

Effects of gap size and UV dosage on decolorization of C.I. Acid Blue 113 wastewater in the UV/H₂O₂ process

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Abstract

The wastewater from textile dyeing industry is difficult to be treated successfully according to both high variability of composition and color intensity. To investigate the effects of reactor gap size and UV dosage on the decolorization of dye wastewater, a commercially available azo dye C.I. Acid Blue 113 was chosen as a model compound. UV/H₂O₂ processes with various gap sizes and setups of plug flow reactor and recirculated batch reactor were proposed to deal with the dye wastewater in this study. The experimental parameters including the design of reactor configurations of annular gap size, and in batch system or plug flow reactors and hydrogen peroxide dosage, UV dosage were investigated. The gap size of reactor was adjusted by different diameter of reactor shells in order to optimize the reactor configuration. The color removal percentage was used to evaluate the treatment efficiency. An optimal hydrogen peroxide concentration of 46.53 mM was observed in this study for highest decolorization rate. Besides, the pseudo-first-order rate constant of 3.14 min⁻¹ was obtained by plug flow reactor with 0.5 cm gap size, 120.70 W/l of UV dosage and 23.27 mM of H₂O₂ dosage. The first-order rate constant, which was about 20 times less than that of plug flow reactor, was obtained 0.1422 min⁻¹ by recirculated batch reactor with 2.0 cm gap size, 7.0 W/l of UV and 23.27 mM of H₂O₂ dosages. Ultimately, we developed an effective pre-treatment or treatment technology for dye wastewater to provide the dyeing industries and dye manufacturers an alternative to meet the effluent standards.

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Keywords: Dyeing wastewater; UV/H₂O₂ process; Azo dye; Decolorization; Plug flow reactor

1. Introduction

The textile industry has been one of the most important industries in Taiwan. Currently, there are more than 250 textile dyeing and processing factories in Taiwan [1]. Effluent streams from dyestuff manufacturing and textile dyeing processes are highly colored and difficult to be decolorized that result into the major environmental problem. The Taiwan Environmental Protection Agency has enforced the National Effluent Standard (NES) of true color as 550 units of American Dye Manufacturers Institute (ADMI) since 2003. Therefore, textile industry faces a tougher environmental challenge.

In the past, most textile dyeing mills applied the biological or combination of physical/chemical precipitation processes that hardly meet the new requirement of NES. While the effluent standard of 400 ADMI was implemented since the year of 1988, Kao et al. found only 35% of 186 dyeing effluent samples could meet the discharge standard [1]. Most of the treatment facilities applied NaOCl as the final polishing step to reduce the effluent color, which could severely damage the ecology of surface water. However, the dye wastewater treatment methods in the past, by adsorption onto activated carbon or coagulants [2,3], mainly transferred the contaminant from wastewater to solid waste that needs further disposal. Meanwhile, the biological process cannot effectively decolorize dye wastewater for most of the synthetic organic dyes, according to the toxicity of some commercial dyes for the biomass [4]. Consequently, the alternative

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technologies can decompose the non-biodegradable azo dyes have to be investigated. Besides, the chemical oxidation by chlorine or ozone is capable to decolorization of dye effluent effective [5], but it is hard to handle these gaseous oxidants. Moreover, chlorination may also produce carcinogenic by-products. Recently, some studies proved that Fenton's reagents [6] and photo-catalytic oxidation with TiO_2 [7] can effectively perform the color removal of dye wastewater. Although Fenton's reaction decolorizes rapidly, meanwhile it produces mass $\text{Fe}(\text{OH})_3$ sludge by coagulation process which needs further disposal. Additionally, the limit of TiO_2 photo-catalytic process was the surface of photo-catalyst as well as more difficult to scale up. Combination of hydrogen peroxide and UV radiation, one of the advanced oxidation processes (AOPs), produces hydroxyl free radicals $\cdot\text{OH}$ to enhance a high-degradation rate of organics in aqueous system. Several studies have reported about the successful application of the $\text{UV}/\text{H}_2\text{O}_2$ process for dye wastewater treatment. Shu et al. reported the feasibility study of degradation of C.I. Acid Red 1 and C.I. Acid Yellow 23 by $\text{UV}/\text{H}_2\text{O}_2$ process positively they also investigated the optimal operating parameters for decolorization of C.I. Acid Black 1 [8,9]. Neamuta et al. [10] demonstrated that the $\text{UV}/\text{H}_2\text{O}_2$ process decolorized three reactive azo dyes, C.I. Reactive Yellow 84, C.I. Reactive Black 5 and C.I. Reactive Red 120. Aleboye et al. [11] also reported the optimal dosage of hydrogen peroxide for the decolorization of C.I. Acid Orange 8, C.I. Acid Blue 74 and Methyl Orange by the $\text{UV}/\text{H}_2\text{O}_2$ process. Similarly, many other researchers took advantage of the $\text{UV}/\text{H}_2\text{O}_2$ process on the dye removal in a small-scale batch reactor [12–15]. However, the study on development of the continuous $\text{UV}/\text{H}_2\text{O}_2$ photo-reactor is scarce.

The aim of this work was to evaluate the effect of reactor configurations such as annular gap size, recirculated batch system and plug flow system on the decolorization of azo dye wastewater. C.I. Acid Blue 113 (AB113) was used as a model dye. The color removal effect of AB 113 was studied by different gap sizes, by batch and plug flow reactors. The reaction rates were calculated for the comparison of the decolorization efficiency between different reactor setups.

2. Experimental

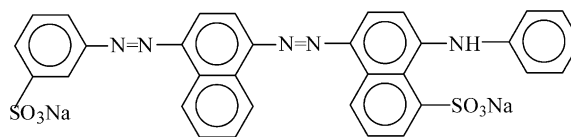
2.1. Materials

Hydrogen peroxide was obtained from Fluka Chemical which is 35% (w/w) Di-azo dye, C.I. Acid Blue 113 (C.I. 26360) was obtained from Aldrich Chemical Co., without further purification. The main characteristics are shown 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 dark.

Table 1
The characteristics of C.I. Acid Blue 113 (AB 113)

Azo dye	C.I. Acid Blue 113
Formula	$\text{C}_{32}\text{H}_{21}\text{N}_5\text{Na}_2\text{O}_6\text{S}_2$
λ_{max} (nm)	566
MW	681.66
Solubility in water (mg/ml)	40

Chemical Structure



2.2. Apparatus

A thin-gap annular photooxidation reactor with plug flow reactor design fitted with a Sterilight® low pressure mercury arc UV lamp (wavelength 253.7 nm, input power of 14 W) in the inner quartz tube of reactor was conducted in the experiments. Water with C.I. Acid Blue 113 flowed through the thin gap between quartz tube and outer stainless steel shell where the oxidation process was produced by various conditions. Fig. 1 is a schematic drawing of the typical thin gap annular photoreactor employed in this work. There were three reactors with different dimensions used in this work as shown in Table 2. The outside diameter of the quartz tube was 2.2 cm. The inside diameter of stainless shell was designed to be 3.20, 5.10 and 6.20 cm. The reactor gap size was adjusted for the quartz tube with different outer stainless shell to be 0.5, 1.45 and 2.0 cm, respectively. There were one lower inlet and one higher outlet fittings mounted on the stainless shell that went

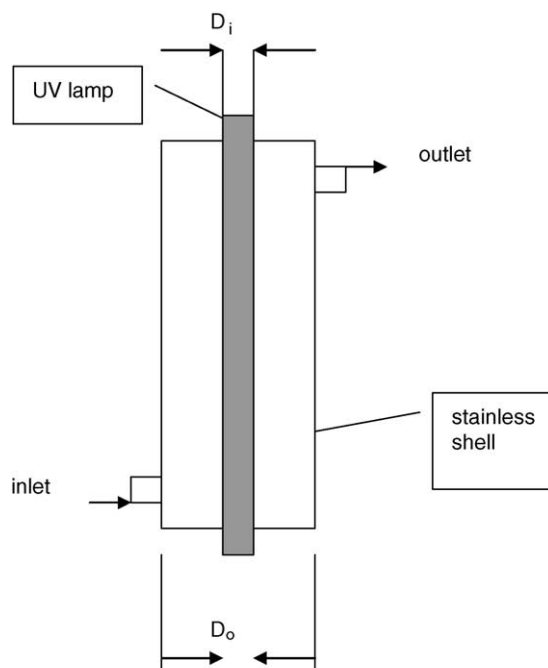


Fig. 1. The schematic drawing of the annular photoreactor employed.

Table 2
The geometry of the annular photoreactor employed in this work

Reactor	D_i (cm)	D_o (cm)	D_i/D_o	Gap size (cm)	Reactor length (cm)	Reactor volume (cm ³)	Annular area (cm ²)
R1	2.2	3.2	0.688	0.5	27.5	116.0	4.241
R2	2.2	5.1	0.431	1.45	27.5	457.3	16.627
R3	2.2	6.2	0.355	2.0	27.5	725.7	26.389

D_i is the inner diameter of annular photoreactor, which is measured as outside diameter of the inner quartz tube and D_o is the outer diameter of the annular photoreactor, which is measured as the inside diameter of the outer stainless shell.

through the flowing dyewater, which was irradiated by the UV lamp to produce photochemical reaction in the thin gap. While the dyewater flowed through the reactor from outlet, it then was discharged or recycled. A recirculated batch reactor, that the effluent from reactor outlet flowed to the stirred tank, then pumped back to the reactor continuously. On the other hand, the dyewater, which flowed through the plug flow reactor, simply discharged.

2.3. Analyses

Optical absorption spectrum on C.I. Acid Blue 113 was determined by a Hitachi U-2000 spectrophotometer. The characterized wavelength of AB 113 was identified for quantitative analysis. Hydrogen peroxide concentration was determined by spectrophotometer method based on the method which Masschelein et al. [16] proposed. A color development by adding cobalt reagent and hexametaphosphate solution to water sample was measured by the absorbance so that the hydrogen peroxide concentration was calculated by advantage of calibration curve.

3. Results and discussion

3.1. The effect of initial hydrogen peroxide concentration

From a previous study, azo dyes with di-azo links were fairly difficult for treatment using either ozonation process or UV-induced ozonation process [17]. In this study, C.I. Acid Blue 113 was investigated to use different hydrogen peroxide dosages and reactor gap size. The initial concentration of hydrogen peroxide is an important parameter for the degradation of azo dyes in the UV/H₂O₂ process. Theoretically, the higher initial hydrogen peroxide concentration, the higher the decomposition rate of the AB 113 is. However, the •OH free radicals reach equilibrium with the concentration of hydrogen peroxide. Over the equilibrium concentration, any increase of the hydrogen peroxide concentration cannot enhance the free radical concentration. Fig. 2 showed the AB113 initial concentration of 40.0 mg/l (29.30 μM) the pseudo-first-order rate constants of the photo-oxidation were implemented significantly, while the hydrogen peroxide dosage increased from 5.82 to 93.06 mM. However, the hydrogen peroxide dosage from 23.27 to 69.79 mM provided hardly increase in the degradation rate. Reversely, increasing the hydrogen peroxide dosage from 69.79 to 93.06 mM caused a deduction effect

on the AB113 degradation. Therefore, the optimal hydrogen peroxide dosage of 46.53 mM was obtained for the degradation of AB 113. Besides, the UV/H₂O₂ process is very effective for decolorization of AB 113 shown in Fig. 2. In 20 min of UV irradiation with hydrogen peroxide dosage of 5.82 and 23.27 mM, 67.5 and 93.5% of decolorization rate were achieved, respectively. Shu et al. [8] investigated the decolorization of C.I. Acid Red 1 and C.I. Acid Yellow 23 by UV/H₂O₂ process. They described an optimal dose of 9.8 mM of H₂O₂ for a 23.56 μM of C.I. Acid Red 1 aqueous solution with initial molar ratio of H₂O₂/dye of 415.96. Neamtu et al. [10] also reported an optimal dose of 24.5 mM of H₂O₂ for a 45.76 μM Disperse Red 354 solution with H₂O₂/dye molar ratio of 534.45. Therefore, the hydrogen peroxide concentration higher than 46.53 mM was concluded to be unprofitable consumption in this study. The optimal molar ratio of H₂O₂/dye was calculated to be 1588.05 for AB113.

In order to describe the experimental results, we develop a mathematic equation for pseudo-first-order decolorization of C.I. Acid Blue 113 by the UV/H₂O₂ process as follows:

$$R = \left(1 - \frac{C}{C_0}\right) \times 100\% = (1 - e^{-kt}) \times 100\% \quad (1)$$

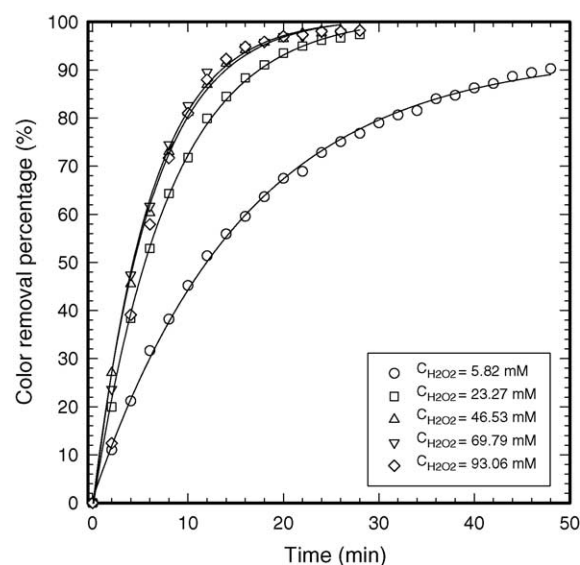


Fig. 2. The color removal percentage of C.I. Acid Blue 113 vs. time under various hydrogen peroxide concentrations in the UV/H₂O₂ process. The operating condition was under different H₂O₂ initial concentrations from 5.82 to 93.06 mM in a 2.01 recirculated batch reactor. C.I. Acid Blue 113 initial concentration was 29.30 μM pH was 5.5.

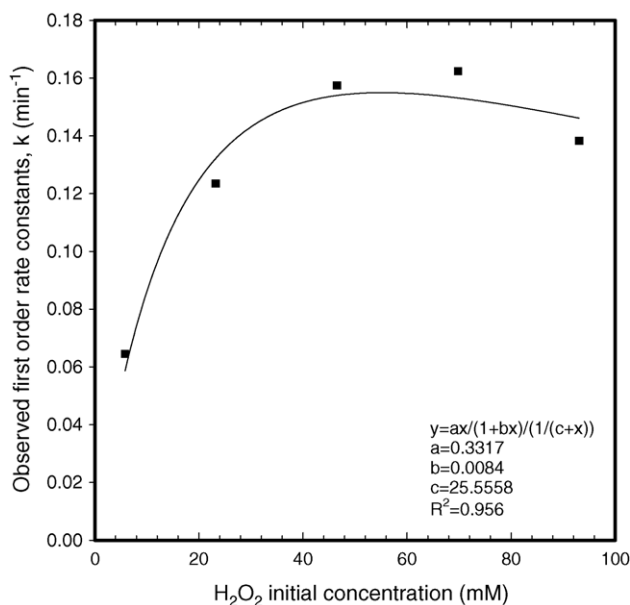


Fig. 3. The pseudo-first-order rate constants vs. hydrogen peroxide concentration for recirculated batch reactor. C.I. Acid Blue 113 initial concentration was $29.30 \mu\text{M}$, pH was 5.5.

where k denotes the observed first-order reaction rate constant, t is the reaction time, and R is the color removal percentage of C.I. Acid Blue 113 at any time t . C_0 denotes the initial C.I. Acid Blue 113 concentration and C is the C.I. Acid Blue 113 concentration at any time t . Thus, k can be obtained by linear regression for each experimental run. The results for k versus hydrogen peroxide dosage were summarized in Fig. 3, that the higher the dosage of hydrogen peroxide, the higher is the first-order rate constant obtained while H_2O_2 dosage increasing to 69.79 mM . The first-order rate constants of 0.1624 and 0.1383 min^{-1} can be obtained for H_2O_2 dosages of 69.79 and 93.06 mM , respectively.

3.2. The effect of annular gap size of the reactor

UV light intensity is a major parameter, which affects the azo dye degradation in the UV/ H_2O_2 process. Theoretically, the higher UV lamp power produces the faster formation of $\bullet\text{OH}$ free radicals, which promotes the higher degradation rate of azo dyes. However, UV irradiates the H_2O_2 while wastewater absorbing UV at the same time in the UV/ H_2O_2

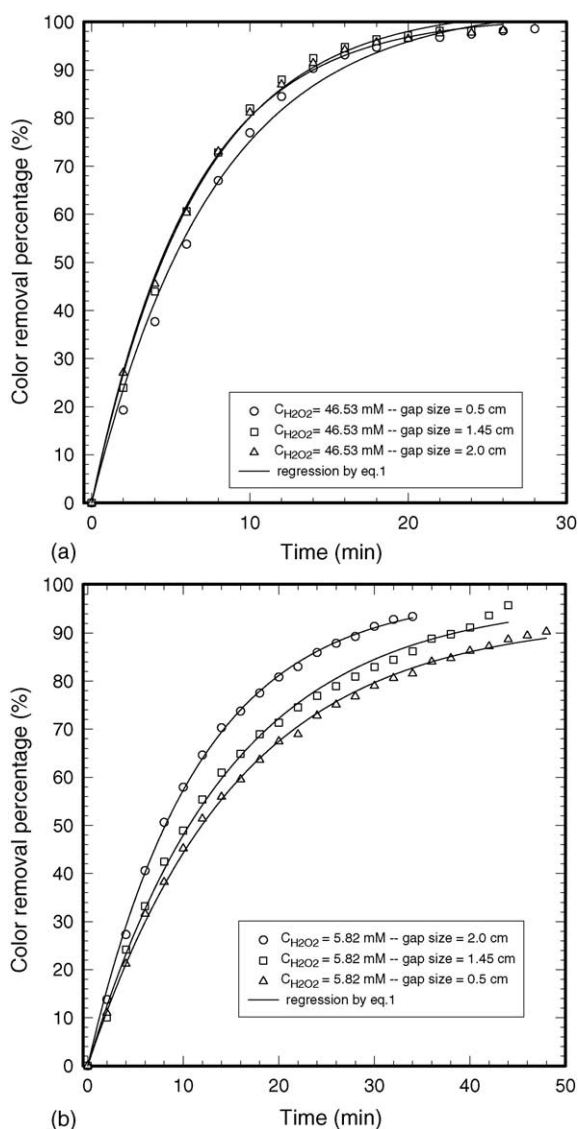


Fig. 4. The color removal percentage of C.I. Acid Blue 113 in recirculated batch UV/ H_2O_2 process under various gap sizes. The operating condition was under H_2O_2 initial dosage (a) 46.53 mM and (b) 5.82 mM in a 2.0 l recirculated batch reactor. C.I. Acid Blue 113 initial concentration was $29.30 \mu\text{M}$ initial pH was 5.5. Reactor gap sizes were 0.5, 1.45 and 2.0 cm , respectively.

Table 3

The observed first-order rate constants and color removal efficiencies at 20 min of reaction time for recirculated batch reactors (RBR) with various annular gap sizes and hydrogen peroxide concentrations

H_2O_2 dosage (mM)	Gap size (cm)	k (min^{-1})	R^2	Color removal efficiency at 20 min (%)
5.82	0.5	0.0645	0.997	67.45
	1.45	0.0682	0.997	71.30
	2.0	0.0877	0.999	80.83
46.53	0.5	0.1416	0.991	96.66
	1.45	0.1501	0.997	97.17
	2.0	0.1575	0.999	96.49

process. Thus, less UV light irradiated the hydrogen peroxide to produce fewer free radicals to reduce the degradation rate while more UV light is absorbed by wastewater. Therefore, the effect of UV absorbance by wastewater was studied by taking advantage of the annular gap size of reactor configuration.

3.2.1. Recirculated batch reactor (RBR)

In this set of experiments, three different gap sizes including 0.5, 1.45 and 2.0 cm, were applied to the degradation of C.I. Acid Blue 113 (AB 113). The average light intensity, which was varied by the gap size, was calculated by dividing the UV light intensity by various reactor volumes. The optimal reactor configuration was obtained for the optimal degradation rate of AB 113 from different gap sizes. Fig. 4(a) shows the decolorization of AB 113 curve in a recirculated batch reactor (RBR) with various gap sizes. The decolorization of AB 113 showed no significant difference among the gap sizes for higher hydrogen peroxide dosage of 46.53 mM. However, larger gap size improved the higher degradation rate of AB 113 significantly for the lower hydrogen peroxide concentration of 5.82 mM as shown in Fig. 4(b). The largest AB 113 degradation rate was obtained in the largest gap size, 2.0 cm. Besides, the observed first-order rate constant and color removal percentage at 20 min of reaction time are summarized in Table 3.

In the RBR, wastewater was pumped through the reactor gap and recycled continuously to keep the same scale of UV lamp for the same amount of wastewater reaction. For high hydrogen peroxide dosage, the decolorization curve showed no significant difference. When there is low hydrogen peroxide concentration, the average reaction rate was reduced reversely.

To discuss these findings, we propose following explanations. The decolorization rate is affected by both UV dosage and hydrogen peroxide dosage significantly. At optimal hydrogen peroxide dosage of 46.53 mM, the decolorization rate is the highest one for each UV dosage. Thus, changing the reactor gap size does not make significant differences on decolorization rates. At lower hydrogen peroxide dosage of 5.82 mM, the UV light efficiency is more important to affect the decolorization rates with varying the gap sizes. Thus, the larger gap size performs a higher decolorization rate because that larger gap size offers more irradiation opportunity for each dye molecule.

3.2.2. Plug flow reactor (PFR)

In this set of experiments, three gap sizes as above were applied to the plug flow reactor (PFR), which performed in the thin gap reactor relatively different from the RBR. The residence time of wastewater in the PFR was adjusted by using different pumping rate. The color removal percentage versus flow rate for various reactors are plotted in Fig. 5(a), which shows the higher flow rate reaches the lower color removal. On the other hand, the higher color removal percentage was

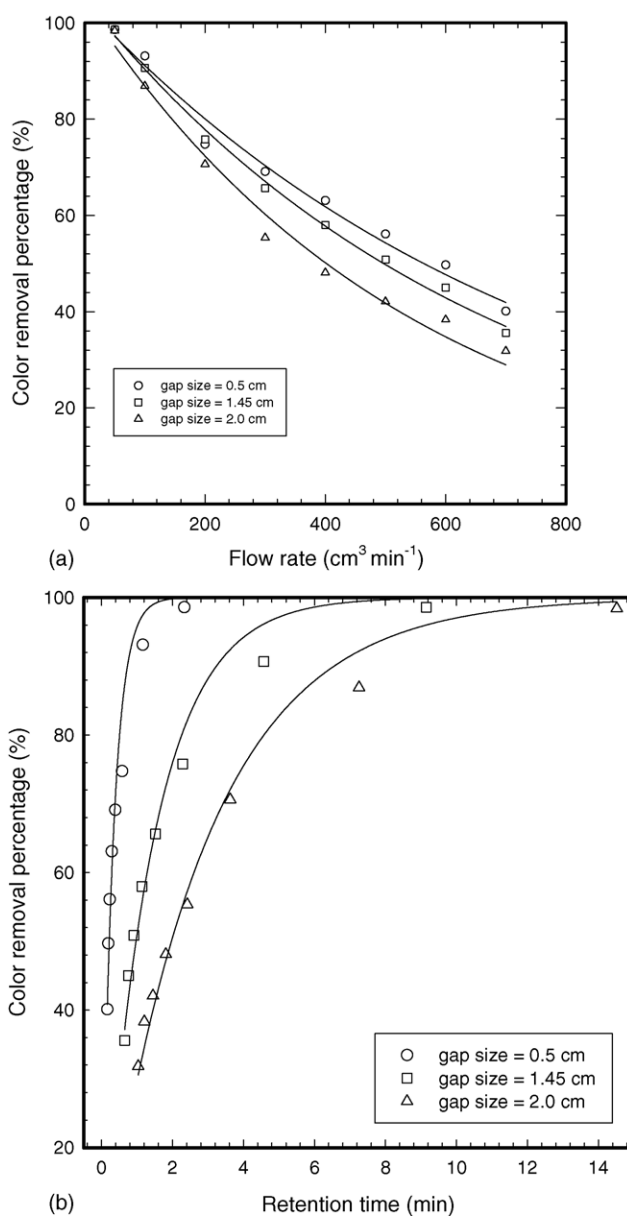


Fig. 5. (a) The color removal percentage of C.I. Acid Blue 113 vs. flow rate in plug flow UV/H₂O₂ process under various gap sizes. (b) The color removal percentage of C.I. Acid Blue 113 vs. retention time in plug flow UV/H₂O₂ reactor under various gap sizes. The operating condition was under H₂O₂ initial dosage 46.53 mM. C.I. Acid Blue 113 initial concentration was 29.30 μ M, initial pH was 5.5. Reactor gap sizes were 0.5, 1.45 and 2.0 cm, respectively.

measured from the outlet of PFR with the longer retention time shown in Fig. 5(b). It shows the higher removal percentage with the smaller gap size that the smallest gap size (0.5 cm) obtained a fastest degradation rate among three gap size reactors.

The investigation of AB 113 decomposition in aqueous solution by the UV/H₂O₂ process was examined under various configuration of photoreactor in the continuous annular PFR. The decomposition of azo dye was assumed to be pseudo-first-order and irreversible reaction in a steady-state

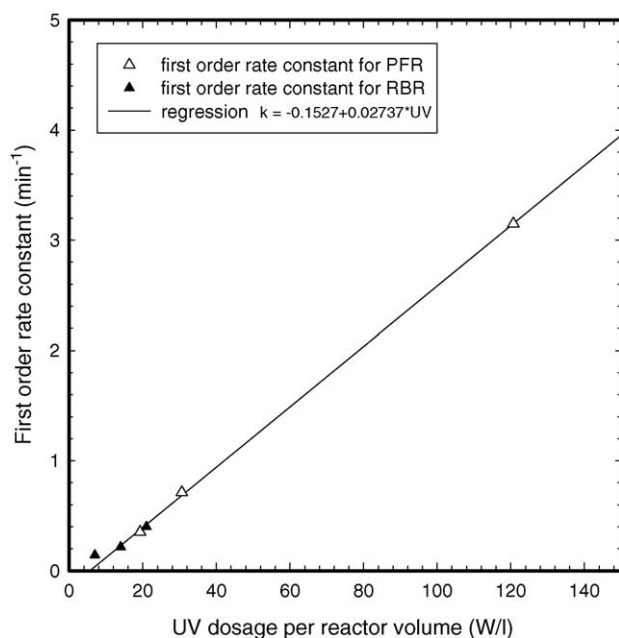


Fig. 6. The pseudo-first-order rate constants vs. volumetric UV dosages for recirculated batch reactor and plug flow reactor.

PFR. Thus, the pseudo-first-order rate constant can be calculated as

$$k = \frac{-\ln(C_{\text{dye, eff}}/C_{\text{dye, in}})}{\tau}$$

Here k denotes the pseudo-first-order rate constant, τ is retention time, $C_{\text{dye, eff}}$ is effluent AB 113 concentration at outlet of the reactor and $C_{\text{dye, in}}$ is the AB 113 concentration at inlet of reactor. The color removal percentage of azo dye at reactor outlet was found to increase with decreasing the reactor gap size at the same volumetric flow rate. For the wastewater flow rate $300 \text{ cm}^3 \text{ min}^{-1}$, the color removal percentages were 69.11, 65.63, and 55.36% for reactor gap size of 0.5, 1.45, and 2.0 cm, respectively. In Fig. 5(b), the higher decolorization efficiency of the AB 113 can be achieved by using an annular reactor with smaller gap size at the same retention time.

Since the decolorization rate is affected by both UV dosage and hydrogen peroxide dosage in the PFR, at fixed hydrogen peroxide dosage of 46.53 mM, the decolorization rate is affected mainly by reactor gap size. In the PFR, each dye molecule flows through the reactor only once. Although the larger gap size offered the longer residence time, but the dye molecules at outer layer of the lamp receive less intensity of UV irradiation. Therefore, the smaller gap size reactor has better decolorization capability and efficiency.

3.3. The effect of unit UV dosage

The unit UV dosage, which applied a UV power input per certain reaction volume, was calculated in W/l. The effect of unit UV dosage on the decolorization of azo dye wastewater was evaluated by reactor configurations, in RBR

or PFR. In RBR various numbers of lamps (from 1 to 3) were applied to have different UV dosages. The first-order rate constants was a function of unit UV dosage shown in Fig. 6, that they increased linearly with unit UV dosage. For H_2O_2 dosage 23.27 mM, the pseudo-first-order rate constant (k) of 3.140 min^{-1} was obtained for PFR in 0.5 cm gap size and 120.70 W/l of UV dosage. For RBR with 2.0 cm gap size, which employed 7 W/l of UV dosage, the k value of 0.142 min^{-1} , which was about 20 times less than that of PFR. This outcome implies no matter what reactor configuration, the reaction rate constant is strongly affected by unit UV dosage so that all rate constant versus UV dosage lay on the straight line in Fig. 6. Therefore, the rate constants of PFRs were about from 2 to 10 times larger than that of RBRs.

4. Conclusions

In this study, the photo-oxidative degradation of C.I. Acid Blue 113 in the UV/ H_2O_2 process was proven to be a promising wastewater treatment technology. Meanwhile, the important outcome from the experiments was the finding of optimum hydrogen peroxide concentration in the UV/ H_2O_2 system. In general, increasing the initial concentration of hydrogen peroxide increased the decomposition rate of AB 113, but there was an optimum value of initial concentration to reach the higher reaction rate. Once, the concentration was overdose with the optimum, the degradation rate of AB 113 was decreased reversely. Besides, the reactor gap size played an important role for the decolorization of AB 113 for both PFR and RBR. Thin-gap PFR was the most powerful design to decolorize AB 113. The largest pseudo-first-order rate constant of 3.140 min^{-1} was obtained for PFR with 0.5 cm gap size and 120.70 W/l of UV dosage. Additionally, the better performance of decolorization for both PFR and RBR could be reached by adjusting the reactor gap size. The results in this work could be used in a scale-up to the commercial reactor for treatment of dye wastewater.

Acknowledgements

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