

## Research Article

# Pretreatment of Color Filter Wastewater towards Biodegradable by Fresnel-Lens-Assisted Solar TiO<sub>2</sub> Photocatalysis

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Received 20 July 2012; Revised 16 August 2012; Accepted 16 August 2012

Academic Editor: Jiaguo Yu

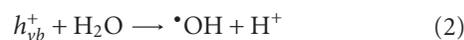
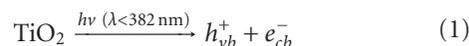
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The pretreatment of color filter wastewater towards biodegradable by Fresnel-lens-enhanced solar TiO<sub>2</sub> photocatalytic process was investigated. The experimental design of response surface methodology (RSM) was employed to assess the effect of critical process parameters (including initial pH, TiO<sub>2</sub> dosage, and reaction time) on pretreatment performance in terms of BOD<sub>5</sub>/COD, COD and TOC removal efficiency. Appropriate reaction conditions were established as an initial pH of 7.5, a TiO<sub>2</sub> dosage of 1.5 g/L with a reaction time of 3 h for increasing the BOD<sub>5</sub>/COD ratio to 0.15, which implied that the treated wastewater would be possibly biodegradable. Meanwhile, the efficiency of COD and TOC removals reached 32.9% and 24.4%, respectively. With the enhancement of Fresnel lens, the required reaction time for improving the biodegradability of wastewater to 0.15 was 1 h only. Moreover, the efficiency of COD and TOC removals was promoted to 37.4% and 25.8%, respectively. This could be mainly due to the concentrated effect of Fresnel lens for solar energy, including an increase of 2 times of solar irradiation and a raising of 15–20°C of wastewater temperature. Consequently, solar TiO<sub>2</sub> photocatalytic process with the use of a PMMA Fresnel lens could offer an economical and practical alternative for the pretreatment of industry wastewater containing diversified biorefractory pollutants with a high concentration of COD such as color filter wastewater.

## 1. Introduction

Organic wastewater from color filter industry generally contains so many residuals such as TMAH (C<sub>4</sub>H<sub>13</sub>NO), PGMEA (C<sub>6</sub>H<sub>12</sub>O<sub>3</sub>), acrylic resin, and pigments, and it is variable in composition and strength at different stages of process. In the presence of biorefractory organic matter, the effluent is usually characterized by its high chemical oxygen demand (COD) and low biodegradability generally expressed as a ratio of biological oxygen demand at day 5 (BOD<sub>5</sub>) to COD, that is, BOD<sub>5</sub>/COD. Advanced oxidation processes (AOPs) have been previously described as a promising option to remove persistent pollutants from contaminated water [1] when conventional water treatment processes are not efficient enough. AOPs are able to produce a highly reactive, nonspecific oxidant, mainly hydroxyl radicals (•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, which result in a high operation cost in AOPs [2]. 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 [3]. In particular, TiO<sub>2</sub> photocatalysis (as shown in (1)–(3)) using solar irradiation has been used as an economically viable process and has attracted great interest in the recent years [4–6]:



However, solar TiO<sub>2</sub> photocatalysis was usually carried out by using solar irradiation directly, resulting in a lower absorption and utilization of solar energy [7, 8]. To improve the efficiency of solar TiO<sub>2</sub> photocatalysis, it is necessary

TABLE 1: Physical and chemical properties of color filter wastewater.

Characteristic	Values
pH	9.8~10.2
COD, mg/L	924~960
BOD <sub>5</sub> , mg/L	22~51
BOD <sub>5</sub> /COD	0.02~0.05
TOC, mg/L	280~303
SS, mg/L	0.3~1.9
TS, mg/L	1080~1160
Color (ADMI value)	1540~1600
TMAH, mg/L	3.2~3.3
Cl <sup>-</sup> , mg/L	1.8~2.0
NO <sub>3</sub> <sup>-</sup> , mg/L	4.8~5.0
SO <sub>4</sub> <sup>2-</sup> , mg/L	1.1~1.2
NH <sub>4</sub> <sup>+</sup> , mg/L	0.7~0.8

to concentrate and maximize solar energy utilization in the process. Moreover, the combination of solar TiO<sub>2</sub> photocatalysis as a preliminary treatment, followed by an inexpensive biological process, seems to be a more attractive option for biorefractory organic wastewater.

In this study, pretreatment of color filter wastewater towards biodegradable using solar TiO<sub>2</sub> photocatalysis enhanced by a high-concentrating Fresnel lens was investigated. A factorial design according to response surface methodology (RSM) was employed to optimize the reaction conditions of critical process parameters (including initial pH of wastewater, TiO<sub>2</sub> dosage, and reaction time) to reach a biodegradable degree of color filter wastewater. Moreover, the effect of Fresnel lens on treatment performance in terms of COD degradation efficiency, mineralization efficiency, and biodegradability (BOD<sub>5</sub>/COD) of color filter wastewater was examined.

## 2. Material and Methods

**2.1. Materials.** The color filter wastewater used in this study was obtained from an electrooptical industry plant located in Hsin-Chu, Taiwan, during 2009-2010. The characteristics of color filter wastewater are shown in Table 1. Basically, the color filter wastewater has the properties of high COD (924–960 mg/L), high TOC (280–303 mg/L), and low biodegradability (BOD<sub>5</sub>/COD: 0.02–0.05). TiO<sub>2</sub> powder (mainly anatase form, mean particle size: 30 nm, BET surface area: 50 ± 15 m<sup>2</sup>/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 color filter wastewater was used and maintained at a preset temperature in a water bath during the experiments. A 3 factors \* 3 levels Box-Behnken experimental design [9] with three replicates at center point according to the methodology of response surface as shown in Table 2 was performed to examine

TABLE 2: Experimental range and levels of the process parameters in this study.

Independent variable	Factor	Range and level		
		-1	0	+1
Initial pH	X <sub>1</sub>	5	7.5	10
TiO <sub>2</sub> dose, g/L	X <sub>2</sub>	0.5	1.0	1.5
Reaction time, hr	X <sub>3</sub>	1	2	3
Y (response) – BOD <sub>5</sub> /COD				

the influence of three critical process parameters (viz., initial pH, TiO<sub>2</sub> dosage and reaction time) on the biodegradability, COD and TOC degradation of wastewater. Moreover, the regression analysis of Minitab R14 software (Minitab Co., USA) was used to figure out the reaction conditions for improving the biodegradability of wastewater. At the RSM runs, the initial pH of wastewater was adjusted to the desired pH by adding 1 N H<sub>2</sub>SO<sub>4</sub>. The wastewater was then 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<sub>280–400 nm</sub> intensity is around 66.5 ± 0.5 W/m<sup>2</sup>. In addition, the wastewater was maintained at 25 ± 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 tested for COD, TOC, and BOD<sub>5</sub>.

As the appropriate values of the process parameters were developed on the basis of RSM application and related regression equation of biodegradability, a Fresnel lens made of PMMA (thickness: 2 mm, pitch: 0.5 mm, facet depth: 0.2 mm, Fresnel circles: 395) was added into solar TiO<sub>2</sub> photocatalytic system with a distance of 16 cm above the level of wastewater in a clear sky condition to investigate the effect of Fresnel lens. The solar irradiation was measured with a LI-250 radiation indicator (LI-COR Co., USA) of pyranometer LI-200SA and a UV<sub>280–400 nm</sub> detector of PMA 2100 (Solar Light Co., USA). The irradiated solar irradiation during the experimental run with Fresnel lens was in the range of 900–1000 W/m<sup>2</sup> (UV<sub>280–400 nm</sub>: 52.4–57.4 W/m<sup>2</sup>). In addition, two blank experiments including direct photolysis reaction and adsorption on TiO<sub>2</sub> only under the experimental conditions of this study were performed. The result indicated that the COD and TOC removal efficiency of color filter wastewater was less than 1%, which implied that the removal of organic pollutants of color filter wastewater due to these effects was negligible in this study.

### 2.3. Analysis

**2.3.1. Chemical Oxygen Demand (COD) Measurement.** COD of solution via a DR 4000 photometer (HACH Co., USA) by using a K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> as the reacting reagent was measured in order to understand the changes on degree of oxidation for color filter wastewater.

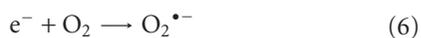
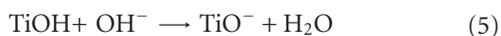
**2.3.2. Total Organic Carbon (TOC) Measurement.** TOC of solution was measured by using a Shimadzu VCPH analyzer (Shimadzu Co., Japan) in order to know the amount of organics in color filter wastewater degraded to CO<sub>2</sub> during oxidation.

**2.3.3. BOD<sub>5</sub> Measurement.** BOD<sub>5</sub> test was measured according to the procedures described in Standard methods 10 [Section 5210D, 10].

The bacteria (2000~4000 mgMLSS/L) used in this test were obtained from a local activation sludge system, operating at industrial wastewater treatment plant. The data showed that the BOD<sub>5</sub> value of untreated color filter wastewater in this study was in the range of 0.02~0.05, indicating that the color filter wastewater was hardly biodegradable.

### 3. Results and Discussion

**3.1. Effect of Initial pH and Dosage of TiO<sub>2</sub>.** Figure 1 displays the two-dimensional contour plots for the biodegradability (BOD<sub>5</sub>/COD), COD, and TOC degradation of color filter wastewater as a function of initial pH and concentration of TiO<sub>2</sub>. As shown in Figure 1, when the pH of wastewater was varied from 10 (the original pH of wastewater) to 5 at the same TiO<sub>2</sub> dosage, the biodegradability of wastewater decreased with decreasing initial pH of wastewater to around a pH of 7.5 and then gradually increased with decreasing initial pH of wastewater to pH 5. This phenomenon was also observed in the degradation of COD and TOC in all the TiO<sub>2</sub> concentration range studied. This can be explained by the surface charge of TiO<sub>2</sub> as a function of pH. The zero point of charge (ZPC) for TiO<sub>2</sub>-P25 is around pH 6.3–6.8 [11]. Therefore, at more acidic pH values (pH < pH<sub>ZPC</sub>), the TiO<sub>2</sub> surface is positively charged as expressed by (4) and at alkaline pH, the surface (pH > pH<sub>ZPC</sub>) is negatively charged as expressed by (5) [12, 13]. Therefore, at pH values below 6.3, the adsorption of wastewater is favourable due to the electrostatic attraction between the organic pollutants of wastewater and positively charged TiO<sub>2</sub> on the surface, leading to a better efficiency with the •OH generated on the surface of TiO<sub>2</sub>. A similar phenomenon was found in the study of Xiang et al. [14]. Moreover, the study of Wang et al. [15] indicated that the positively charged TiO<sub>2</sub> could prompt the transfer of photoinduced electrons to the oxygen adsorbed on the surface of TiO<sub>2</sub>. Consequently, the superoxide ion would be produced as shown in (6) and the recombination of electron hole on the surface of TiO<sub>2</sub> would be probably inhibited:



As the pH was above 6.8, the organic pollutants of wastewater were subjected to electrostatic repulsion between themselves and the negative surface of TiO<sub>2</sub>. Hence, the

adsorption of the organic pollutants of wastewater is less, leading to a decrease in degradation efficiency. Similar results were also observed in the TiO<sub>2</sub> photocatalytic degradation of a power station effluent [16] and the adsorption of Congo red on the surface of NiO [17]. Nevertheless, Barka et al. [18] pointed out that more OH<sup>-</sup> may react with the holes generated from the photoexcitation of TiO<sub>2</sub> and produced more •OH radicals as described by (3), leading to a higher degradation efficiency. Hence, the biodegradability and degradation efficiency of color filter wastewater treated in the alkaline condition (pH 10) was found to be higher than those treated in the neutral pH. In general, the biodegradability and degradation efficiency of color filter wastewater was in the order of pH 5 > pH 10 > pH 7.5 under all TiO<sub>2</sub> concentration range studied.

On the other hand, as shown in Figure 1, the concentration of TiO<sub>2</sub> also showed an obvious effect on the biodegradability and degradation efficiency of color filter wastewater. Ordinarily, more catalyst will substantially result in more generation of hydroxyl radicals until an optimum catalyst concentration is achieved. Hence, the results showed that, under all pH range studied (5–10), the increase of catalyst concentration from 0.5 to 1.5 g/L increased the degradation efficiency. This fact may be due to the increase in the number of organic pollutants adsorbed and more oxidation of organics [19].

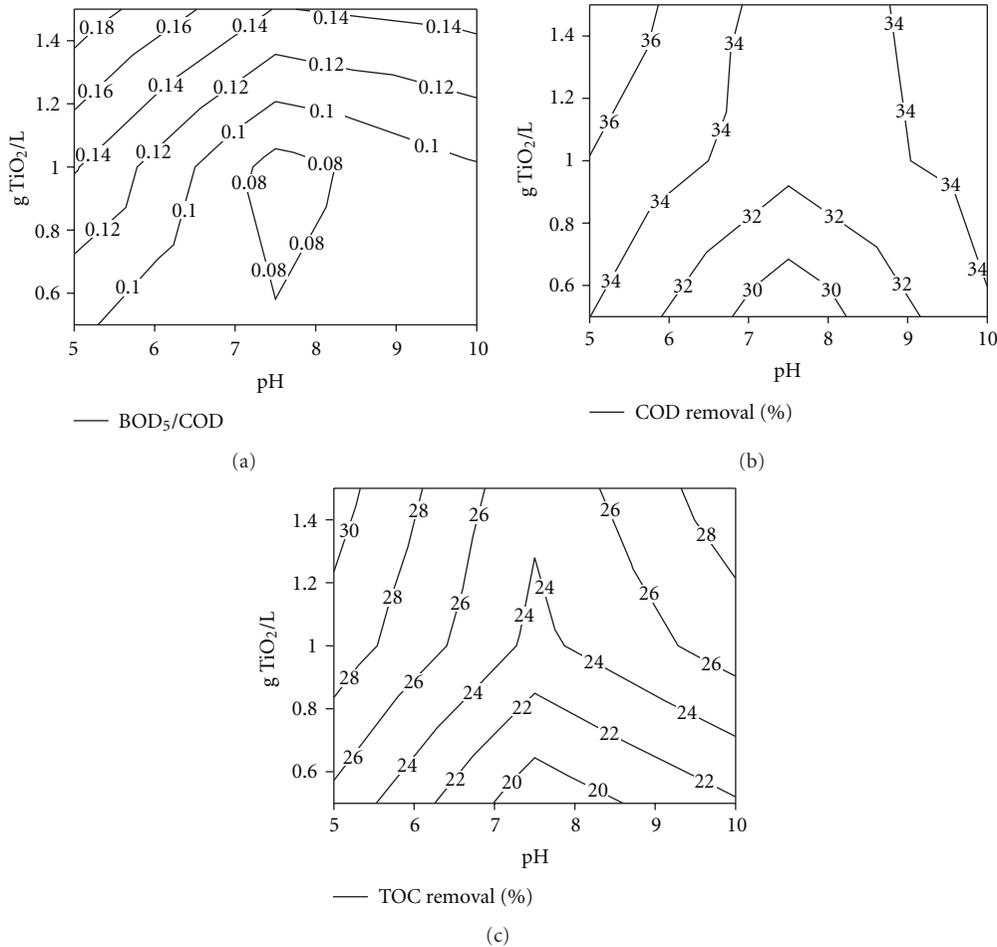
In addition, the experimental results allow the development of a second-order polynomial multiple regression equation as described by (7), which could be used to assess the effect of critical process parameters (viz., initial pH, TiO<sub>2</sub> dosage and reaction time) on pretreatment performance in terms of the biodegradability of wastewater. The regression model had a high value of coefficient of determination ( $r^2 > 0.96$ ). This implies that the process efficiency could be predicted well by the second order polynomial regression equations under the conditions studied. Moreover, a neutral pH must be considered for a better operation of the following biological treatment. Accordingly, an appropriate reaction condition was established as an initial pH value of 7.5, a TiO<sub>2</sub> dosage of 1.5 g/L with a reaction time of 3 h for increasing the ratio of BOD<sub>5</sub>/COD ratio to 0.15, which means the treated wastewater reaching a possibly biodegradable level [20]:

$$\begin{aligned} Y_{\text{BOD}_5/\text{COD}} = & 0.166 - 0.010X_1 + 0.035X_2 \\ & + 0.027X_3 - 0.033X_1^2 - 0.026X_2^2 \\ & - 0.051X_3^2 - 0.027X_1X_2 - 0.015X_1X_3 \\ & - 0.003X_2X_3, \quad r^2 = 0.962. \end{aligned} \quad (7)$$

**3.2. Effect of Fresnel Lens.** Table 3 showed the effect of Fresnel lens on the degradation efficiency and biodegradability of color filter wastewater under the reaction condition with an initial pH of 7.5 and a TiO<sub>2</sub> dosage of 1.5 g/L. It was found that the concentrating effect of Fresnel lens for solar energy could result in an increase of 2 times of solar light intensity as indicated by an increase in UV<sub>280–400 nm</sub> intensity from 54.9 W/m<sup>2</sup> to 110.3 W/m<sup>2</sup>, accompanied with a raising of

TABLE 3: Effect of Fresnel lens on the degradation efficiency and biodegradability of color filter wastewater.

Solar light source and reaction time	UV <sub>280–400 nm</sub> Intensity, W/m <sup>2</sup>	Wastewater temperature, °C	COD removal, %	TOC removal, %	AOS	BOD <sub>5</sub> /COD
Solar light + Fresnel lens, 1 h	110.3	35–45	37.4	25.8	0.01	0.150
Suntest 500 W/m <sup>2</sup> , 1 h	66.5	25	25.9	20.3	−0.40	0.112
Suntest 500 W/m <sup>2</sup> , 2 h	66.5	25	29.1	22.6	−0.15	0.120
Suntest 500 W/m <sup>2</sup> , 3 h	66.5	25	32.9	24.4	−0.02	0.145

FIGURE 1: Contour of the biodegradability (a) and degradation efficiency (b) and (c) of color filter wastewater as a function of initial pH and TiO<sub>2</sub> dosage (reaction time: 3 h).

heat irradiation in terms of 15~20°C increase in wastewater temperature in this study. Consequently, a 37.4% of COD and a 25.8% of TOC degradation of color filter wastewater were achieved in a reaction time of 1 h with the assistance of Fresnel lens, in contrast to a 32.9% of COD and a 24.4% of TOC degradation in 3 h reaction by an artificial solar irradiation with an UV<sub>280–400 nm</sub> intensity of 66.5 W/m<sup>2</sup>.

Moreover, the degree of oxidation of color filter wastewater during solar photocatalysis could significantly affect the biodegradability of solution. The average oxidation state (AOS) of organic carbon could be used to monitor the change in the degree of oxidation of pollutants [1]. The

average oxidation state of the organic carbon was calculated by.

$$\text{AOS} = 4 - 1.5 \times \frac{\text{COD}}{\text{TOC}}, \quad (8)$$

in which the unit of COD and TOC is mg/L. The AOS value indicates how chemical substances in the effluent become more oxidized. A higher AOS value implies a higher degree of oxidation. Theoretically, the AOS has a value of +4 for CO<sub>2</sub>, the most oxidized state of C, and −4 for CH<sub>4</sub>, the most reduced state of carbon. As shown in Table 3, the AOS values increased from −0.73 for untreated color filter wastewater

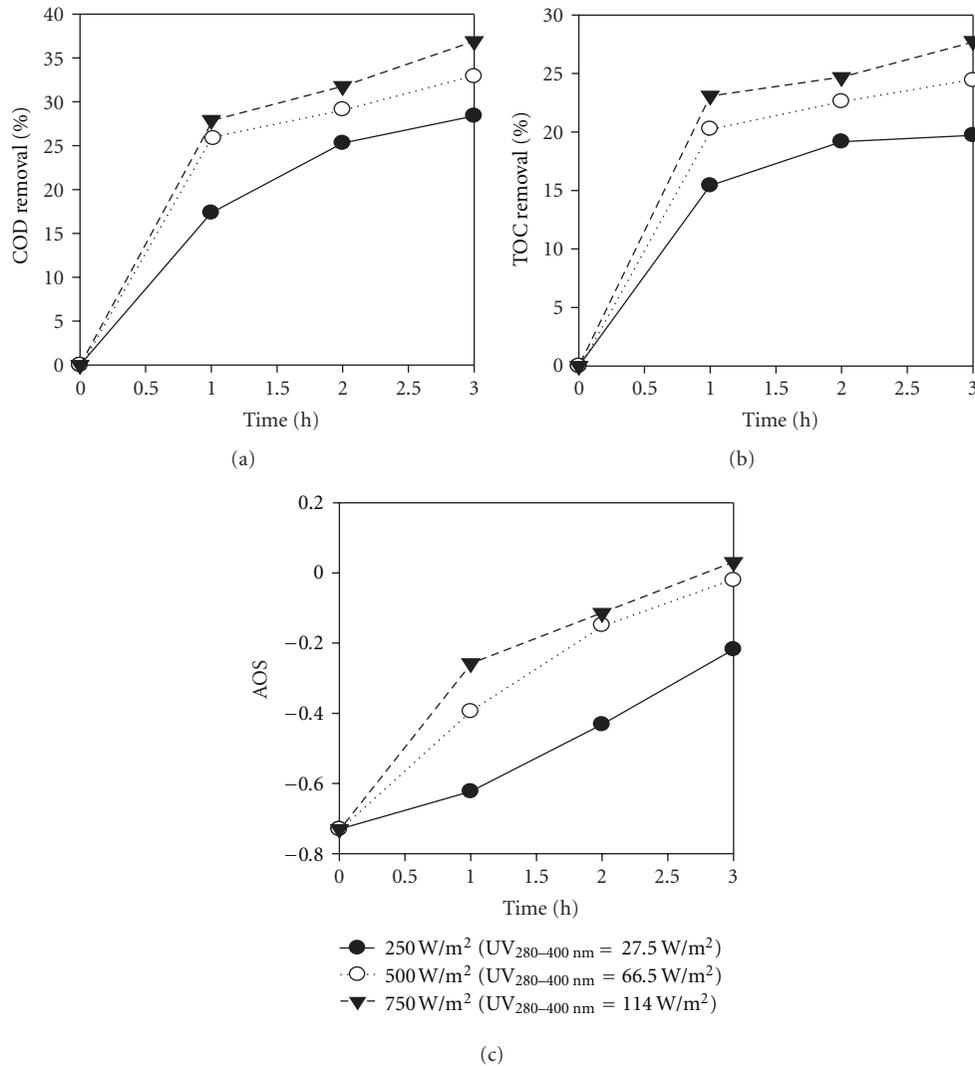


FIGURE 2: Effect of solar light intensity on the degradation of color filter wastewater (wastewater temperature:  $25 \pm 0.5^\circ\text{C}$ ).

to 0.01 and  $-0.42$  for treated color filter wastewater at a reaction time of 1 h with and without using Fresnel lens, respectively. This result implied that a higher degree of oxidation happened, leading to a further improvement in the biodegradability of color filter wastewater in Fresnel-lens-assisted system. The required reaction time to reach the criteria of a possible biodegradability of wastewater, which a  $\text{BOD}_5/\text{COD}$  value of 0.15 was usually selected, and it was, therefore much less for the Fresnel-lens-assisted system.

Basically, the degradation efficiency of wastewater increased with increasing light intensity in the  $\text{TiO}_2$  photocatalytic process [21]. As shown in Figure 2, the result illustrated that the higher the solar light intensity, the higher the COD and TOC degradation was. A 10% increase of the COD and TOC degradation was observed with raising solar light intensity from 250 ( $\text{UV}_{280-400 \text{ nm}}$ :  $27.5 \text{ W/m}^2$ ) to  $750 \text{ W/m}^2$  ( $\text{UV}_{280-400 \text{ nm}}$ :  $114 \text{ W/m}^2$ ). This could be because a higher light irradiation increased the generation of electron-hole pairs and then produced more oxidizing species such as  $\cdot\text{OH}$

radical. A similar phenomenon was observed in the study of Liu et al. [22]. 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  $31.5 \text{ W/m}^2$ , indicating a positive effect of increasing light irradiation.

Furthermore, the degradation efficiency of wastewater probably increased with increasing the temperature of wastewater. The study of Daneshvar et al. [23] indicated that the effect of wastewater temperature on the degradation efficiency of wastewater may not be significant because the adsorption capability of  $\text{TiO}_2$  may decrease and the recombination of electron hole may accelerate. However, the study of Barka et al. [24] found that the degradation efficiency of dye wastewater increased with raising the wastewater temperature from 20 to  $40^\circ\text{C}$  due to the enhanced motivation energy of wastewater, leading to increasing the frequency of collision between pollutants and  $\cdot\text{OH}$ . As shown in Figure 3, a 10% increase of the COD and TOC degradation was

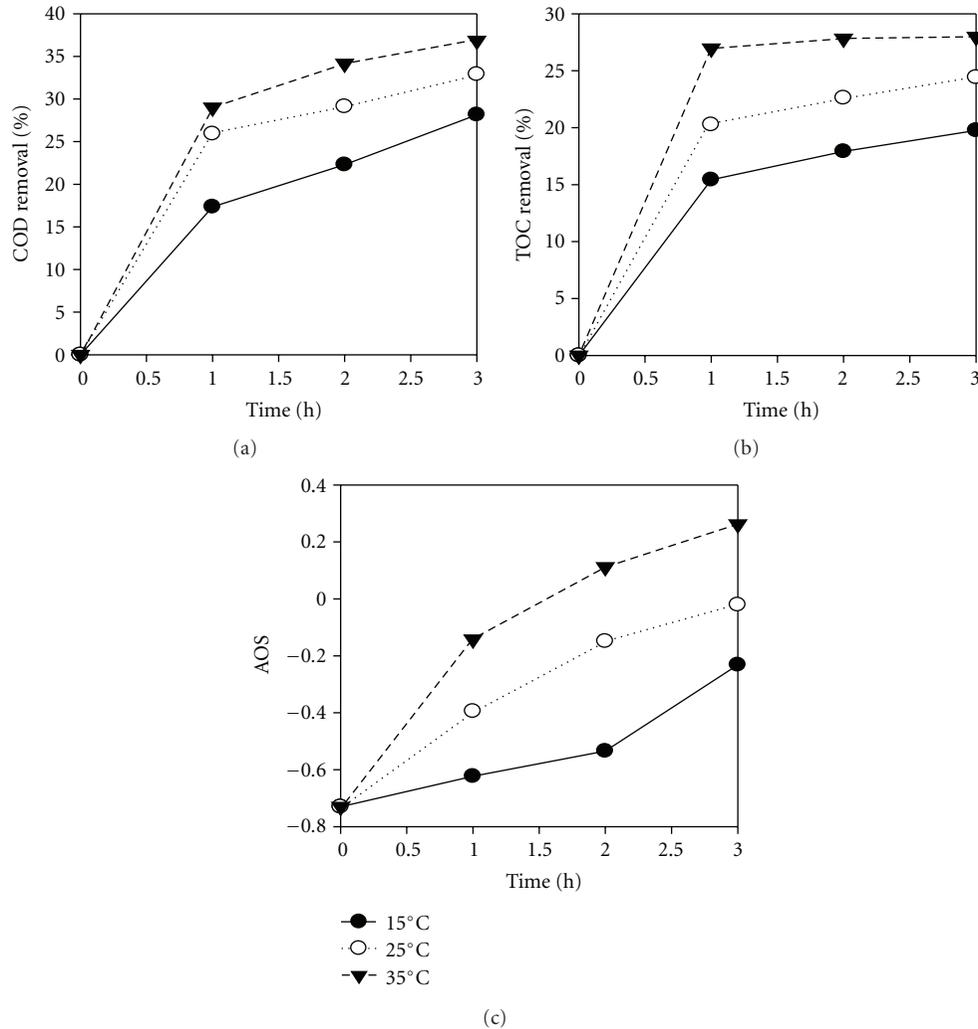


FIGURE 3: Effect of wastewater temperature on the degradation of color filter wastewater (solar light intensity: 500 W/m<sup>2</sup> (UV<sub>280-400 nm</sub>: 66.5 W/m<sup>2</sup>)).

observed with raising wastewater temperature from 15 to 35°C. Similarly, the results of Lin and Lee [25] illustrated that the degradation efficiency of MX-5B dye wastewater improved 15% while the temperature of water was increased from 22 to 40°C in a TiO<sub>2</sub> photocatalytic process. This is because a higher water temperature increased the reaction rate between •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 then persistent promotion of •OH production. Secondly, the raise of water temperature would be higher due to the effect of solar heat irradiation, which provides additional positive effect on the performance of solar photocatalytic process. By the way, quantitative determination of the concentration of hydroxyl radicals produced during photocatalysis may provide more solid explanation for the promotion effect with the assistance of Fresnel lens. Xiang et al. [26] reported that the photoluminescence (PL) technique using coumarin as a probe molecule of •OH radicals is an effectively probing method for indirect

determination of hydroxyl radical concentration. However, hydroxyl radicals had a short lifetime and high reactivity influencing its detection efficiency. Newton and Milligan [27] had reported that the trapping efficiency of •OH formed in the TiO<sub>2</sub> photocatalysis was about 5–11% even by the PL technique. Therefore, though the measurement of •OH concentration was not performed in this study, the promotion effect of Fresnel lens on solar TiO<sub>2</sub> photocatalysis is still clear according to the results, namely, the increase of biodegradability, COD, and TOC removal efficiency of wastewater.

To quantitatively analyze the effect of solar light intensity and solar heat irradiation in terms of wastewater temperature on the degradation of color filter wastewater, a pseudo-first-order model was applied to obtain the rate constants as shown in Tables 4 and 5, respectively. It was found that both the COD and TOC degradation rate of color filter wastewater increased significantly with increasing solar light intensity and wastewater temperature. The effect of wastewater temperature was more obvious than that of solar light intensity on the degradation rate of color filter wastewater.

TABLE 4: Effect of solar light intensity on the degradation rate constant of color filter wastewater<sup>a</sup>.

Solar Light Intensity	<sup>b</sup> $k_{\text{COD}}$ , hr <sup>-1</sup>	<sup>c</sup> $k_{\text{TOC}}$ , hr <sup>-1</sup>
250 W/m <sup>2</sup> (UV <sub>280–400 nm</sub> : 27.5 W/m <sup>2</sup> )	0.154	0.118
500 W/m <sup>2</sup> (UV <sub>280–400 nm</sub> : 66.5 W/m <sup>2</sup> )	0.197	0.147
750 W/m <sup>2</sup> (UV <sub>280–400 nm</sub> : 114 W/m <sup>2</sup> )	0.218	0.165

<sup>a</sup>Wastewater temperature: 25 ± 0.5°C.

<sup>b</sup> $k_{\text{COD}}$ : pseudo-first-order rate constant based on the degradation of COD in solution.

<sup>c</sup> $k_{\text{TOC}}$ : pseudo-first-order rate constant based on the degradation of TOC in solution.

TABLE 5: Effect of water temperature on the degradation rate constant of color filter wastewater<sup>a</sup>.

Wastewater temperature	<sup>a</sup> $k_{\text{COD}}$ , hr <sup>-1</sup>	<sup>b</sup> $k_{\text{TOC}}$ , hr <sup>-1</sup>
15°C	0.140	0.116
25°C	0.197	0.147
35°C	0.235	0.193

<sup>a</sup>solar light intensity: 500 W/m<sup>2</sup> (UV<sub>280–400 nm</sub>: 66.5 W/m<sup>2</sup>).

<sup>b</sup> $k_{\text{COD}}$ : pseudo-first-order rate constant based on the degradation of COD in solution.

<sup>c</sup> $k_{\text{TOC}}$ : pseudo-first-order rate constant based on the degradation of TOC in solution.

#### 4. Conclusions

Solar energy could be concentrated efficiently by using Fresnel lens and had a significant effect on the increase of UV<sub>280–400 nm</sub> light intensity of solar irradiation and the temperature of wastewater, leading to a positive effect on the performance of solar photocatalytic process. A biodegradability of 0.15 and a COD degradation of 27.4% and a TOC degradation of 25.8% of color filter wastewater were achieved in 1 h reaction under the reaction conditions of an initial pH of 7.5, a TiO<sub>2</sub> concentration of 1.5 g/L, and an assistance of Fresnel lens. Consequently, the solar TiO<sub>2</sub> photocatalytic process with the use of a PMMA Fresnel lens can offer an economical and practical alternative for the pretreatment of color filter wastewater towards biodegradable, making color filter wastewater be treated effectively by a biological process possible.

#### Acknowledgments

Many thanks to the kind sponsorship of National Science Council, Taiwan (Project no.: NSC 98–2221-E-239-004), without which this work would not have been possible.

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