Hindawi Publishing Corporation
International Journal of Photoenergy
Volume 2012, Article ID 303586, 7 pages
doi:10.1155/2012/303586

Research Article

Solar Photocatalytic Degradation of Azo Dye in Aqueous TiO_2 Suspension Assisted by Fresnel Lens

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Received 29 May 2012; Accepted 24 August 2012

Academic Editor: Meenakshisundaram Swaminathan

Solar TiO_2 photocatalytic process assisted by a Fresnel lens was investigated for treating an azo dye wastewater of Acid Orange 10 (AO10). Response surface methodology (RSM) was employed to assess the effect of critical process parameters (including initial pH of wastewater, concentration of TiO_2, and reaction time) on treatment performance in terms of COD and TOC degradation efficiency. Optimized reaction conditions based on the analysis of RSM were established under an initial pH of 6.0, a concentration of TiO_2 of 1 g/L, and a reaction time of 2 h for reaching a 90% COD and TOC degradation of AO10 wastewater. With the assistance of Fresnel lens, the TOC degradation rate of AO10 wastewater increased significantly from 0.606 h^{-1} and 0.289 h^{-1} to 1.477 h^{-1} and 0.866 h^{-1} in summer (June) season ($UV_{280–400\,nm}$ nm: 39.9–44.8 W/m^2) and winter (December) season ($UV_{280–400\,nm}$ nm: 23.9–26.9 W/m^2), respectively. This could be mainly due to the concentrating effect of Fresnel lens for solar energy, resulting in an increase of 2∼2.5 times of solar light intensity and a raising heat irradiation in terms of 10∼15 °C of wastewater temperature. These results revealed that solar energy could be concentrated effectively by using Fresnel lens and showed a significant promoting effect on the TiO_2 photocatalytic degradation of dye wastewater.

1. Introduction

Over 100,000 different types of dyes are commercially available and 700,000 tons are produced yearly all over the world. Nearly 50% of these dyes are azo-type dyes [1]. Azo dyes, aromatic moieties linked together by azo (–N=N–) chromophores, represent the largest class of dyes used in textile processing and other industries. The release of these compounds into the environment is undesirable, because the color matters and their toxic breakdown products can be mutagenic [2]. In addition, due to the complex aromatic structure and stability of the azo-dyes, conventional biological treatments are ineffective for degradation and mineralization of the dye molecules [3]. Instead, activated carbon adsorption or coagulation is commonly used. However, new environmental laws may consider the spent adsorbents or sludge as hazardous waste and require further treatment. Consequently, intensive research for novel technologies with higher efficiency and less amount of waste generated has been stimulated. Advanced oxidation processes (AOPs) have been previously described as a promising option to remove persistent pollutants from contaminated water [4]. AOPs are able to produce a highly reactive, nonspecific oxidant, mainly hydroxyl radicals ($^{\bullet}OH$). The hydroxyl radical possesses inherent properties that enable it to attack refractory organic pollutants in water to achieve a complete mineralization. However, the production of photons with artificial light sources requires significant electrical energy demand and UV lamp consumption, leading to a high operation cost in AOPs [5]. Alternatively, solar energy is essentially unlimited and its utilization is ecologically benign. In the wastewater treatment sector, solar technology has been extensively used as an alternative to UV lamps to reduce the operation cost in AOPs [6]. In particularly, TiO_2 photocatalysis (1)–(3) using solar irradiation has been used as an economically viable process and has attracted great interest in recent years [7]. However, solar TiO_2 photocatalysis was usually carried out by using solar irradiation directly, resulting in a lower

absorption and utilization of solar energy [8]. To improve the efficiency of solar TiO_2 photocatalysis, it is necessary to maximize the absorption of solar energy.

$$TiO_2 \xrightarrow{h\nu(\lambda < 382\,\text{nm})} h^+_{vb} + e^-_{cb} \quad (1)$$

$$h^+_{vb} + H_2O \longrightarrow {}^\bullet OH + H^+ \quad (2)$$

$$h^+_{vb} + OH- \longrightarrow {}^\bullet OH \quad (3)$$

In this study, treatment of an azo dye-Acid Orange 10 (AO10) wastewater towards highly mineralization using solar TiO_2 photocatalysis enhanced by high-concentrating Fresnel lens was investigated. Response surface methodology (RSM) was employed to obtain the optimal reaction conditions of critical process parameters (including initial pH of wastewater, TiO_2 concentration, and reaction time) to reach a 90% of COD and TOC degradation of dye wastewater. Moreover, the effect of Fresnel lens on treatment performance in terms of color, COD, and TOC degradation efficiency of AO10 dye wastewater was examined.

2. Materials and Methods

2.1. Materials. AO10 ($C_{16}H_{10}N_2O_7S_2Na_2$) with a purity of 84% was purchased from the Sigma-Aldrich Co. (USA) and used without further purification. The chemical properties of AO10 are shown in Table 1. An initial AO10 concentration of 50 mg/L was prepared for all experimental runs. TiO_2 powder P25 (mainly anatase form, with a mean particle size of 30 nm and a BET surface area of $50 \pm 15\,m^2/g$) from Degussa Co. (Frankfurt, Germany) was used in this study. All other chemicals used in this study were analytical grade and used as received.

2.2. Procedures. All experiments were carried out in a batch mode. A 1 L glass beaker containing 200 mL of AO10 solution was used. The initial pH of the solution was adjusted to the desired pH by adding 1 N H_2SO_4 or 1 N NaOH. In this study, a 3-factor * 3-level experimental design with three replicates at center point according to the methodology of response surface [9] as shown in Table 2 was applied to investigate the influence of three factors (namely, initial pH, TiO_2 concentration and reaction time) for COD and TOC degradation efficiency of AO10 wastewater. At the RSM runs, the prepared dye solution was placed into the photoreactor and irradiated by a 1500 W Xe lamp in an Atlas Suntest CPS+ solar simulator (Atlas Co., USA) emitting artificial solar light with a spectral distribution resembling the solar spectrum (300–800 nm) in which the $UV_{280-400\,nm}$ intensity is around $67 \pm 0.5\,W/m^2$. In addition, the AO10 solution was maintained at $25 \pm 0.5°C$ in a water bath. During the experiments, the pH of the solution was monitored using a pH meter (SP-701LI 120, Suntex Co., Taiwan) equipped with a glass electrode. Samples were withdrawn from the reactor at preset time intervals and then stored at 4°C for the following ADMI, COD, TOC, and IC analysis.

As the optimal values of the process parameters were developed on the basis of RSM application and related equations, a Fresnel lens made of PMMA (thickness: 2 mm, pitch: 0.5 mm, facet depth: 0.2 mm, and Fresnel circles: 395) was added into solar TiO_2 photocatalytic system with a distance of 16 cm above the level of wastewater. To investigate the effect of Fresnel lens in summer (June) and winter (December) seasons, a similar reactor without Fresnel lens was also performed under the same natural solar irradiation using the experimental conditions obtained from RSM runs. A schematic diagram of the photoreactor using Fresnel lens is shown in Figure 1. In addition, two blank experiments including direct photolysis reaction and adsorption on TiO_2 only under the experimental conditions of this study were performed. The result indicated that the mineralization efficiency of AO10 solution was less than 2%, which implied that the mineralization of AO10 solution due to these effects was slight in this study.

2.3. Analysis

2.3.1. American Dye Manufacturing Institute (ADMI) Measurement. The color of AO10 solution was determined with a DR 4000 photometer (HACH Co., USA) for ADMI measurement. The efficiency of decolorization was calculated on the basis of ADMI reduction of solution.

2.3.2. Chemical Oxygen Demand (COD) Measurement. COD of solution via a DR 4000 photometer (Hach Co., USA) by using a $K_2Cr_2O_7$ as the reacting reagent was measured in order to understand the changes in the degree of oxidation for AO10 wastewater.

2.3.3. Total Organic Carbon (TOC) Measurement. TOC of solution was measured by using a Shimadzu VCPH analyzer (Shimadzu Co., Japan) in order to know the amount of AO10 molecules degraded to CO_2 during oxidation.

2.3.4. Ion Chromatography (IC) Analysis. To quantify the degradation product—oxalate ($C_2O_4^{2-}$) and acetate (CH_3COO^-)—an ion-chromatographic system (Dionex ICS-1000) equipped with an IonPac AS12A column (L: 200 mm, ID: 4.0 mm) was used. Aqueous solutions of 2.7 mM Na_2CO_3 and 0.3 mM $NaHCO_3$ were used as eluents. Analysis was performed under a flow rate of 1.5 mL/min and operated on an isocratic mode.

3. Results and Discussion

3.1. Optimization of Solar Photocatalytic Treatment of AO10 Wastewater. Figure 2 displays the three-dimensional response surface plots for percent of COD and TOC degradation efficiencies of AO10 wastewater as a function of initial pH and concentration of TiO_2. As shown in Figure 2, when the pH of AO10 wastewater was varied from 5 ($X_1 = -1$) to 9 ($X_1 = 1$), the degradation efficiency reached a maximum at pHs 5.5–6.5 followed by a decrease of COD and TOC degradation efficiency in the range 6.5–9.0 in all the TiO_2 concentration ranges studied. This phenomenon can be explained by the surface charge of TiO_2 as a function

Table 1: Chemical characteristics of alizarin violet AO10.

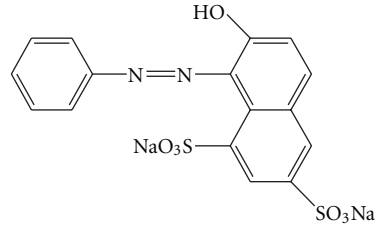
Dye	Chemical structure	λ_{max} (nm)	MW, g/mol	Category
Acid Orange 10 ($C_{16}H_{10}N_2O_7S_2Na_2$) (C.I. number 16230)		478	452.37	Azo

Table 2: Experimental range and levels of the process independent variables in this study.

Independent variable	Factor	Range and level		
		−1	0	+1
Initial pH	X_1	5.0	7.0	9.0
TiO_2, g/L	X_2	0.5	1.0	1.5
Reaction time, hr	X_3	1.0	1.5	2.0
Y (response)—COD or TOC degradation, %				

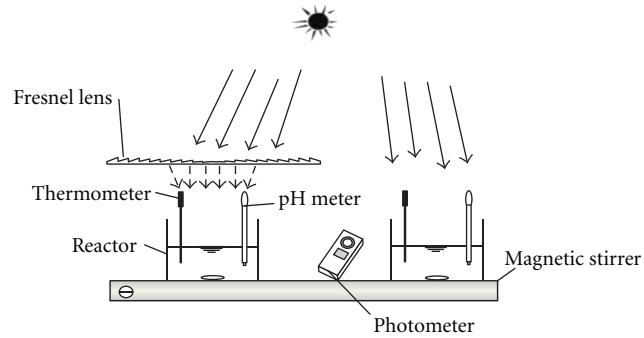


Figure 1: Schematic diagram of the solar photocatalytic reactor with and without Fresnel lens.

of pH. The zero point of charge (ZPC) for TiO_2-P25 is around pH 6.3–6.8 [10]. Therefore, at more acidic pH environment ($pH < pH_{ZPC}$), the TiO_2 surface is positively charged as expressed by (4), and at alkaline pH, the surface ($pH > pH_{ZPC}$) is negatively charged as expressed by (5) [11]. AO10 in water is negatively charged because the two sodium sulfonate group is hydrolyzed to form dye anion and sodium ions as expressed by (6). At pH values below 6.3, the adsorption of AO10 is favorable due to the electrostatic attraction between the fully ionized sulfonic group and positively charged TiO_2 on the surface. Above pH 6.8, AO10 is subjected to electrostatic repulsion between itself and the negative surface of TiO_2. Hence, the adsorption of the AO10 dye is less and the degradation efficiency decreased. Similar result was also observed in the photocatalytic degradation of Acid Orange 7 [12]. However, the effect of initial pH of dye solution was not significant because of some carboxyl acid intermediates such as acetate and oxalate were produced, leading to a gradually decreased pH of solution, and then the reaction of (4) may be dominant.

$$\mathrm{TiOH} + \mathrm{H^+} \longrightarrow \mathrm{TiOH_2^+}, \quad \mathrm{pK_{a1}} = 4.95 \tag{4}$$

$$\mathrm{TiOH} + \mathrm{OH^-} \longrightarrow \mathrm{TiO^-} + \mathrm{H_2O}, \quad \mathrm{pK_{a2}} = 7.80 \tag{5}$$

$$\text{dye-}(\mathrm{SO_3Na})_2 \longrightarrow \text{dye-}\left(\mathrm{SO_3^-}\right)_2 + 2\mathrm{Na^+}. \tag{6}$$

On the other hand, as shown in Figure 2, the effect of TiO_2 concentration was much more considerable than that of initial pH on the COD and TOC degradation of AO10 wastewater. In general, more catalysts will substantially result in generation of more hydroxyl radicals until an optimum catalyst concentration is achieved. Hence, the results showed that, within the pH range studied (5–9), the increase of catalyst concentration from 0.5 to 1.0 g/L increased the degradation efficiency. This fact may be due to the increase in the number of dye molecules adsorbed and more oxidation of dye [13]. Above this value, no obvious improvement is obtained by increasing the concentration of catalyst. This may be due to an increased opacity of the suspension and the shielding effect of light with an excess of TiO_2 particles, consequently leading to a decrease in the formation of $^{\bullet}OH$ radicals. Accordingly, the optimum concentration of the catalyst for efficient solar photodegradation of AO10 would be around 1.0 g/L. This result was consistent with those reported in the literature [14] for the TiO_2 photocatalytic degradation of Remazol Red dye.

On the basis of RSM application, the empirical relationship between the dye degradation efficiency (Y) and the independent variables is developed and listed in Table 3. The regression model had a high value of coefficient of determination ($r^2 > 0.97$). This implies that the process efficiency could be predicted well by the second-order polynomial regression equations under the conditions studied.

Based on the model equations in Table 3, the optimal values of the process parameters were established as an initial pH of 6.0, an initial concentration of TiO_2 of 1 g/L, and a reaction time of 2 h for reaching a 90% COD and TOC degradation of AO10 wastewater. In order to confirm the optimum conditions of AO10 degradation, a five-replicate and t-test analyses were performed. The results showed that the average COD and TOC degradation efficiency were 90.5% and 90.4%, respectively, and the 95% of confidence intervals for COD and TOC degradation efficiency were 89.7~91.3% and 89.4~90.8%, respectively. Consequently,

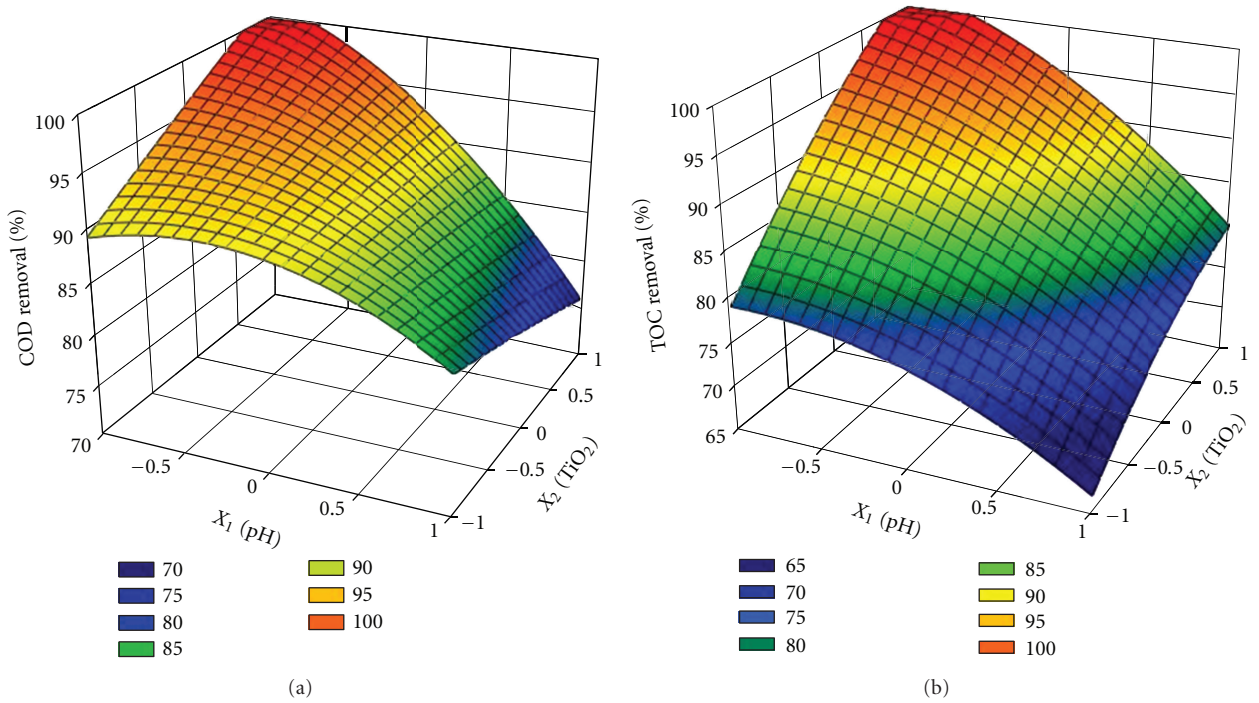


Figure 2: Response surface for (a) COD and (b) TOC degradation efficiency of AO10 wastewater as a function of initial pH and TiO_2 concentration. (Reaction time: 2 h, light intensity ($UV_{280–400\,nm}$: 66.5 W/m^2, water temperature: 25 ± 0.5°C).

Table 3: Polynomial regression equation of AO10 degradation on the basis of COD and TOC removal.

Polynomial regression equation	r^2
[a] $Y_{COD} = 81.0 + X_1 + 9.7X_2 + 15.3X_3 - 3.9\,X_1{}^2 - 0.2\,X_2{}^2 - 4.6\,X_3{}^2 - 5X_1X_2 - 6.9X_1X_3 - 8.3X_2X_3$	0.971
[a] $Y_{TOC} = 74.1 - 5X_1 + 10.5X_2 + 18.7X_3 - 3.2X_1{}^2 - 2\,X_2{}^2 - 5.7\,X_3{}^2 - 2.6X_1X_2 - 3.7X_1X_3 - 1.3X_2X_3$	0.997

[a] Y_{COD}: the COD degradation efficiency of AO10 wastewater.
[b] Y_{TOC}: the TOC degradation efficiency of AO10 wastewater.

the credibility of the optimal conditions obtained in this study was acceptable.

3.2. Effect of Fresnel Lens on the Degradation Efficiency of AO10 Wastewater. To investigate the effect of Fresnel lens, photocatalytic oxidation of AO10 wastewater with or without Fresnel lens was performed simultaneously under natual solar irradiation using the optimal experimental conditions obtained from RSM runs.

Basically, it was found that the concentrating effect of Fresnel lens for solar energy could result in an increase of 2.2~2.5 and 1.8~2.0 times of solar light irradiation in summer (June) and winter (December) seasons, respectively, as shown in Table 4. Also, a raising heat irradiation in terms of 10~15°C of wastewater temperature was observed in this study. Figures 3 and 4 showed the effect of Fresnel lens on the COD, TOC degradation, and decolorization efficiency of AO10 wastewater in summer (June) and winter (Dec.) season, respectively. As shown in Figure 3, a 99% of COD and a 94% of TOC degradation of AO10 wastewater were achieved with the assistance of Fresnel lens, in contrast to a 94% of COD and a 74% of TOC degradation in solar photocatalytic process without Fresnel lens observed within a reaction of 2 h. The decolorization efficiency of AO10 wastewater was also increased 29% as using Fresnel lens for a reaction of 1 h only. Moreover, it was found that the degradation efficiency of AO10 wastewater with the aid of Fresnel lens at a reaction of 1 h was close to that without the assistance of Fresnel lens at a reaction time of 2 h. This could be due to a higher light irradiation and water temperature that increased the rate of generation of oxidizing species such as •OH radical. This result implied that the higher the solar light irradiation applied, the higher the generation of electron-hole pairs and •OH radicals. A similar phenomenon was observed in the study of Liu et al. [15]. Their result indicated that the TOC degradation efficiency of Acid Yellow 17 solution increased from 5.1% to 53.2% as the intensity of UV light increased from 12.4 to 31.5 W/m^2, indicating a positive effect of increasing light irradiation. In addition, the results of Lin and Lee [16] indicated that the degradation efficiency of MX-5B dye wastewater improved 15% while the temperature of water was increased from 22°C to 40°C in TiO_2 photocatalytic process. This is due to a higher

Table 4: Effect of Fresnel lens on the degradation rate constant of AO10 wastewater.

Solar photocatalytic process*	[a]k_{COD}, h^{-1}	[b]k_{TOC}, h^{-1}	$UV_{280–400\,nm}$, W/m^2	[c]ΔT, °C
Without fresnel lens	0.792	0.606	39.9–44.8 (June)	8 ~ 10
	0.438	0.289	23.9–26.9 (Dec.)	6 ~ 8
With fresnel lens	2.307	1.477	96.8–112.1 (June)	14 ~ 15
	1.799	0.866	48.5–53.8 (Dec.)	14 ~ 16

*Operation condition: pH_0: 6.0, $[TiO_2]_0$ = 1.0 g/L; reaction time: 2 h;
[a]k_{COD}: pseudo-first order rate constant based on the degradation of COD in solution;
[b]k_{TOC}: pseudo-first order rate constant based on the degradation of TOC in solution;
[c]ΔT: final solution temperature—initial solution temperature.

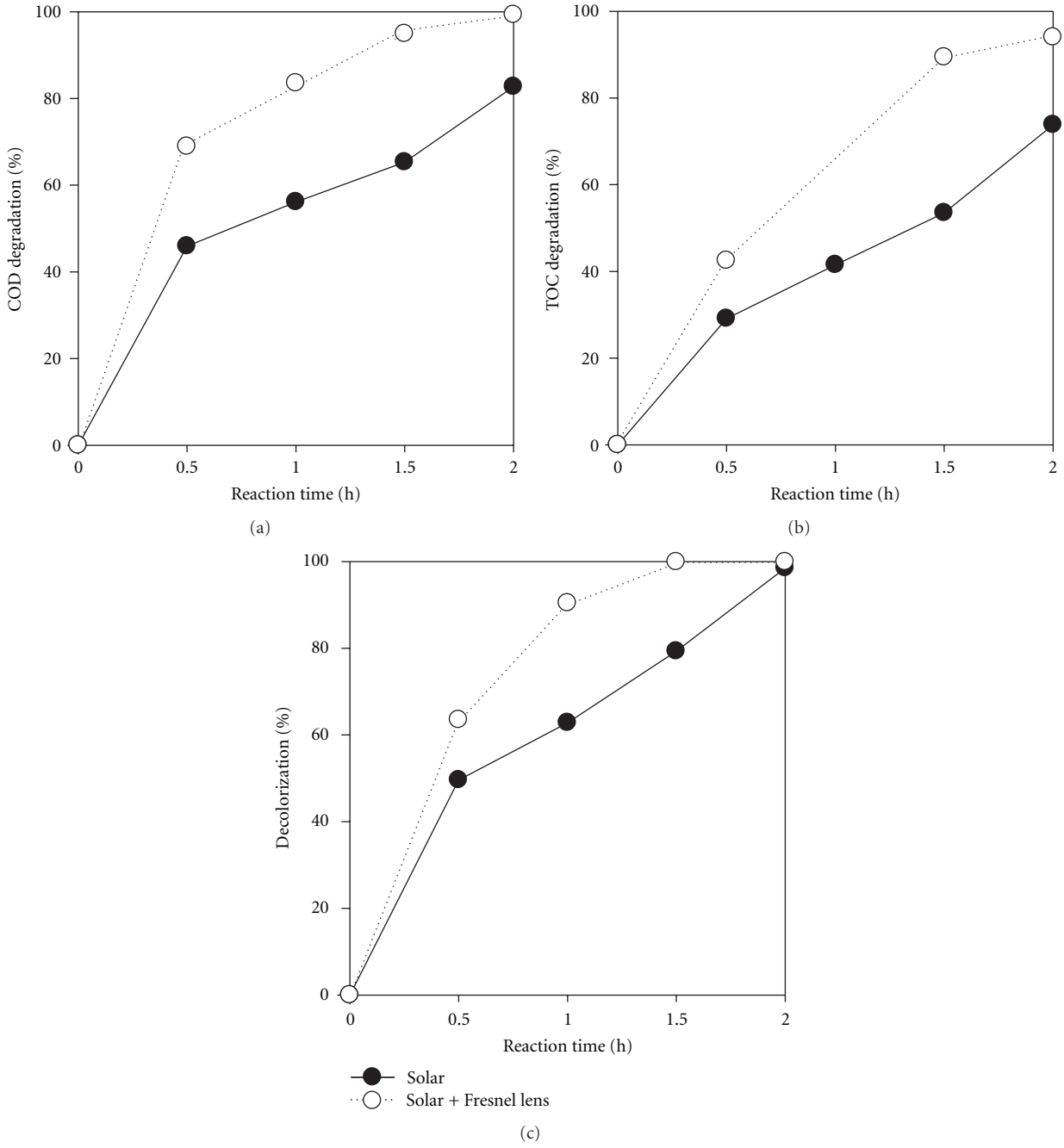


Figure 3: Effect of Fresnel lens on the degradation efficiency of AO10 dye wastewater in summer season (June).

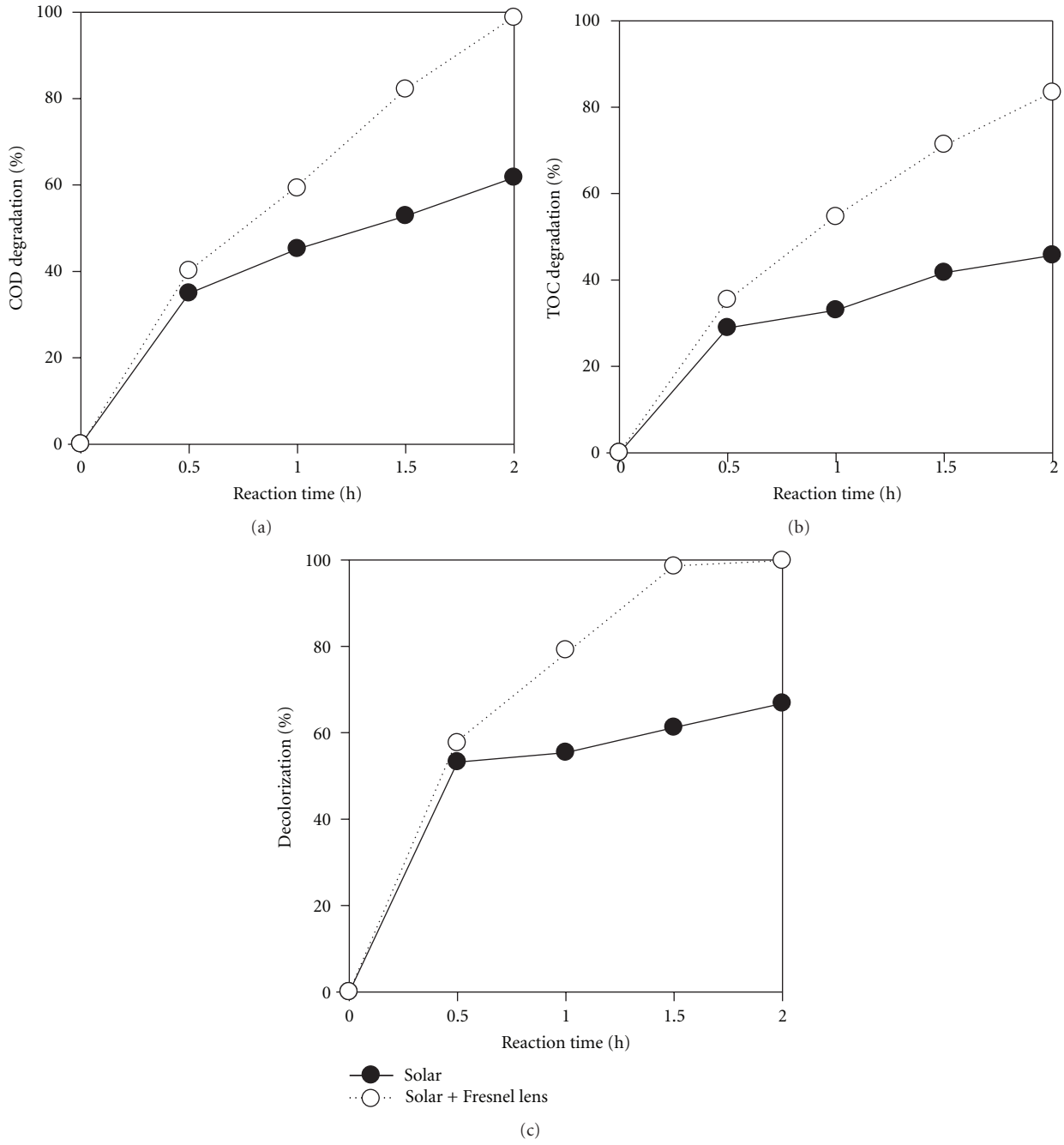


Figure 4: Effect of Fresnel lens on the degradation efficiency of AO10 dye wastewater in winter season (December).

water temperature that increased the reaction rate between $^{\bullet}$OH and organic molecules. Accordingly, two promotion effects were found with the assistance of Fresnel lens. First, the increase of solar light irradiation could enhance the excitation of electron hole and hence persistent promotion of $^{\bullet}$OH production. Second, the raise of water temperature would be higher due to the effect of solar heat irradiation, which renders additional positive effect on the performance of solar photocatalytic process.

To quantitatively analyze the effect of Fresnel lens on the degradation of AO10 wastewater, a pseudo-first-order model was applied to obtain the rate constants. It was found that both the COD and TOC degradation efficiencies of AO10 wastewater, with or without Fresnel lens, followed the pseudo-first-order reaction kinetics as indicated by high correlation coefficients ($r^2 > 0.90$). It was obvious that a significant enhancement for the degradation rate of AO10 wastewater was achieved by using Fresnel lens. As the rate constant shown in Table 4, the COD and TOC degradation rate of AO10 wastewater increased a factor of 2.9 and 2.4, respectively, in summer (June) season and a factor of 4.1 and 3.0, respectively, in winter (December)

season. The promotion effect of Fresnel lens was more significant in winter season. This may be due to a lower solar irradiation (23.9~26.9 W/m^2) and a lower initial water temperature (15~18°C) in winter season, leading to a much lower production of $^{\bullet}$OH radicals in the solar photocatalytic process without the assistance of Fresnel lens.

4. Conclusions

Optimized reaction conditions based on the application of RSM were established as an initial pH of 6.0, a TiO_2 concentration of 1.0 g/L, and a reaction time of 2 h for more than a 90% of COD and TOC degradation of AO10 wastewater in solar TiO_2 photocatalytic process. Solar energy could be concentrated efficiently by using Fresnel lens and had a significant effect on the increasing of $UV_{280–400\,nm}$ light intensity of solar irradiation and the temperature of wastewater, leading to a positive effect on the performance of solar photocatalytic process. Consequently, the solar TiO_2 photocatalytic process with the use of a low cost of PMMA Fresnel lens can offer an economical and practical alternative for the treatment of dye wastewater.

Acknowledgment

Many thanks are due to the kind sponsorship of the National Science Council, Taiwan (Project no. NSC 99-2221-E-239-011), without which this work would not have been possible.

References

[1] I. D. Mall, V. C. Srivastava, N. K. Agarwal, and I. M. Mishra, "Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analyses," *Chemosphere*, vol. 61, no. 4, pp. 492–501, 2005.

[2] C. Bauer, P. Jacques, and A. Kalt, "Photooxidation of an azo dye induced by visible light incident on the surface of TiO_2 ," *Journal of Photochemistry and Photobiology A*, vol. 140, no. 1, pp. 87–92, 2001.

[3] Z. Zhang and H. Zheng, "Optimization for decolorization of azo dye acid green 20 by ultrasound and H_2O_2 using response surface methodology," *Journal of Hazardous Materials*, vol. 172, no. 2-3, pp. 1388–1393, 2009.

[4] F. Al Momani, "Impact of photo-oxidation technology on the aqueous solutions of nitrobenzene: degradation efficiency and biodegradability enhancement," *Journal of Photochemistry and Photobiology A*, vol. 179, no. 1-2, pp. 184–192, 2006.

[5] L. A. Pérez-Estrada, S. Malato, A. Agüera, and A. R. Fernández-Alba, "Degradation of dipyrone and its main intermediates by solar AOPs. Identification of intermediate products and toxicity assessment," *Catalysis Today*, vol. 129, no. 1-2, pp. 207–214, 2007.

[6] M. I. Maldonado, P. C. Passarinho, I. Oller et al., "Photocatalytic degradation of EU priority substances: a comparison between TiO_2 and Fenton plus photo-Fenton in a solar pilot plant," *Journal of Photochemistry and Photobiology A*, vol. 185, no. 2-3, pp. 354–363, 2007.

[7] S. Malato, P. Fernández-Ibáñez, M. I. Maldonado, J. Blanco, and W. Gernjak, "Decontamination and disinfection of water by solar photocatalysis: recent overview and trends," *Catalysis Today*, vol. 147, no. 1, pp. 1–59, 2009.

[8] A. Durán and J. M. Monteagudo, "Solar photocatalytic degradation of reactive blue 4 using a Fresnel lens," *Water Research*, vol. 41, no. 3, pp. 690–698, 2007.

[9] G. E. P. Box, W. G. Hunter, and J. S. Hunter, *Statistics for Experimenters: An Introduction to Design. Data Analysis and Model Building*, Wiley, New York, NY, USA, 1st edition, 1978.

[10] E. Evgenidou, K. Fytianos, and I. Poulios, "Semiconductor-sensitized photodegradation of dichlorvos in water using TiO_2 and ZnO as catalysts," *Applied Catalysis B*, vol. 59, no. 1-2, pp. 81–89, 2005.

[11] S. Lakshmi, R. Renganathan, and S. Fujita, "Study on TiO_2-mediated photocatalytic degradation of methylene blue," *Journal of Photochemistry and Photobiology A*, vol. 88, no. 2-3, pp. 163–167, 1995.

[12] P. Bansal, D. Singh, and D. Sud, "Photocatalytic degradation of azo dye in aqueous TiO_2 suspension: reaction pathway and identification of intermediates products by LC/MS," *Separation and Purification Technology*, vol. 72, no. 3, pp. 357–365, 2010.

[13] M. S. T. Gonçalves, A. M. F. Oliveira-Campos, E. M. M. S. Pinto, P. M. S. Plasência, and M. J. R. P. Queiroz, "Photochemical treatment of solutions of azo dyes containing TiO_2," *Chemosphere*, vol. 39, no. 5, pp. 781–786, 1999.

[14] K. Soutsas, V. Karayannis, I. Poulios et al., "Decolorization and degradation of reactive azo dyes via heterogeneous photocatalytic processes," *Desalination*, vol. 250, no. 1, pp. 345–350, 2010.

[15] C. C. Liu, Y. H. Hsieh, P. F. Lai, C. H. Li, and C. L. Kao, "Photodegradation treatment of azo dye wastewater by UV/TiO_2 process," *Dyes and Pigments*, vol. 68, no. 2-3, pp. 191–195, 2006.

[16] Y. C. Lin and H. S. Lee, "Effects of TiO_2 coating dosage and operational parameters on a TiO_2/Ag photocatalysis system for decolorizing procion red MX-5B," *Journal of Hazardous Materials*, vol. 179, no. 1–3, pp. 462–470, 2010.