 0.8317 | 1.1232 | 1.7837 | 2.1930 |

formation of $OH^{\bullet}$ by photolysis of hydrogen peroxide; and (2) the reaction between $OH^{\bullet}$ and $H_2O_2$. Theoretically, the higher volumetric UV dosage ($D$) may irradiate $OH^{\bullet}$ radical readily faster so as to lead the higher decolorization rate. By plotting the $k_{obs}$ versus $D$, an approximately linear relationship can be obtained as shown in Fig. 3. Thus, the $k_{obs}$ can be characterized by linear dependence on volumetric UV dosage at various $H_2O_2$ concentrations. Meanwhile, the decolorization of AB1 was negligible resulting into all six lines forcefully passing through the origin in absence of UV light. This relationship can be described by following Eq. (3).

$$k_{obs} = k_I D \tag{3}$$

where, $k_{obs}$ is linear proportional to volumetric UV dosage, $D$ and $k_I$ is the slope of each line. By linear regression, $k_I$ can be modeled as function of initial hydrogen peroxide concentration ($C_{h0}$) from 3.54 to 42.48 mM and obtained from the slopes in Fig. 3. In addition, there is a second $x$-axis plotted by the concentration ratio of initial hydrogen peroxide to dye of $C_{h0}/C_{d0}$ for observation of the important ratio effectiveness. In figure, the decolorization rate increases linearly while $C_{h0}$ at low ratio of $C_{h0}/C_{d0}$ of about 100–500. By increasing the ratio of $C_{h0}/C_{d0}$ greater than 800, the decolorization rate increases slightly. Yet, once the ratio of $C_{h0}/C_{d0}$ is continuously incrementing, higher than 1200, the decolorization rate decreases due to remaining hydrogen peroxide in solution which competes the $OH^{\bullet}$ radicals with dye. Accordingly, the results indicated the nonlinear relationship between $k_I$ and $C_{h0}$ in some experimental situations because $OH^{\bullet}$ radicals irradiated by the UV/$H_2O_2$ process were competed by dye and $H_2O_2$ of overdose. Hence, we suggest combining two terms of $a \times C_{h0}/(b + C_{h0})$ and competition term or inhibition constant of $1/(1 + C_{h0}/k_c)$. In Fig. 4, the proposed rate expression fits very well with experimental data. The constants obtained in this regression model are $a = 0.0038$, $b = 17.5312$, $k_c = 53.7634$, and $R^2 = 0.980$. Meanwhile, an optimum $C_{h0}/C_{d0}$ can be found in a range from 500 to 1000. Similarly, the observations of optimum $C_{h0}/C_{d0}$ and $C_{h0}$ also were mentioned by other investigators such as 851 by Cisneros et al.; 826–1100 by Ince; 859 by Galindo and Kalt; and 400 by Colonna et al. [9,10,6,7]. The rate expression model can be then rearranged as following Eq. (4).

$$k_I = \frac{0.0038 \times C_{h0}}{(17.5312 + C_{h0})\left(1 + \frac{C_{h0}}{53.7634}\right)} \tag{4}$$

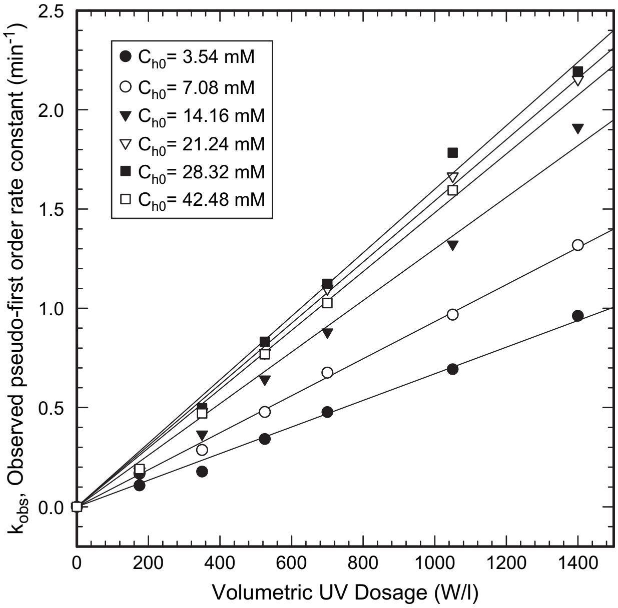

Fig. 3. Observed pseudo-first order rate constants versus volumetric UV dosage at various hydrogen peroxide concentrations.

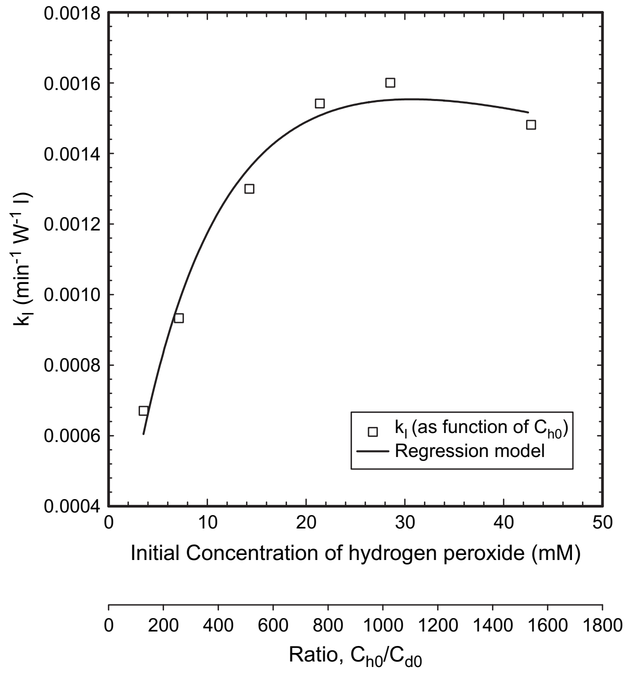

Fig. 4. The second order rate constant, $k_I$, which is as function of initial hydrogen peroxide concentration. The second axis denotes ratio of initial hydrogen peroxide concentration to initial dye concentration.

where, $C_{h0}$ denotes the initial concentration of hydrogen peroxide. By substituting $k_I$ in Eq. (3), we can calculate the $k_{obs}$ which the empirical kinetic model predicts. The experimental results by combining UV with hydrogen peroxide for the initial dye concentration of $2.758 \times 10^{-2}$ mM shown in Fig. 5. The model prediction was compared with experimental calculation data at volumetric UV dosage of 350, 700, and 1400 W/l. As a result, the model performs adjacently fit to the experimental data in all experimental runs. The model prediction and experimental results are consistent in such circumstance of operating parameters.

### 3.3. Integrating effects of pH and initial dye concentration

Except the consideration of UV dosage and hydrogen peroxide concentration in kinetic model expression mentioned above, two more parameters such as pH and initial dye concentration were added in order to enlarge the applications in real case. By raising pH, decolorization rates of dye fall under the UV/$H_2O_2$ process because hydrogen peroxide generally decomposes into water and oxygen rather than hydroxyl radicals in alkaline condition. Initially, the pH was 5.25 for $2.758 \times 10^{-2}$ mM of AB1 and 7.08 mM of $H_2O_2$ solution. By adding 1 N NaOH solution pH was raised to 6.95, 9.05, and 11.0. The observed decolorization rate of AB1 decreased while increasing pH according to the alkalinic catalytic decomposition of $H_2O_2$. Additionally, three more adjustments were performed by adding HCl solution to decrease the pH of 2.96 and 1.98. The decolorization rate of AB1 under pH 2.96 can lightly increase than that under pH 5.25. However, once the pH was lower than 2.96, the rate decreased oppositely. Thus, a very narrow operation window, pH range of about 3.0–5.15 for high rates can be obtained, as shown in Fig. 6. This means that the unsuccessful treatment of wastewater contaminated with AB1 can be performed with pH higher than 5.15 and less than 3.0. Also, it is not recommended by adjusting the pH to the narrow window of 3.0–5.15 in order to approach indistinguishable rate increase. To uncover pH effect, the ratio of $k_{obs}$ of the decolorization at each pH level is divided by $k_{obs}$ at pH 5.15 and a pH correlation index ($\varphi_{pH}$) can be obtained. The ratios then were plotted versus pH as illustrated in Fig. 6 which shows the most suitable pH for operating conditions. An expression equation of $\varphi_{pH}$ was developed by the experimental data. Since the $k_{obs}$ decreases at higher pH value, a similar approach was used for pH effect modeling as well as that for $C_{h0}$ in Eq. (4). The effect of pH that the model performed in very good prediction can be expressed by $\varphi_{pH}$, shown in Fig. 6. By nonlinear regression, the $\varphi_{pH}$ can be found as follows (Eqs. (5) and (6)):

$$\varphi_{pH} = \frac{4.0502 \times pH}{(1 + 0.3112 \times pH)(3.1733 + pH)} \tag{5}$$

$$k_{obs} = k_I \times D \times \varphi_{pH} \tag{6}$$

where, $\varphi_{pH}$ denotes the pH correlation index.

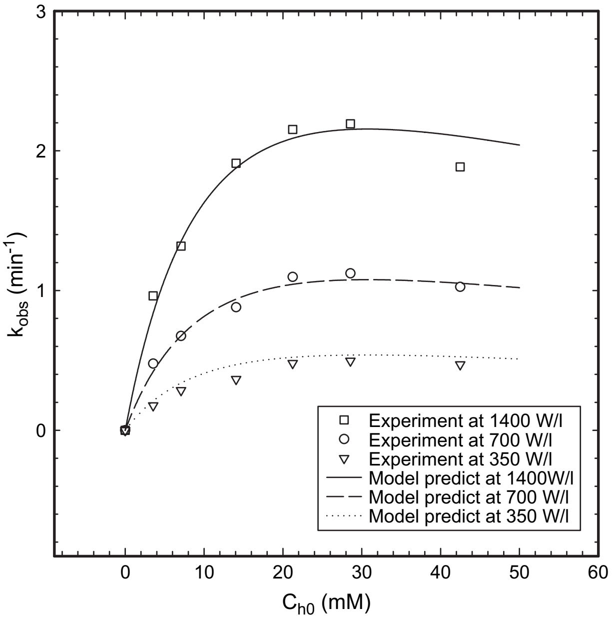

Fig. 5. The comparison of experimental measured and model predicted $k_{obs}$ for various volumetric UV dosages and hydrogen peroxide concentrations. Initial dye concentration is $2.758 \times 10^{-2}$ mM.

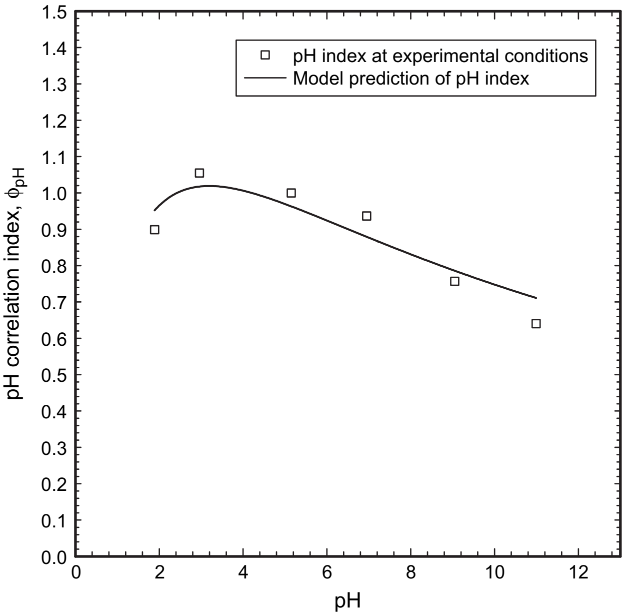

Fig. 6. The experimental measured and model predicted pH index ($\varphi_{pH}$) as a function of pH. Initial dye concentration is $2.758 \times 10^{-2}$ mM and hydrogen peroxide concentration is 7.08 mM. UV dosage is 350 W/l.

Besides, the other parameter included in the model enlargement was the effect of initial dye concentration ($C_{d0}$) on the decolorization rate of AB1 as shown in Fig. 7. Some researchers reported that the observed rate constant ($k_{obs}$) increases by decreasing initial dye concentration [6,16]. An initial dye concentration correlation index ($\varphi_c$) was developed by experimental data under three volumetric UV dosages (700, 1050, 1400 W/l) and three initial dye concentrations ($2.758 \times 10^{-2}$, $4.137 \times 10^{-2}$, $5.516 \times 10^{-2}$ mM). $\varphi_c$ is defined as the experimental $k_{obs}$ divided by the model calculated $K_{obs}$ using Eqs. (3) and (4) at $C_{d0}$ of $2.758 \times 10^{-2}$ mM. The nine of $\varphi_c$ values were then plotted versus $1/C_{d0}$ as in Fig. 7. By linear regression, expression equation of $\varphi_c$ can be found as follows (Eq. (7)):

$$\varphi_c = -0.0562 + 2.0216 \times 10^{-3} \times \frac{1}{C_{d0}} \tag{7}$$

where, $\varphi_c$ denotes the initial dye concentration correlation index. $k_{obs}$ of $C_{d0}$ other than $2.758 \times 10^{-2}$ mM can be estimated using following Eq. (8).

$$k_{obs} = k_I \times D \times \varphi_c \tag{8}$$

From Fig. 7, the effect of initial dye concentration can be expressed by $\varphi_c$ which performs in very good prediction of experimental results. For example, at initial dye concentration of $5.516 \times 10^{-2}$ mM the correlation index, $\varphi_c$, was calculated to be 0.463. For hydrogen peroxide concentration of 28.32 mM and UV dosage of 1400 W/l, the $k_{obs}$ was estimated by Eq. (8) to be 1.037 min$^{-1}$ which is very close to the experimental data of 0.971 min$^{-1}$. Ultimately, summarizing the modeling for a batch UV/$H_2O_2$ reactor can be finalized as follows (Eq. (9)):

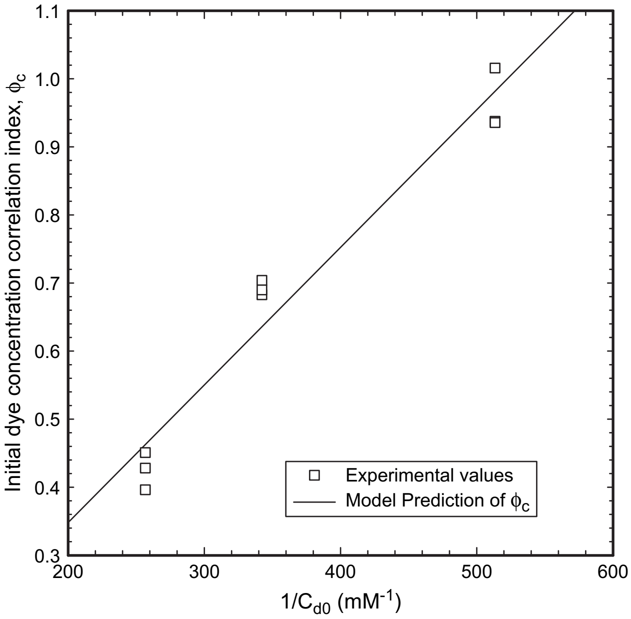

Fig. 7. The experimental measured and model predicted initial dye concentration index ($\varphi_c$) as a function of ($1/C_{d0}$). UV dosages are 700, 1050, 1400 W/l and initial dye concentrations are 2.758, 4.137, $5.516 \times 10^{-2}$ mM, respectively. The hydrogen peroxide concentrations are 14.16, 21.24, 28.32 mM.

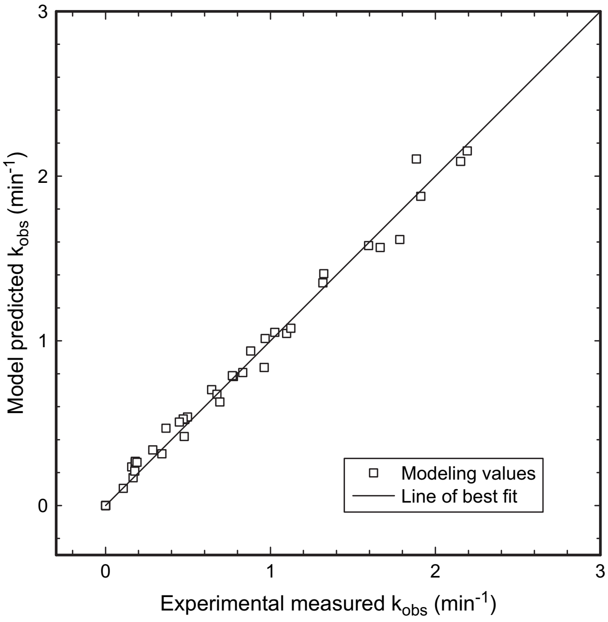

Fig. 8. Model predicted $k_{obs}$ versus experimental measured $k_{obs}$ of 36 experimental runs shown in Table 1.

$$-\frac{dC_d}{dt} = \frac{0.0038 \times C_{h0} \times D \times C_d}{(17.5312 + C_{h0})\left(1 + \frac{C_{h0}}{53.7634}\right)} \times \varphi_c \times \varphi_{pH} \tag{9}$$

Comparision of the experimentally measured $k_{obs}$ with predicted $k_{obs}$ calculated by model Eq. (9) is shown in Fig. 8. The model of rate expression equation attempts to predict and validate the experimental results accurately. Substantially, the model predicts fairly well while $R^2$ of 0.989 by various operating parameters such volumetric UV dosage, initial hydrogen peroxide concentration, pH and initial dye concentration. Therefore, our proposed model demonstrates successfully the prediction of observed decolorization rate constants of AB1 in a UV/$H_2O_2$ reactor.

## 4. Conclusions

The UV induced hydrogen peroxide oxidation (UV/$H_2O_2$) is a powerful technology for decolorizing AB1. While UV radiation alone, or hydrogen peroxide oxidation alone can hardly decolorize the dye. Therefore, the decolorization rates of AB1 were determined in the presence of hydrogen peroxide with UV radiation.

The operation parameters such as volumetric UV dosage, initial hydrogen peroxide concentration, pH, and initial dye concentrations, significantly influence the reaction rates. Kinetic model developed in this study can predict the observed reaction rate constants ($k_{obs}$) in a very good agreement with experimental results. To maximize the reaction rate, an optimum $C_{h0}/C_{d0}$ can be identified in a range from 500 to 1000 for AB1 in the giving system. The observations of optimum $C_{h0}/C_{d0}$ also were mentioned by other investigators. Therefore, we suggest introducing a competition term or inhibition term, $1/(1 + C_{h0}/k_c)$ into the proposed model.

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