

Decolorization of azo dye acid black 1 by the UV/H₂O₂ process and optimization of operating parameters

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Abstract

An advanced oxidation process, UV/H₂O₂, was applied for decolorization of a di-azo dye (acid black 1). The effects of operating parameters such as hydrogen peroxide dosage, UV dosage and initial dye concentration, on decolorization have been evaluated. The acid black 1 solution was completely decolorized under optimal hydrogen peroxide dosage of 21.24 mmol/l and UV dosage of 1400 W/l in less than 1.2 min. The decolorization rate followed pseudo-first order kinetics with respect to the dye concentration. The rate increased linearly with volumetric UV dosage and nonlinearly with increasing initial hydrogen peroxide concentration. It has been found that the degradation rate increased until an optimum of hydrogen peroxide dosage, beyond which the reagent exerted an inhibitory effect. For real case application, an operation parameter plot of rate constant was developed. To evaluate the electric power and hydrogen peroxide consumption by UV/H₂O₂ reactor, 90% color removal was set as criteria to find the balance between both factors.

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1. Introduction

Textile industry is one of the most important industries among Taiwan's economic development contribution in last few decades. There are about 10,000 kinds of dyes used in textile industry. The industry wastewater was concerned because of its quality and quantity, so that Taiwan EPA issued the stricter effluent standards to enforce the decolorization and elimination of pollutants in wastewater before discharging into surface water body. Therefore, technologies of dye wastewater decolorization become more and more important to follow the regulatory enforcement.

High levels of environmental contamination are produced in effluents of textile dyeing and finishing industries, due to high color intensity and chemical oxygen demand (COD). Some azo dyes, dye precursors, and their degradation prod-

ucts such as aromatic amines were known to be carcinogenic by Brown and DeVito [1]. Textile dyestuffs with complicated aromatic structures resisted the degradation in conventional biological wastewater treatment system. The United States Environmental Protection Agency's (U.S. EPA) Water Engineering Research Laboratory first reported that 11 out of 18 studied azo dyes were substantially unaffected by the activated sludge process [2]. Some other studies [3–4] showed the similar results that azo dyes were very difficult to be biodegraded under aerobic conditions. Some biological treatment processes using anaerobic condition were studied to effectively decolorize azo dyes [5–6]. However, most of the textile industries employed traditional activated sludge process for their wastewater treatment in Taiwan. Thus, textile industries have difficulties meeting the new color regulation using their aerobic biological and chemical coagulation treatment technology [7]. That implies textile dyeing industries should pursue efficient technique as pre-treatment or polishing processes to decolorize the highly colored wastewater. Consequently, the alternative and innovative technologies of the

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refractory azo dyes have to be explored urgently. In general, by adsorption onto activated carbon or chemical coagulation were employed to deal with dye wastewater [8,9]. However, these treatment methods mainly transferred the contaminant from wastewater into solid wastes that the spent activated carbon and coagulant sludge need further and ultimate disposal eventually. Thus, textile industries were compelled to consider the alternative technologies for dealing with wastewater problems in order to meet the effluent standards and cost economical as well.

One of the advanced oxidation processes (AOPs), which combine UV radiation and hydrogen peroxide (UV/H₂O₂), may provide a better solution for textile effluents. AOPs are widely used to decompose various hazardous organics in industrial wastewater and groundwater. The extensive literature in this field has been reviewed by Venkatadri and Peters [10]. In the system, the free radicals (OH•) are dominant species with the potential ability to oxidize most of organic contaminants, which are mineralized into carbon dioxide and water in wastewater. The formation of free radicals is fairly affected by the amount of UV radiation absorbed by H₂O₂, initial concentration of hydrogen peroxide, and initial concentration of contaminants. Sometimes, to reach effectiveness of treatment requires large light power and oxidant dosage so that cost increases in comparison with traditional treatments such as coagulation and adsorption. Thus, optimizing the operating parameters, the UV/H₂O₂ process can be a feasible and economical method. UV/H₂O₂ process appears 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 investigators have reported the successful applications of the UV/H₂O₂ process of dye wastewater treatment. Shu et al. [11] demonstrated that the UV/H₂O₂ process was able to decolorize acid red 1 (AR1) and acid yellow 23. They also found that initial hydrogen peroxide concentration was a very important operating parameter, which affected the pseudo-first order reaction rate. Besides, an optimal molar ratio of hydrogen peroxide to dye concentration (H₂O₂/dye) of AR1 was about 416, while 500 demonstrated by Colonna et al. [12]. Similarly, Galindo and Kalt [13] showed the optimal ratio of H₂O₂/dye of acid orange 7 to be calculated as 1754. Moreover, there were some other similar observations of optimal H₂O₂/dye ratio for various dyes by the researchers [14–18].

The aim of this work was to evaluate the possibility of treatment alternative for AB1 dye wastewater by UV/H₂O₂ process. Also, the operating parameters such as hydrogen peroxide dosage, UV dosage, and initial dye concentration were determined to find the optimum conditions. Besides, rate constants were obtained and discussed relationship with the operation parameters. Meanwhile, setting criteria of 90% color removal was used to evaluate both of the best utilization factors of electric power and hydrogen peroxide consumption by the UV/H₂O₂ reactor.

2. Experimentation

2.1. Materials

Hydrogen peroxide was obtained from Fluka Chemical (30% w/w). The acid black 1 (AB1) was obtained from Aldrich Chemical Co. and used without further purification. The characteristics such as wavelength, molecular weight, dye contents and structure of AB1 are given in Table 1. Reagents for the measurement of hydrogen peroxide were all ACS analytical reagent grade from Fisher Scientific Co., and the stock solution was refrigerated and stored in the dark.

2.2. Apparatus

The New England Photochemical Co. Model RPR-100 photochemical reactor, which fitted with 16 RPR-1849/2537 Å low pressure mercury arc UV lamps (wavelength 253.7 nm, 35 W per lamp) along the inner wall of reactor, was employed in this study. Thus, a total of 560 W input power may be applied in a 500 ml quartz stirred vessel. The UV intensity readings for 253.7 nm were 12,800 and 21,000 μW/cm² at reactor center and 2 in. from lamp base on manufacturer's test report, respectively. Photons were measured as $1.65 \times 10^{16} \text{ s}^{-1} \text{ cm}^{-3}$. A UVP made UVX radiometer was used to make sure the UV lamps were in good conditions. The completely mixing of solution was achieved using nitrogen bubbling. The pH was monitored by a pH controller and monitor device.

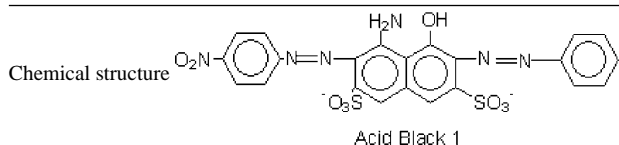
A quartz vessel, which contained 400 ml tap water with various dye concentration, and hydrogen peroxide dosage, was reacted in the photo-oxidation reactor with various UV dosages. Samples were withdrawn at time intervals and analyzed by the spectrophotometer.

2.3. Analyses

Optical absorption spectrum of AB1 was determined by a Cray DMS-300 spectrophotometer. The concentration correlation can be quantified by absorption analysis of the characterized wavelength of 618 nm for AB1 by linear regression. Hydrogen peroxide concentration was determined by spectrophotometer method based on the method, which was proposed by Masschelein et al. [19]. By adding 1.0 ml of Co(II) reagent and 1.0 ml of hexa-*meta*-phosphate solution to 80 ml

Table 1
The characteristics of acid black 1

Azo dyes	Formula	λ_{max} (nm)	MW	Dye contents (%)
Acid black 1	C ₂₂ H ₁₄ N ₆ Na ₂ O ₉ S ₂	618	616.50	85



sample and making up to 100 ml with saturated bicarbonate solution, a green color is developed for the measurement of the absorbance at 260 nm. The hydrogen peroxide concentration was obtained with respect to absorbance by linear regression of calibration curve.

3. Results and discussion

The experimental tests for AB1 decolorization were studied by various operating parameters such as UV light intensity, initial concentrations of hydrogen peroxide and dye. AB1 was one of eleven non-biodegradable dyes studied by EPA [2] and identified as the most difficult to be decolorized among eight azo dyes by the ozonation [20].

3.1. Reaction rate expression

The decolorization of AB1 over time as function of UV light intensity in a 400 ml bench scale photochemical reactor was shown in Fig. 1. Meanwhile the initial concentration of hydrogen peroxide was 7.08 mmol/l and that of AB1 was 20 mg/l (2.758×10^{-2} mmol/l). The major decolorization rate expression of AB1 can be expressed as follows:

$$-\frac{dC_A}{dt} = k_1 C_A C_{OH\cdot} + k_2 C_A C_{HO_2\cdot} \quad (1)$$

where C_A represents AB1 concentration, t expresses time, $C_{HO_2\cdot}$ denotes the peroxy radical concentration, and $C_{OH\cdot}$ denotes the hydroxyl radical concentration. Assuming hydroxyl radical and peroxy radical concentration reach equilibrium instantaneously with excess hydrogen peroxide. Thus, the $C_{OH\cdot}$ and $C_{HO_2\cdot}$ can be viewed as a constant. The

oxidation potential of peroxy radical is much less than hydroxyl radical, and it is negligible. Therefore, the rate expression equation is then simplified into a pseudo-first order kinetic model.

$$-\frac{dC_A}{dt} = k_{obs} C_A \quad (2)$$

where k_{obs} represents a pseudo-first order kinetic constant. By integrating the both sides, the equation can be expressed as follows:

$$-\ln\left(\frac{C_A}{C_{A0}}\right) = k_{obs} t \quad (3)$$

where C_{A0} represents initial concentration of AB1. Base on the above rate expression equations, the logarithmic changes in normalized AB1 concentration (C_A/C_{A0}) with time were shown in Fig. 2. The observed pseudo-first order rate constants of UV/ H_2O_2 reaction were calculated by linear regression, 0.6755 and 1.1232 min^{-1} for UV intensity of 700 and 1400 W/l, respectively. The square of the relative coefficients (R^2) of six experimental tests by linear regression was in the range from 0.982 to 0.998. The straight lines can be obtained by plotting $-\ln(C_A/C_{A0})$ versus time shown in Fig. 2 so that explained a pseudo-first order reaction assumption was reasonable.

3.2. Effect of initial hydrogen peroxide concentration

The observed pseudo-first order rate constants (k_{obs}) of the dye decolorization versus hydrogen peroxide dosage were plotted in Fig. 3 while UV intensity varied from 175 to 1400 W/l. The hydrogen peroxide concentration was stoichiometrically over-dosaged and was measured to be relatively unchanged during the experiments. There existed maximum rate constants particularly when hydrogen peroxide concentrations of 21.24–28.32 mmol/l and high UV intensity of 1400 W/l. Increasing of H_2O_2 concentration greater than 28.32 mmol/l, the decolorization rate slowly decreased. However, the rates nearly accelerated while UV dosages were lower than 700 W/l, and the hydrogen peroxide concentrations were greater than 21.24 mmol/l. Explanation of this scenario was that increasing photolysis of H_2O_2 by incrementing its concentration may be counterbalanced by $OH\cdot$ scavenging by H_2O_2 . That means excess H_2O_2 reacts with $OH\cdot$ and competes with dye in the solution while the photolysis is processing at the same time. Therefore, the optimum of hydrogen peroxide concentration observed for the maximum AB1 decolorization was between 21.24 and 28.32 mmol/l. There was a second x-axis made by C_{H_0}/C_{A0} scale and labeling which expressed the importance of initial concentration ratio of hydrogen peroxide to dye. Here, C_{H_0} denotes initial concentration of hydrogen peroxide. We found the optimum ratio of C_{H_0}/C_{A0} was from 500 to 800. The observations of optimal C_{H_0}/C_{A0} also were mentioned the ratio C_{H_0}/C_{A0} of 851 and 826–1100 by Cisneros et al. [17] and Ince [15], respectively.

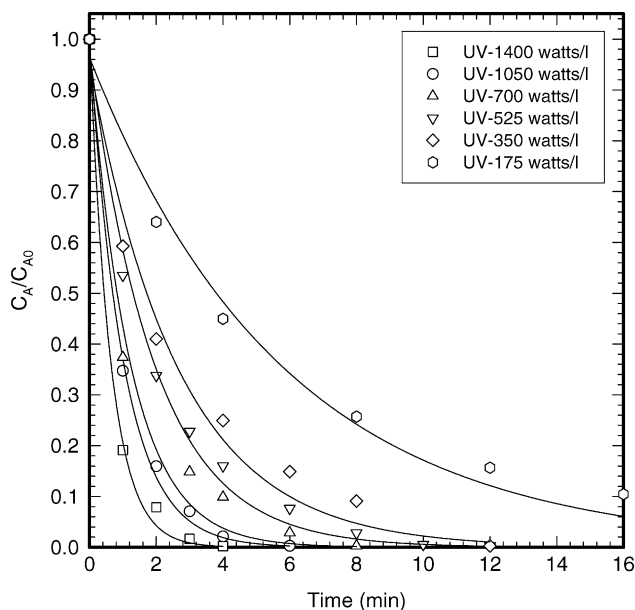


Fig. 1. The normalized concentration (C_A/C_{A0}) of AB1 vs. time as a function of volumetric UV dosage while 2.758×10^{-2} mmol/l of initial dye concentration and 7.08 mmol/l of hydrogen peroxide concentration.

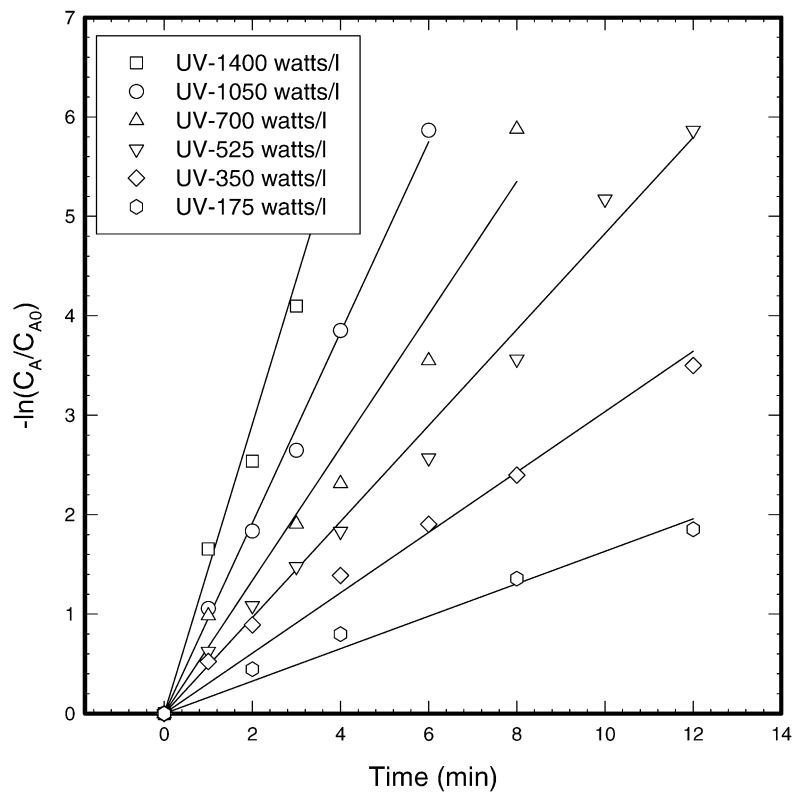


Fig. 2. The first order rate expression of AB1 vs. time as a function of volumetric UV dosage while 2.758×10^{-2} mmol/l of initial dye concentration and 7.08 mmol/l of hydrogen peroxide concentration.

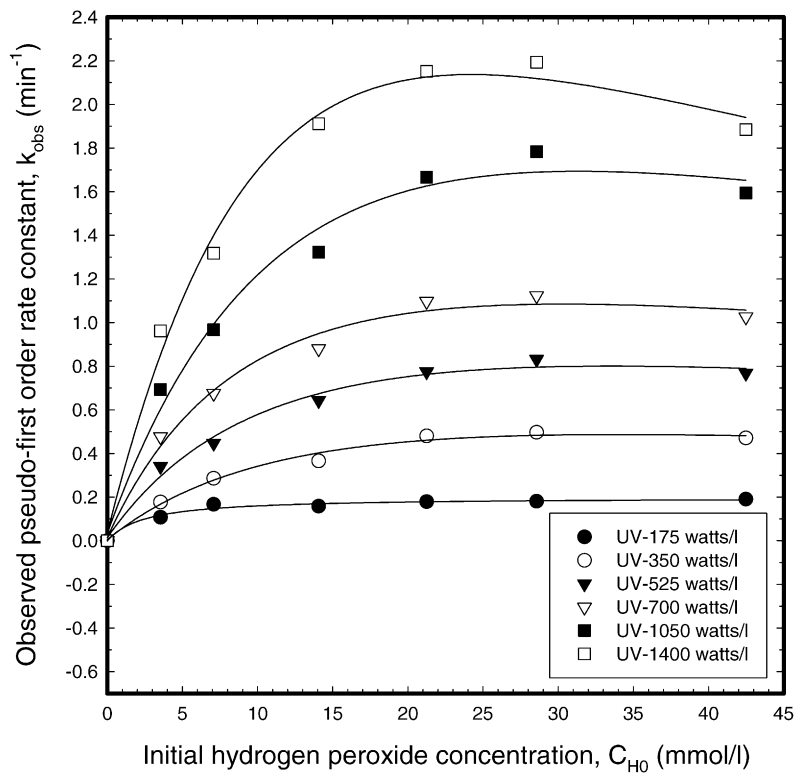


Fig. 3. Observed pseudo-first order rate constants vs. initial hydrogen peroxide concentration at various volumetric UV dosages.

3.3. Effect of volumetric UV light dosage

The experiments were conducted to verify the observed decolorization mainly caused by the photo-oxidation reaction. While in the presence of hydrogen peroxide without UV radiation, the decolorization was nearly negligible. Once combining UV radiation and hydrogen peroxide, AB1 could be decolorized in a relatively high reaction rate because of the hydroxyl radical generation from coupling of UV irradiation and hydrogen peroxide. Fig. 4 shows an approximately linear relationship between k_{obs} and UV dosage. Theoretically, the higher dye decolorization rate in the higher UV lamp power is in the result of faster formation of OH^\bullet free radical. Thus, the k_{obs} increases by UV dosage increasing, while the same initial H_2O_2 concentration. The well-known disadvantage of the UV/ H_2O_2 process is the poor absorption of H_2O_2 in the UV region. The amount of UV radiation absorbed by H_2O_2 plays an important role in the formation of plentiful OH^\bullet in the solution. Since the photolysis of H_2O_2 is enhanced to produce abundant OH^\bullet in the dye solution to be used for decolorization.

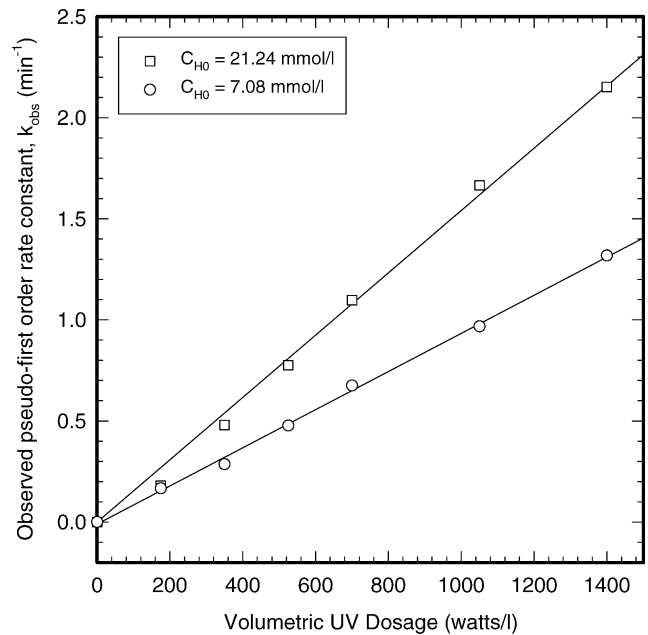


Fig. 4. Observed pseudo-first order rate constants vs. volumetric UV dosage at initial hydrogen peroxide concentration of 21.24 mmol/l.

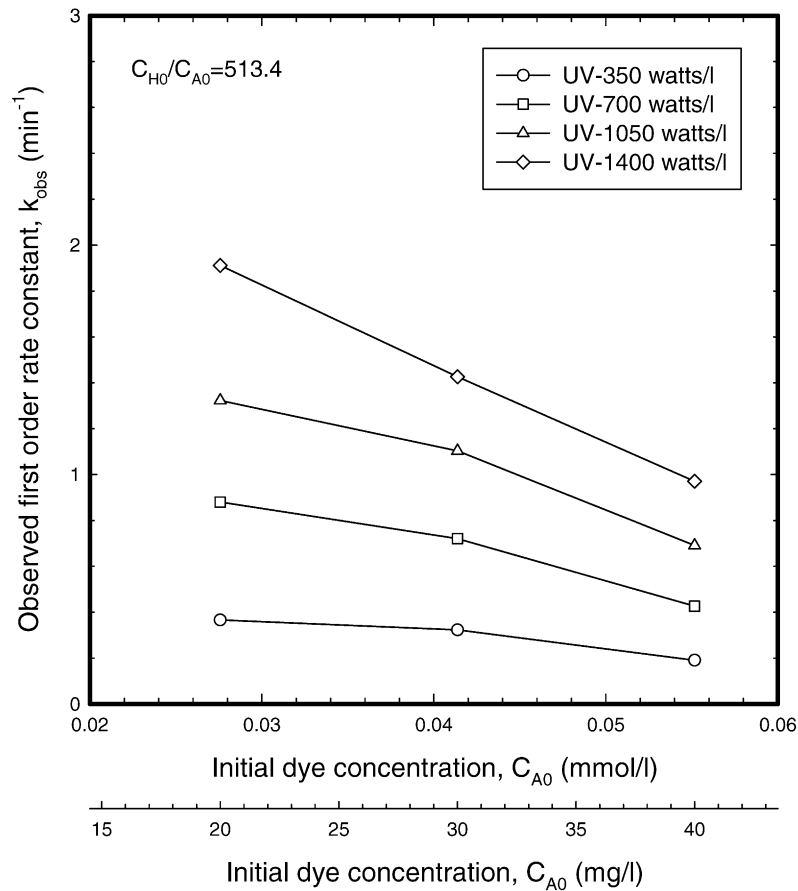


Fig. 5. The observed first order rate constant as function of initial AB1 concentration. UV dosages were 350, 700, 1050, and 1400 W/l and initial dye concentrations were 2.758×10^{-2} , 4.137×10^{-2} , and 5.516×10^{-2} mmol/l, respectively, while the hydrogen peroxide concentrations of 14.16, 21.24, and 28.32 mmol/l.

3.4. Effect of initial dye concentration

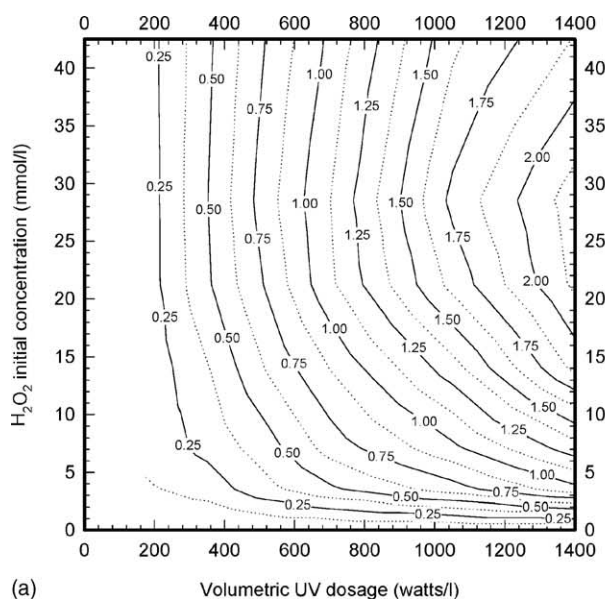
The effect of initial dye concentration (C_{A0}) on the decolorization rate (k_{obs}) was shown in Fig. 5 by plotting the rate constants versus C_{A0} . Meanwhile, the experimental conditions were three initial dye concentrations of 2.758×10^{-2} , 4.137×10^{-2} , and 5.516×10^{-2} mmol/l, also the fixed concentration ratio of hydrogen peroxide to dye ($C_{H_2O_2}/C_{A0}$) of 513.4 for each experimental test, and four UV dosage (350, 700, 1050, and 1400 W/l) employed as well. It is interested to find that k_{obs} declines significantly by raising initial dye concentration while UV dosage of 1400 W/l, yet was only slightly affected while 350 W/l. The results were similar to the observations by other investigators that the declining pseudo-first order rate constants with respect to increasing initial dye concentrations [21].

3.5. Selection of operating parameters

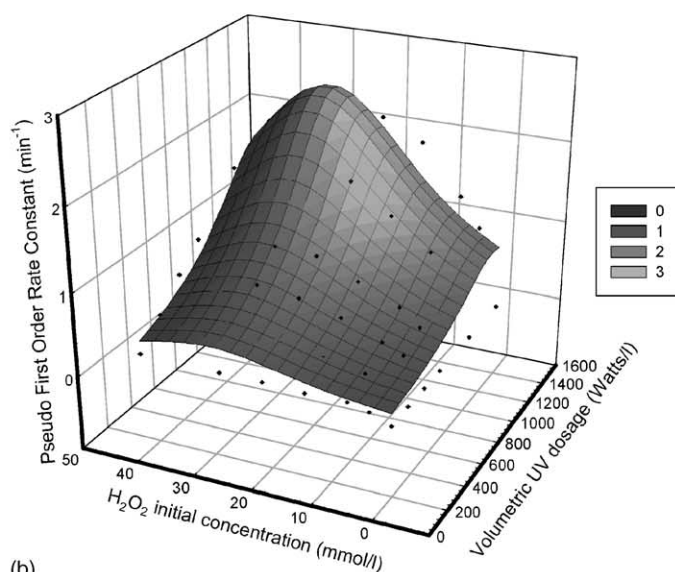
Although the decolorization rate was affected by initial hydrogen peroxide concentration and UV dosage significantly, yet the selection of operating parameters considers both the economic and technological feasibility. Therefore, a contour plot was generated in order to observe the first order rate constant which shows as a function of hydrogen peroxide concentration and UV dosage in Fig. 6a. The lines of isoconcentration represent the observed rate constants, which provide the future user easily determine constants under certain experimental conditions. From this figure, the best operating region was located while the higher UV dosage and hydrogen peroxide concentration in the range of 20–35 mmol/l. A 3-D plot of k_{obs} versus initial concentration of hydrogen peroxide and volumetric UV dosage can be presented in Fig. 6b,

which also help the evaluation of best rate constant within given parameters. The decolorization rate increased as a function of increasing UV dosage. However, increasing hydrogen peroxide until extremely high dosage, the inhibitory effect performed and deducted the rates oppositely. To help textile industries meeting ADMI < 550 effluent color standard, 90% color removal was used to evaluate the power and retention time needed for decolorizing AB1. Besides, the retention time needed can be estimated while we set 90% color removal of AB1 because that power consumed by UV/H₂O₂ reaction can be obtained by multiplying the UV dosage and retention time. Fig. 7a indicates power needed for 90% color removal versus hydrogen peroxide dosage. From the plot, higher hydrogen peroxide dosage needed lower power for 90% color removal so that for hydrogen peroxide dosage of 42.48 mmol/l only needed about 25.3×10^{-3} to 35.3×10^{-3} kWh/l of electric power. As for hydrogen peroxide dosage of 3.54 mmol/l, a power consumption as high as 75.8×10^{-3} kWh/l was needed for same removal efficiency. In other words, at the same hydrogen peroxide dosage, the reactor equipped with higher power UV lamp has higher color removal efficiency but needs lower energy consumption. Fig. 7b presents the retention time needed for 90% color removal as function of hydrogen peroxide and UV dosage. Both the more dosage of hydrogen peroxide and UV, the less time achieved the 90% color removal. The reactor equipped with low energy of 175 W/l UV light source needs more than 10 min to reach 90% color removal. Yet, only needs less than 5 min while UV dosage was higher than 700 W/l. Also, the retention time only slightly changes for all cases of UV dosages once the hydrogen peroxide concentration was higher than 21.24 mmol/l.

Moreover, plotting both the retention time and electric power needed for 90% color removal versus UV dosage, the



(a)



(b)

Fig. 6. (a) The contour plot of operating parameters. (b) A 3-D operating parameters plot. The observed first order rate constant as function of volumetric UV dosages and hydrogen peroxide concentrations. Initial dye concentration was 2.758×10^{-2} mmol/l.

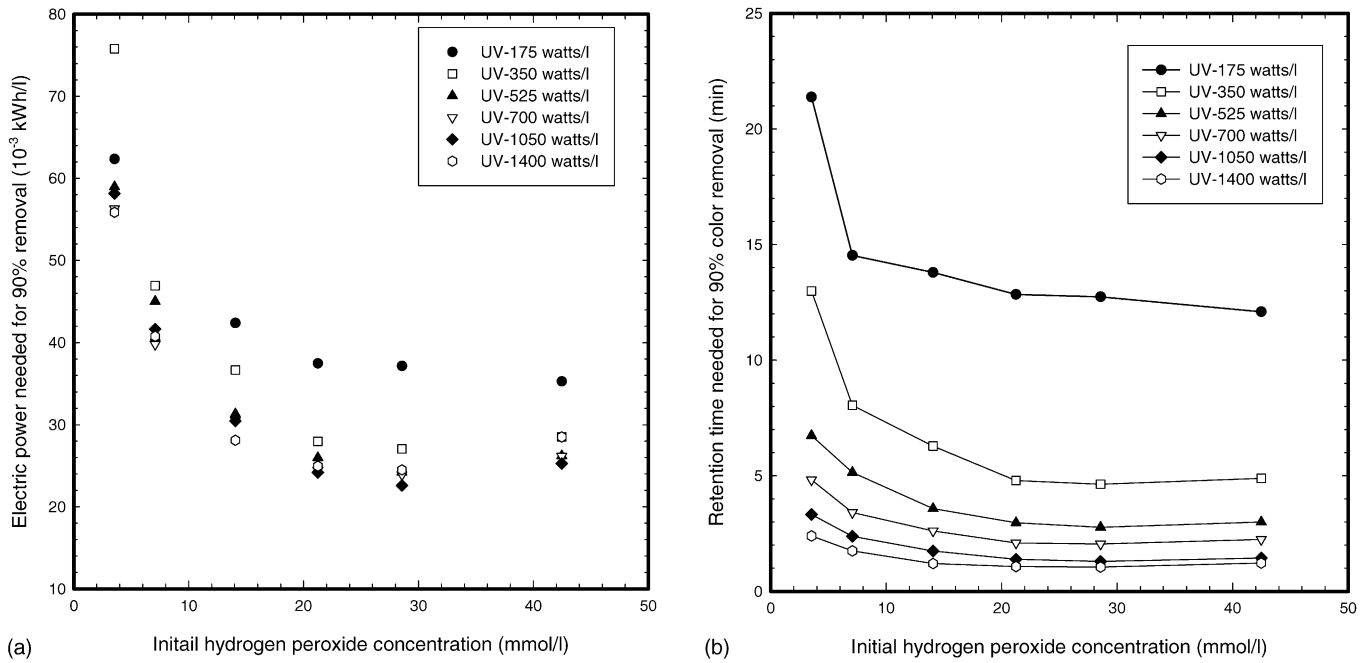


Fig. 7. (a) The electric power consumed for 90% color removal vs. hydrogen peroxide concentration at various UV dosages. (b) The retention time needed for 90% color removal vs. hydrogen peroxide concentration at various UV dosages. Initial dye concentration was 2.758×10^{-2} mmol/l.

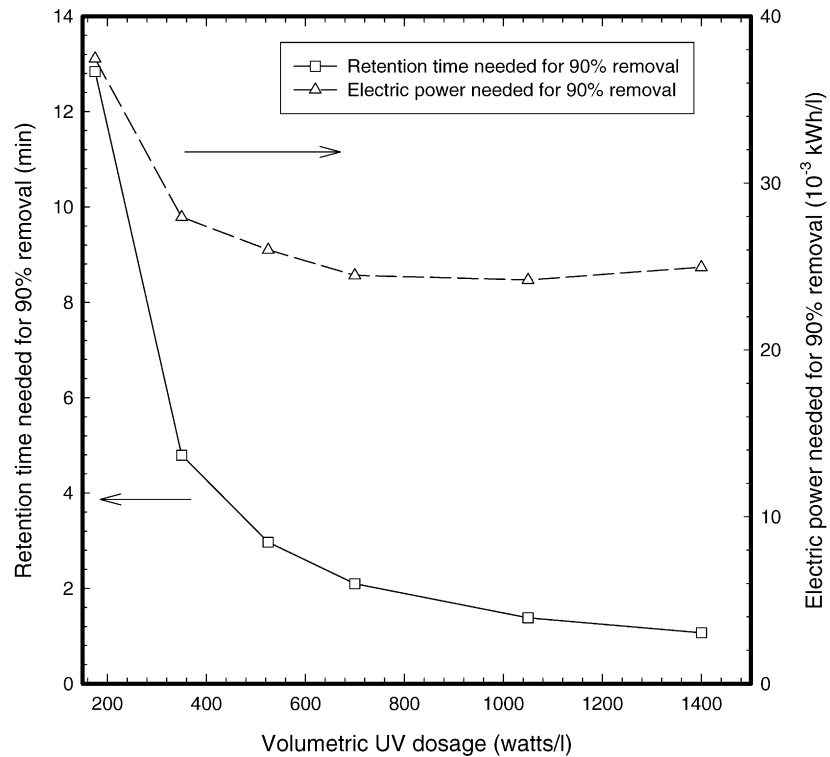


Fig. 8. The comparison of retention time and electric power needed for 90% color removal as function of UV dosage. Initial dye concentration was 2.758×10^{-2} mmol/l and hydrogen peroxide concentration was 21.24 mmol/l under the optimal condition.

optimal operating conditions of them can be obtained while the hydrogen peroxide dosage of 21.24 mmol/l (the optimum from Section 3.2), as shown in Fig. 8. Both the retention time and electricity needed for 90% color removal decrease with increasing of UV dosage. It continuously falls with slow rate, while UV dosage was higher than 700 W/l and 90% color removal, yet the electric power needed changes finitely. Thus, 700 W/l was chosen as the optimal UV dosage, because that though the operation cost of electricity consumption was the same within 700, 1050, and 1400 W/l, but the equipment cost of 700 W/l significantly was lower than the others.

4. Conclusion

The experimental results showed that the UV/H₂O₂ process can be a suitable pretreatment method for complete decolorization of dye wastewater from textile industries under the optimal operating conditions. The decolorization rates of AB1 were determined and affected significantly by the UV dosage, hydrogen peroxide dosage, and initial dye concentrations. Meanwhile, the results showed the 90% decolorization of AB1 can be reached within 21.4 min, while hydrogen peroxide concentration varies from 3.75 to 42.8 mmol/l and UV dosage of 175–1400 W/l. It is not cost effective to use hydrogen peroxide dosage more than 21.24 mmol/l. Ultimately, the optimal operation conditions can be determined while UV dosage of 700 W/l and hydrogen peroxide dosage of 21.24 mmol/l to reach the best color removal efficiency.

Acknowledgements

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