

Research Article

Treatment of Color Filter Wastewater by Fresnel Lens Enhanced Solar Photo-Fenton Process

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Treatment of color filter wastewater using solar photo-Fenton process enhanced by high-concentrating Fresnel lens was investigated in this paper. Optimal reaction conditions based on response surface methodology (RSM) were established as under an initial pH of 5, a $[\text{H}_2\text{O}_2]_0/\text{COD}_0$ ratio of 1~1.35 and a $[\text{H}_2\text{O}_2]_0/[\text{Fe}^{2+}]_0$ ratio of 15 for a reaction time of 60 min, which could reach a readily biodegradable level, that is, the biodegradability (BOD_5/COD) of wastewater was more than 0.3. With the assistance of Fresnel lens, the solar photo-Fenton process increased the COD degradation rate and mineralization rate by a factor of 4.5 and 6.5, respectively. In addition, the microtoxicity (TU_{50}) of wastewater was almost diminished after a 60 min of treatment, whereas the microtoxicity of treated wastewater without the assistance of Fresnel lens remained a TU_{50} value of 1.166. This could be mainly due to the concentrating effect of Fresnel lens for solar energy, resulting in an increase of 2~3 times of solar light intensity and a raising heat irradiation in terms of 15~30 °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 photo-Fenton reaction for treating color filter wastewater.

1. Introduction

Organic wastewater from color filter industry generally contains so many residuals such as TMAH ($\text{C}_4\text{H}_{13}\text{NO}$), PGMEA ($\text{C}_6\text{H}_{12}\text{O}_3$), acrylic resin, and pigments, and it is variable in composition and strength at different stages of process. The effluent is usually characterized by its high chemical oxygen demand (COD), low biodegradability (BOD_5/COD), and with microtoxicity, implying the presence of refractory organic matter. Therefore, biological treatment processes are susceptible for treatment of color filter wastewater. 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. For that reason, 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 ($^{\bullet}\text{OH}$). 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 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 alternative to UV lamps to reduce the operation cost in AOPs [3]. In particular, photo-Fenton process using solar irradiation has been used as an economically viable process and has attracted great interest in recent years [4]. However, solar photo-Fenton process was usually carried out by using solar irradiation directly, resulting in a lower absorption and utilization of solar energy [5]. To improve the efficiency of solar photo-Fenton process, it is necessary to maximize the absorption of solar energy.

TABLE 1: Characteristics of color filter wastewater.

Item	Range
pH	10.4~10.7
UV ₂₅₄	2.000~2.046
COD, mg/L	1674~1766
BOD ₅ , mg/L	152~230
BOD ₅ /COD	0.08~0.13
TOC, mg/L	405~430
SS, mg/L	2.4~3.0
TS, mg/L	1145~1440
Color (ADMI value)	1100~1400

In this study, the degradation and mineralization of color filter wastewater using solar photo-Fenton process enhanced by high-concentrating Fresnel lens was investigated. This lens is made of PMMA plastic materials. Response surface methodology (RSM) was employed to obtain the optimal reaction conditions of critical process parameters (initial pH of wastewater, $[\text{H}_2\text{O}_2]_0/\text{COD}_0$ and $[\text{H}_2\text{O}_2]_0/[\text{Fe}^{2+}]_0$) to reach a readily biodegradable degree of color filter wastewater. Moreover, the effect of Fresnel lens on treatment performance in terms of COD degradation efficiency, mineralization efficiency, biodegradability, and microtoxicity of color filter wastewater was examined.

2. Materials 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. The characteristics of color filter wastewater are shown in Table 1. Basically, the color filter wastewater has the properties of high COD, low biodegradability, and with microtoxicity. Hydrogen peroxide (H_2O_2) with a concentration of 35% was supplied by Panreac Co., EU. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Panreac Co., EU) with a purity of 99% was used as a source of ferrous ion. 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-factor *3-level RSM experimental design with three replicates at center point as shown in Table 2 was applied. The color filter wastewater was placed into the photoreactor and irradiated by artificial solar light with an intensity of 500 W/m^2 by using an ATLAS Suntest CPS+ solar simulator (ATLAS Co., USA). 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 a reaction time of 60 min, tested for H_2O_2 consumption according to the method reported by Sella [6] and iron as Fe^{2+} ion determined by $\text{Fe(II)/1,10-phenanthroline}$ complex at 510 nm [7] using a Hitachi (Japan) U-2001 spectrophotometer instantly, and then quenched with sodium hydrogen sulfite to avoid further

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	3	4	5
g H_2O_2 /g COD	X_2	1.0	1.5	2.0
$[\text{H}_2\text{O}_2]_0/[\text{Fe}^{2+}]_0$	X_3	5	10	15

reactions. The remaining samples were then stored at 4°C for the following ADMI, COD, TOC, BOD₅, and microtoxicity analysis.

As the optimal values of the process parameters were developed on the basis of RSM application and related equations, a Fresnel lens that was made of PMMA (thickness: 2 mm, pitch: 0.5 mm, facet depth: 0.2 mm, Fresnel circles: 395) was added into solar photo-Fenton system with a distance of 16 cm above the level of wastewater. To investigate the effect of Fresnel lens, a similar reactor without Fresnel lens was also performed under the same actual solar irradiation. A schematic diagram of the photoreactor using Fresnel lens is shown in Figure 1.

2.3. Analytical Methods

2.3.1. Color Measurement of Color Filter Wastewater. A DR 4000 spectrophotometer (HACH Co., USA) was used for color measurement in terms of ADMI (American Dye Manufacturers Institute) values. The decolorization efficiency was calculated on the basis of ADMI reduction in color filter wastewater.

2.3.2. COD and TOC Measurement. COD (Chemical Oxygen Demand) of wastewater was carried out via a DR 4000 photometer (HACH Co., USA) by using a $\text{K}_2\text{Cr}_2\text{O}_7$ reagent. TOC (Total Organic Carbon) of wastewater was measured by a Shimadzu VCPH analyzer (Shimadzu Co., Japan).

2.3.3. BOD₅ Measurement. BOD₅ test was measured according to the procedures described in Standard methods [7] Section 5210D. The bacteria (2000~4000 mgMLSS/L) used in this test were obtained from local activation sludge system, operating at industrial wastewater treatment plant. The data showed that the BOD₅ value of untreated color filter wastewater in this study was 0.08~0.13, indicating that the color filter wastewater was not readily biodegradable.

2.3.4. Microtoxicity Measurement. The microtoxicity of each sample was measured using an SDI M500 (SDI Co., USA) analyzer. Microtoxicity is expressed as EC_{50} (5 min, 15°C), which was defined as the effective concentration of solution for a 50% reduction of the luminescence of the bacterium *Photobacterium phosphoreum*. A lower EC_{50} value indicates a higher amount of toxic constituent presented in the pollutant solution. The EC_{50} values are expressed as percentage (% v/v) of the sample [8, 9]. In addition, EC_{50} values could be transformed to toxicity units (TU_{50}), which was equal to

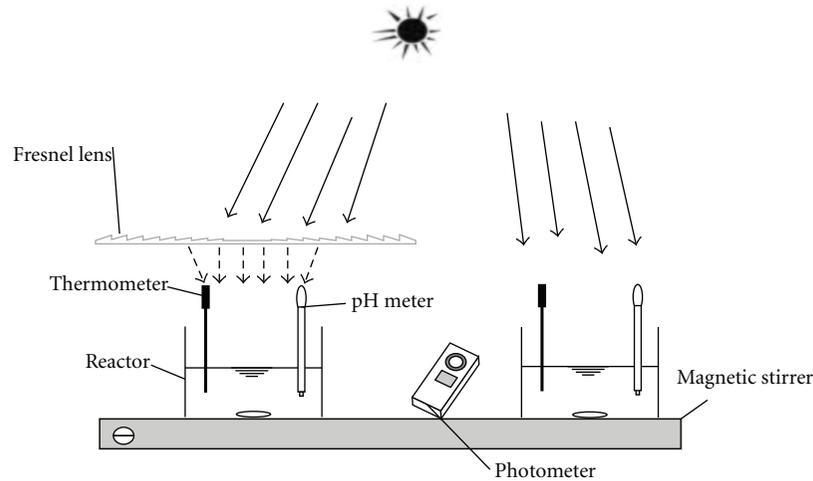


FIGURE 1: Schematic diagram of the solar photoreactor with and without Fresnel lens.

$1/EC_{50}$. The EC_{50} of color filter wastewater was measured, and it was 76~78%. Toxicity Unit (TU_{50}) was, therefore, in the range of 1.25~1.30 for color filter wastewater. In this study, the TU_{50} value was used to trace the change in toxicity of color filter wastewater due to solar photo-Fenton treatment.

3. Results and Discussion

3.1. Optimization of Solar Photo-Fenton Treatment of Color Filter Wastewater. On the basis of RSM application, the empirical relationship between the biodegradability of color filter wastewater (Y) and independent variables studied are shown as follows:

$$\begin{aligned}
 Y_{BOD_5/COD} &= 0.4770 + 0.0066X_1 + 0.0968X_2 - 0.1251X_3 \\
 &\quad - 0.0374X_1^2 - 0.0291X_2^2 - 0.0084X_3^2 - 0.0795X_1X_2 \\
 &\quad - 0.0628X_2X_3 - 0.0565X_2X_3, \\
 r^2 &= 0.904.
 \end{aligned}
 \tag{1}$$

The regression model (1) had a high value of coefficient of determination ($r^2 > 0.90$). This implies that the process efficiency could be predicted properly by the polynomial regression equations under the conditions studied. Based on the model equation, the optimal values of the process parameters were established as under a pH of 5, a $[H_2O_2]_0/COD_0$ ratio of 1~1.35, and a $[H_2O_2]_0/[Fe^{2+}]_0$ ratio of 15 for a reaction time of 60 min, which could reach a readily biodegradable level, that is, the biodegradability (BOD_5/COD) of wastewater was more than 0.3. In order to confirm the optimum conditions, five replicates and t -test analysis were performed. The results showed that the average of BOD_5/COD was 0.306 and the 95% of confidence intervals for BOD_5/COD was 0.290~0.322. Consequently, the credibility of the optimal conditions obtained in this study was acceptable.

3.2. Effect of Fresnel Lens on the Degradation Efficiency of Wastewater. Basically, it was found that the concentrating effect of Fresnel lens for solar energy could result in an increase 2~3 times of solar light irradiation and a raising heat irradiation in terms of 15~30°C of wastewater temperature in this study. Figure 1 showed the effect of Fresnel lens on COD and TOC degradation efficiency of color filter wastewater. As shown in Figure 2, an 85% of COD and a 70% of TOC degradation of color filter wastewater were achieved with the assistance of Fresnel lens, in contrast to a 48% of COD and a 32% of TOC degradation in solar photo-Fenton process with a solar irradiation of 1,000 W/m^2 was observed within 60 min. The decolorization efficiency of color filter wastewater also increased 17% as using Fresnel lens. Moreover, it was found that the degradation efficiency of color filter wastewater with the use of Fresnel lens at a reaction time of 30 min was higher than that without the assistance of Fresnel lens at a reaction time of 60 min. This could be due to a higher light irradiation and because water temperature increased the reaction rate between hydrogen peroxide and any form of ferrous/ferric ion, thus increased the rate of generation of oxidizing species such as $\cdot OH$ radical [10]. A similar phenomenon was also found in the study of Will et al. [11]. Its result indicated that the TOC degradation efficiency of phenol wastewater was 45% and 55% for a solar irradiation of 450 W/m^2 and 750 W/m^2 , respectively. In addition, the study's results of Rodriguez et al. [12] showed that the degradation efficiency of textile wastewater increased while the temperature of water was improved obviously from 30°C to 60°C in photo-Fenton process.

To quantitatively analyze the effect of Fresnel lens on degradation of color filter 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 color filter wastewater with or without Fresnel lens followed the pseudo-first-order reaction kinetics as indicated by high correlation coefficient ($r^2 > 0.90$) (Table 3). It was obvious that a significant enhancement for the degradation rate of color filter wastewater was achieved by using Fresnel lens. As

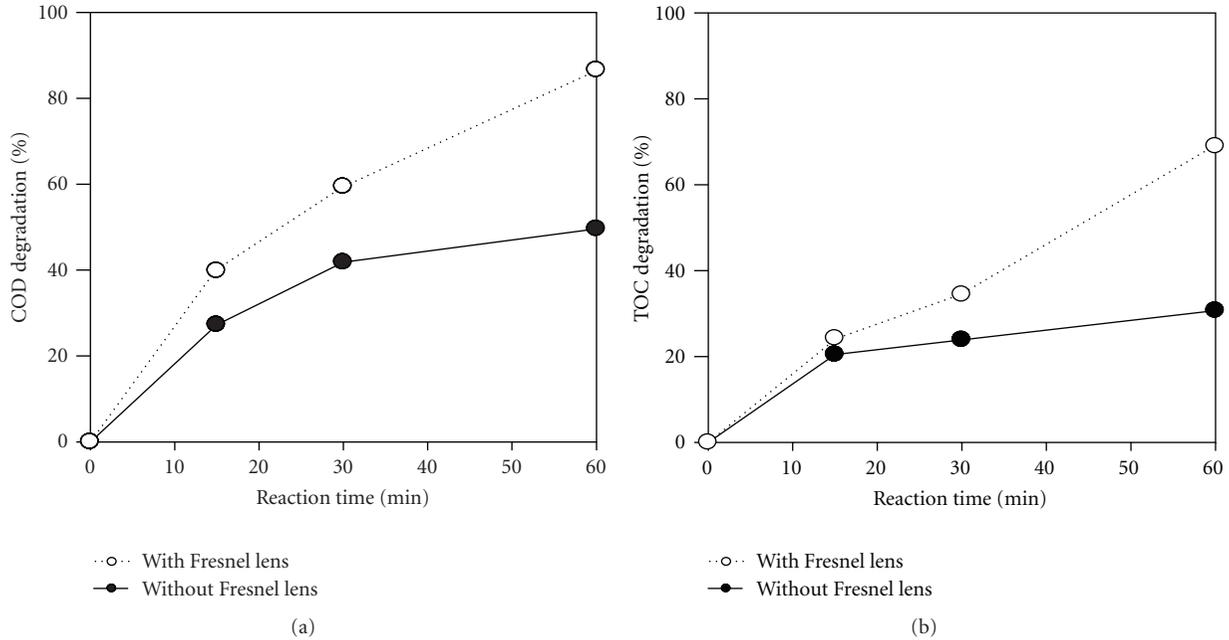


FIGURE 2: Effect of Fresnel lens on the degradation efficiency of (a) COD and (b) TOC of color filter wastewater in solar photo-Fenton process (initial pH: 5.0; $H_2O_2/COD = 1.25$ g/g; $[H_2O_2]_0/[Fe^{2+}]_0 = 15$).

TABLE 3: Effect of Fresnel lens on the degradation rate constant of color filter wastewater.

Solar Photo-Fenton Process	^a k_{COD}, min^{-1}	^b k_{TOC}, min^{-1}	^c $UV_{a+b}, \text{W/m}^2$
Without Fresnel lens	0.0076 ± 0.00079	0.0032 ± 0.00050	54.82
With Fresnel lens	0.0342 ± 0.00232	0.0208 ± 0.00170	138.09

* Operation condition: pH₀: 5.0, 1.25 g H₂O₂/g COD, $[H_2O_2]_0/[Fe^{2+}]_0 = 15$.

^a k_{COD} : pseudo-first-order rate constant based on the degradation of COD in solution for 95% confidence coefficient.

^b k_{TOC} : pseudo-first-order rate constant based on the degradation of TOC in solution for 95% confidence coefficient.

^c UV_{a+b} : UV light (280–400 nm) intensity.

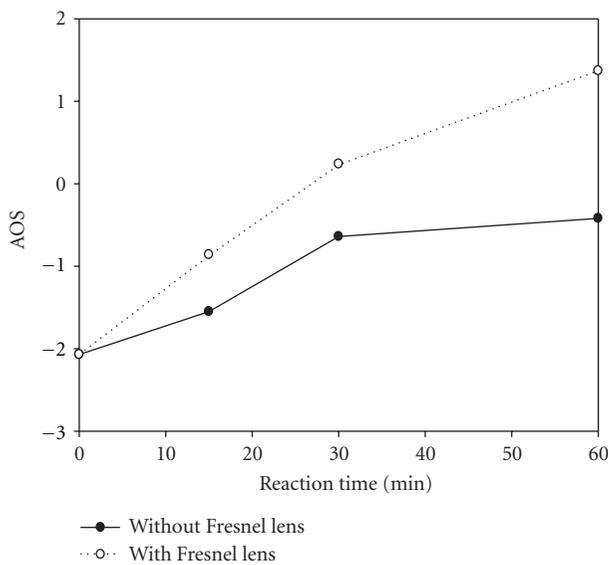


FIGURE 3: Effect of Fresnel lens on AOS of color filter wastewater in solar photo-Fenton process (initial pH: 5.0; $H_2O_2/COD = 1.25$ g/g; $[H_2O_2]_0/[Fe^{2+}]_0 = 15$).

the rate constant shown in Table 3, the COD degradation rate and mineralization rate of color filter wastewater increased a factor of 4.5 and 6.5, respectively, mainly due to the UV_{a+b} light intensity increasing 2.5 times with assistance of Fresnel lens.

3.3. *Effect of Fresnel Lens on the Biodegradability of Wastewater.* The degree of oxidation and produced intermediates of color filter wastewater during solar photo-Fenton treatment could affect significantly the biodegradability of solution [13]. Average oxidation state (AOS) could be used to monitor the change in the degree of oxidation [14]. The average oxidation state of the organic carbon was calculated by

$$AOS = 4 - 1.5 \times \frac{COD}{TOC}, \quad (2)$$

in which the unit of COD and TOC is mol O₂/L and mol C/L, respectively. 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 CO₂, the most oxidized state of C, and -4 for CH₄, the most reduced state of carbon. As shown in Figure 3, the untreated color

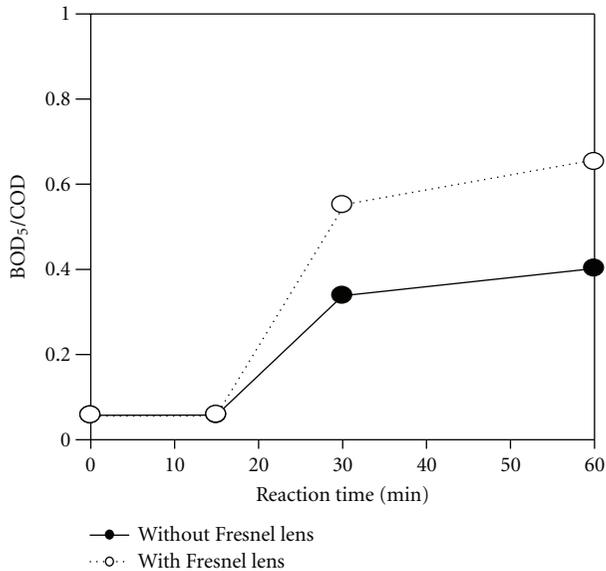


FIGURE 4: Effect of Fresnel lens on the biodegradability of color filter wastewater in solar photo-Fenton process (initial pH: 5.0; $H_2O_2/COD = 1.25$ g/g; $[H_2O_2]_0/[Fe^{2+}]_0 = 15$).

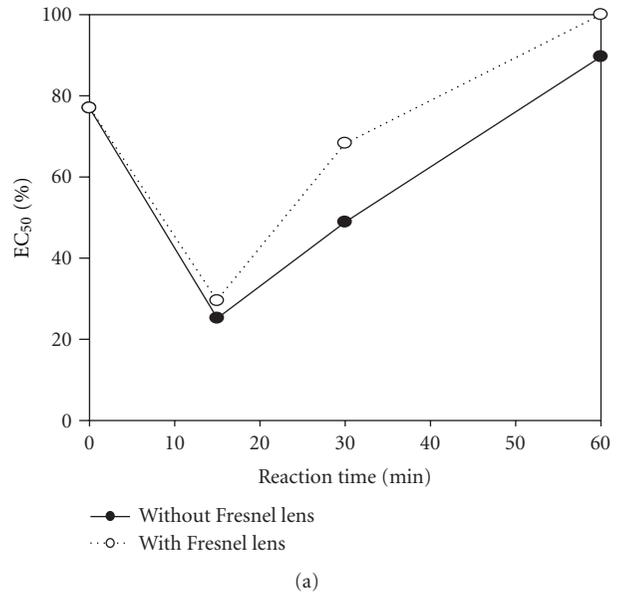
filter wastewater has an AOS value of -2.07 and the AOS values increased to 1.37 and -0.42 at a reaction time of 60 min with and without using Fresnel lens, respectively. This result implied that a higher degree of oxidation happened in Fresnel-lens-assisted system. Figure 4 showed the effect of Fresnel lens on BOD_5/COD of color filter wastewater. It was found that the Fresnel-lens-assisted solar photo-Fenton process could improve furthermore in the biodegradability of color filter wastewater. The required reaction time to reach the criteria of a ready biodegradability of wastewater, in which a BOD_5/COD value of 0.3 was usually selected, was less as a result for the Fresnel-lens-assisted system.

3.4. Effect of Fresnel Lens on the Microtoxicity of Wastewater.

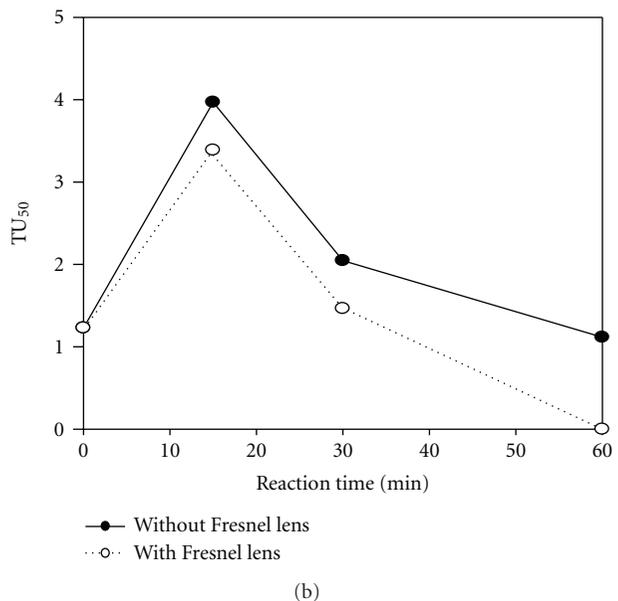
The effect of Fresnel lens on the microtoxicity of color filter wastewater in solar photo-Fenton process was shown in Figure 5. It was found that the microtoxicity of color filter wastewater increased obviously at a reaction time of 15 min, which may be due to more toxic intermediates generated at initial reaction stage. A similar result was also found in the study of González et al. [8]. However, the TU_{50} value decreased almost to 0 in the Fresnel-lens-assisted system as reaction was proceeding to 60 min, while the solar photo-Fenton process without Fresnel lens remained a TU_{50} value of 1.116.

4. Conclusion

With the assistance of Fresnel lens, the efficacy of solar photo-Fenton process enhanced considerably in terms of the COD degradation rate, mineralization rate, and biodegradability of color filter wastewater. In addition, the TU_{50} value of wastewater was almost diminished after a 60 min of treatment, whereas the microtoxicity of treated wastewater



(a)



(b)

FIGURE 5: Effect of Fresnel lens on the microtoxicity of color filter wastewater in solar photo-Fenton process (initial pH: 5.0; $H_2O_2/COD = 1.25$ g/g; $[H_2O_2]_0/[Fe^{2+}]_0 = 15$).

without the assistance of Fresnel lens remained a TU_{50} value of 1.166. This could be mainly due to the concentrated effect of Fresnel lens for solar energy, resulting in an increase of 2~3 times of solar light intensity and a raising heat irradiation in terms of 15~30°C of wastewater temperature. Accordingly, solar energy could be concentrated effectively by using Fresnel lens and showed a significant promoting effect on the performance of solar photo-Fenton process for treating color filter wastewater.

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