Kinetics and Products of Photo-Fenton Degradation of Triazophos

KUNDE LIN, DONGXING YUAN,* MENG CHEN, AND YONGZHI DENG

Key Laboratory of Marine Environmental Science, Ministry of Education,
Environmental Science Research Center, Xiamen University, Xiamen 361005, China

Triazophos is a contaminant of wastewater at manufacturing facilities, and remediative treatment may be needed. While toxicity and persistence limit the effectiveness of biological and physicochemical methods, photo-Fenton processes are promising. UV-Fenton and solar-Fenton processes were applied to degrade triazophos. The optimum parameters were 50 mmol/L H_2O_2, 0.3 mmol/L $FeSO_4$, and pH 3.0. The decomposition of triazophos by a photo-Fenton process followed first-order kinemics. At 30 °C, the half-life of triazophos in a UV-Fenton process ranged from 9.1 min at 2.0×10^5 Lx to 27.3 min at 1.0×10^5 Lx. At 35 °C and with solar irradiation luminance, it ranged within 1.0×10^5 -1.2×10^5 Lx; the half-life of triazophos in the solar-Fenton process was 11.2 min. Five major degradation products, *O,O*-diethyl phosphorothioic acid, monoethyl phosphorothioic acid, phosphorothioic acid, 1-phenyl-3-hydroxy-1,2,4-triazole, and phenylsemicarbazine, were tentatively identified as their corresponding trimethylsilyl derivatives with a gas chromatography−mass spectrometer. The possible degradation pathway of triazophos was proposed. The results indicate the potential use of a solar-Fenton treatment for triazophos-contaminated water.

KEYWORDS: Triazophos; photo-Fenton; photolysis; photocatalysis; photodegradation

INTRODUCTION

Triazophos (CAS Registry 24017-47-8) is the common name for *O,O*-diethyl *O*-1-phenyl-1H-1,2,4-triazol-3-yl phosphorothioate (**Figure 1**). It is a moderately toxic and broad spectrum, nonsystemic organophosphorus pesticide (OP). It has been put into agricultural use since the late 1970s on various crops such as cotton, maize, paddy, and vegetable. In recent years, most high toxic and high residual OPs, for example, methamidophos, parathion, and methyl parathion, were banned from use on crops by the Agriculture Department of China. As a good alternative, less toxic and residual triazophos has more widespread applications.

Wastewater discharged from the manufacture of triazophos contains as high as 10 μg/mL triazophos, which is toxic and refractory to the aquatic environment. Because of its toxicity and persistence, triazophos wastewater is difficult to treat via many biological and physicochemical processes. In recent years, increasing attention has been focused on advanced oxidation processes (AOPs) that provide hydroxyl radicals (•OH) to completely oxidize organic compounds to the harmless products CO_2 and H_2O. Various AOPs, i.e., UV/O_3 (*1*, *2*), UV/H_2O_2 (*3*, *4*), and photo-Fenton (*4*−*9*), have been applied to treat wastewater containing pesticides or other persistent organic compounds. Treatment by UV/O_3 and UV/H_2O_2 requires a large amount of oxidant and UV irradiation to obtain effective photolysis, which makes them high cost. The photo-Fenton

* To whom correspondence should be addressed. Tel: (86)+592 2184820. Fax: (86)+592 2180655. E-mail: yuandx@jingxian.xmu.edu.cn.
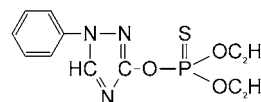
Figure 1. Chemical structure of triazophos.

process, by comparison, is feasible and economical due to its efficient use of longer wavelength irradiation.

In the photo-Fenton reactions, Fe^{2+} ions are oxidized by H_2O_2 and an equivalent amount of $Fe(OH)^{2+}$ and OH• is produced (eq 1). The $Fe(OH)^{2+}$ ion can absorb light at wavelengths up to 410 nm, providing another OH• and Fe^{2+} (eq 2) (*10*). With the catalyst Fe^{2+} ion, the photo-Fenton process can be conducted more efficiently even with longer wavelength light, as compared to the processes of UV/O_3 and UV/H_2O_2 that require light with wavelengths less than 300 nm.

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + OH\bullet \qquad (1)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH\bullet \qquad (2)$$
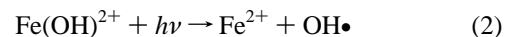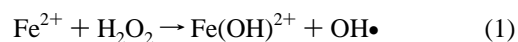
The photo-Fenton process has been adopted to destruct pollutants, such as pesticides (*4*−*9*), phenolic compounds (*11*−*13*), aniline (*14*), nitrotoluene (*15*), explosives (*16*), dyes (*17*), bisphenol A (*18*), and landfill leachates (*19*).

The intent of this study was to explore the application of the photo-Fenton process to degrade triazophos in aqueous media. Therefore, the parameters affecting the degradation of triazophos with the UV-Fenton process such as the amounts of H_2O_2, $FeSO_4$, and pH value were evaluated. The decomposition

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kinetics of triazophos using UV-Fenton and solar-Fenton processes were investigated. The major products formed during the photochemical oxidation of triazophos in UV-Fenton process were identified.

MATERIALS AND METHODS

Instrumentation. The analysis of triazophos residue extracted from the aqueous solutions was performed by gas chromatography (GC) with a flame photometric detector (FPD) operated in the phosphorus mode (Agilent Technologies Inc., Palo Alto, CA) with the following conditions: injection port, 250 °C; splitless injection; 1 μL injection volume; capillary column, SPB1701 (Supelco), 30 m × 0.32 mm i.d. and 0.25 μm film thickness; column temperature program, 160−20 °C/ min −260 °C (6 min); gases and flow rates, carrier gas nitrogen 1.5 mL/min, make up gas nitrogen 25 mL/min, air 100 mL/min, hydrogen 75 mL/min; detector, 250 °C. The retention times of triazophos and triphenyl phosphate were 8.91 and 9.13 min, respectively.

The identification of derivatives of degradation products of triazophos was performed on a Varian 3900 GC directly connected to a Saturn 2000 ion trap mass spectrometer (Varian, Palo Alto, CA). The mass spectrometer operated in the electron impact auto mode with 70 eV of ionization energy was used for full scan in a m/z range from 60 to 500 Da. Other parameters were as follows: standard injection port, 250 °C; splitless injection; 1 μL injection volume; capillary column, VF-5 MS (Varian), 30 m × 0.25 mm i.d. and 0.25 μm film thickness; column temperature program, 80 (3 min)−10 °C/min −280 °C (7 min); carrier gas flow rate, helium 1.0 mL/min; manifold, trap, and transfer line temperatures were set at 40, 180, and 280 °C, respectively.

Chemicals and Reagents. Triazophos with a purity higher than 97.5% was purchased from Kefa New Technology Development Ltd. Co. (Shenyang, China). High-performance liquid chromatography grade ethyl acetate, methanol, and dichloromethane were purchased from Tedia Company (Fairfield, OH). Triphenyl phosphate with a purity higher than 99% was purchased from Acros Organics (Geel, Belgium). The derivatization reagent *N,O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) containing 1 vol % by volume trimethylchlorosilane (TMCS) was purchased from Supelco Inc. (Bellefonte, PA). The hydrogen peroxide solution (30%, v/v) was purchased from Shanghai Yuanda Peroxide Co., Ltd. (Shanghai, China). Analytical reagents, ferrous sulfate (FeSO$_4$·7H$_2$O), anhydrous sodium sulfate, hydrochloric acid, sodium hydroxide, and sulfuric acid were purchased from Shanghai Chemical Reagents Co. (Shanghai, China).

Preparation of Solutions. A triazophos stock solution of 2 mg/mL and a triphenyl phosphate solution of 10 μg/mL were prepared by dissolving the analytes in methanol, respectively. Standard solutions were prepared by diluting the stock solution with methanol. All of the above solutions were stored in a freezer at −4 °C while not in use. A 0.1 mol/L FeSO$_4$ solution was prepared from a given amount of FeSO$_4$· 7H$_2$O with deionized water. All reaction solutions were prepared by diluting stock solutions into 100 mL of deionized water. Before it was diluted, the methanol was evaporated with gentle nitrogen gas.

Experimental Setup. Experiments utilizing the UV-Fenton process were performed in a batch reactor. The high-pressure mercury lamp (Philips HPR 125 W, Belgium) hanging above the glass vessel (Φ 12 cm × 15 cm) and emitting the light in the wavelength range of 300− 600 nm was used to simulate the solar irradiation. The irradiation flux of the lamp could be controlled by adjusting the height of the lamp. In this study, the irradiation luminance was changed from 1.0 × 10^5 to 2.0 × 10^5 Lx. The emission spectrum of the lamp is presented in **Figure 2**. A circulating water jacket system was positioned outside the reaction vessel to maintain the designed temperature. Constant agitation of the reaction solution was ensured by a magnetic stirrer. The reactor remained open to the atmosphere, allowing the contact of water and air.

Solar-Fenton experiments were carried out on the top of a building on the Xiamen University campus, using 15 mL quartz tubes. The emission spectrum of solar irradiation is shown in **Figure 2**.

Direct Photolysis without Additives. The reaction solutions each containing 10.0 μg/mL of triazophos were taken for photolyses. Neither FeSO$_4$ nor H$_2$O$_2$ was added. With the lamp irradiation luminance of 2.0 × 10^5 Lx and the temperature at 30 °C, the reaction was carried
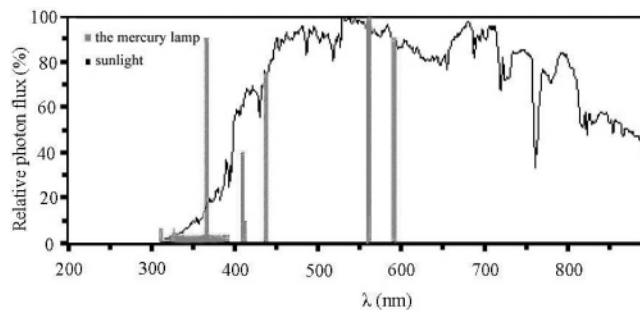

Figure 2. Emission spectra of sunlight and the mercury lamp.

out for 24 h. Under the solar luminance between 4.3 × 10^4 and 1.2 × 10^5 Lx and the temperature between 27.5 and 33 °C, the reaction was continued for 8 h (8:30 AM to 16:30 PM).

Photo-Fenton Degradation Procedure. The lamp was warmed for 5 min before the UV-Fenton reaction. The reaction solution (100 mL) containing 10 μg/mL triazophos was introduced into the reactor. The solution pH was adjusted to the designated value with 10% (v/v) H$_2$-SO$_4$ solution. A given amount of FeSO$_4$ solution was added and well mixed with the reaction solution before the H$_2$O$_2$ solution was added. The time upon the H$_2$O$_2$ added was set as the reaction start time.

For the solar-Fenton treatment, 10 mL of solution containing 10 μg/ mL triazophos was placed in quartz tubes. The time at which the H$_2$O$_2$ solution was added was recorded as the reaction start time. After a certain time, 0.4 mL sample was taken from the reaction solution and the triazophos residues in the sample were immediately extracted with dichloromethane.

Determination of Triazophos Residue in Sample Solutions. The determination of triazophos residue in solutions was carried out on the basis of the EPA method 1657 (*20*). The collected sample was transferred into a 250 mL separatory funnel and diluted with 50 mL of deionized water. One hundred microliters of triphenyl phosphate of 10 μg/mL was added as a surrogate for data quality control. The sample was then extracted three times, each with 10 mL of dichloromethane and vigorous shaking for 2 min. The duration of exaction was about 15 min. The organic phases were collected and combined together. The extract was filtered with a glass funnel filled with anhydrous sodium sulfate and then evaporated to nearly dryness with a gentle nitrogen stream in a 40 °C water bath. The final volume of 1.0 mL was made with ethyl acetate, and the extract sample was ready for GC analysis.

The recoveries of triazophos with the concentration of 1.0 μg/mL were 86.6−96.2%, and the relative standard deviation (RSD) was 5.3% ($n = 3$). Linearity was observed between 0.2 and 20.0 μg/mL with the correlation coefficient of 0.9996 ($n = 6$). The method detection limit of triazophos was 0.05 μg/mL. Recoveries of triphenyl phosphate was 92.1−95.6% with an RSD of 2.3% ($n = 3$).

Identification of Photodegradation Products. UV-Fenton degradation of triazophos was carried out at 30 °C, 2.0 × 10^5 Lx with other parameters kept optimized. The sample for photodegradation product identification was collected at the end of one half-life (9.1 min). One hundred milliliters of sample was acidified to pH 2 with 10% (v/v) H$_2$SO$_4$ and freeze-dried to dryness, and the residue was dissolved with 50 mL of ethyl acetate. The moisture in the extract was removed with anhydrous sodium sulfate, and then, the extract was concentrated to 0.5 mL with a gentle nitrogen stream and in a 40 °C water bath. To silylate the extracted compounds, the extract and silylating reagent BSTFA−1%TMCS, 100 μL each, were well mixed in a septum-capped glass vial and allowed to react for 2 h in a 60 °C water bath. The large amount of excess BSTFA−1%TMCS ensured complete derivatization. An aliquot of 1 μL of silylated extract sample was taken for GC-MS analysis.

RESULTS AND DISCUSSION

Direct Photolysis without Additives. No triazophos degradation in either solution was observed. From the absorption spectrum of triazophos, it had been found that the absorption range was between 200 and 280 nm. However, as shown in
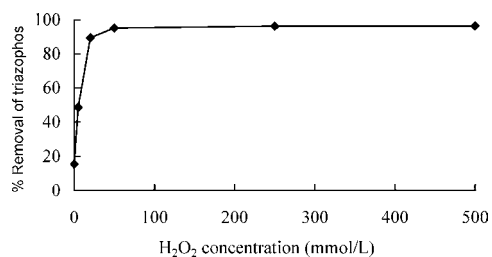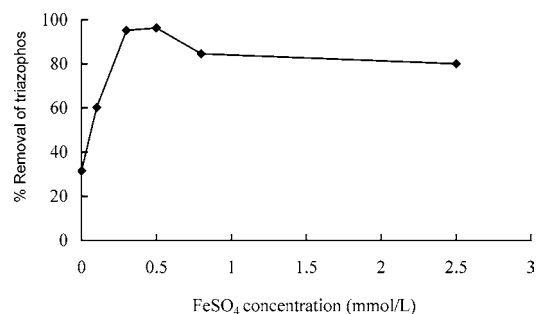
Figure 3. Effect of H_2O_2 concentration on the percent removal of triazophos with the UV-Fenton process. Conditions: triazophos, 10.0 μg/mL; FeSO$_4$, 0.3 mmol/L; pH 3.0; temperature, 30 °C; irradiation flux, 2.0 × 10^5 Lx; and reaction for 1 h.

Figure 4. Effect of FeSO$_4$ concentration on the percent removal of triazophos with the UV-Fenton process. Conditions: triazophos, 10.0 μg/mL; H$_2$O$_2$, 50 mmol/L; pH 3.0; temperature, 30 °C; irradiation flux, 2.0 × 10^5 Lx; and reaction for 1 h.

Figure 2, the emission of the mercury lamp and the sun in that range is extremely weak. This indicated that the triazophos could hardly utilize the irradiation from the mercury lamp and the sun for photodegradation.

Effect of Concentration of H$_2$O$_2$, FeSO$_4$, and pH. The diagram of percent removal of triazophos vs H$_2$O$_2$ concentration is plotted in **Figure 3**. In the absence of H$_2$O$_2$, the percent removal of triazophos was only 15.5%. Removal increased sharply with the addition of H$_2$O$_2$ and reached 95.2% when H$_2$O$_2$ concentration was increased to 50 mmol/L. More H$_2$O$_2$ solution resulted in more OH• radicals and provided greater triazophos oxidation. Removal was not increased further when H$_2$O$_2$ concentration was above 50 mmol/L. This may be due to H$_2$O$_2$ decomposition and recombination of OH• radicals at the high concentration. Furthermore, H$_2$O$_2$ can react with OH• radicals as a scavenger (*21*). The optimal concentration of H$_2$O$_2$ for the best removal of triazophos in the photo-Fenton process was thus considered as 50 mmol/L.

Ferrous in the photo-Fenton process acts as a photocatalyst. To choose the optimal amount of FeSO$_4$ added in the reaction solution, a set of tests was performed. **Figure 4** illustrates the percent removal of triazophos as a function of FeSO$_4$ concentration. Triazophos removal was only 31.6% in the absence of FeSO$_4$ but increased to 95.2% when 0.3 mmol/L FeSO$_4$ was added. Increasing the FeSO$_4$ concentration to 0.5 mmol/L had little effect on the degradation rate. When the FeSO$_4$ concentration was greater than 0.8 mmol/L, brown turbidity formed in the reaction solution and hindered the irradiation absorption necessary for the photolysis, resulting in a decrease of the removal of triazophos. It was considered that the concentration of FeSO$_4$ should be as low as possible to avoid the brown turbidity. The desirable FeSO$_4$ concentration in this study was chosen as 0.3 mmol/L.

Even though the photo-Fenton reaction can be maintained at a neutral pH range, the pH value for triazophos degradation
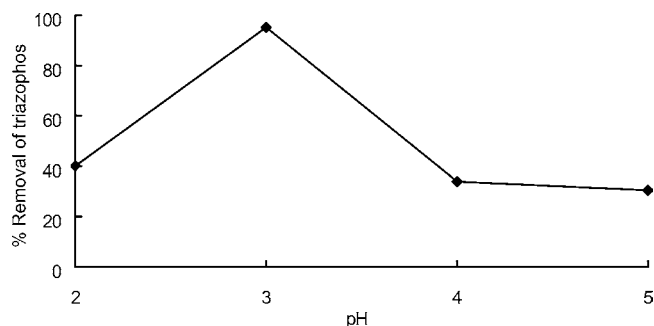

Figure 5. Effect of pH on the percent removal of triazophos with the UV–Fenton process. Conditions: triazophos, 10.0 μg/mL; H$_2$O$_2$, 50 mmol/L; FeSO$_4$, 0.3 mmol/L; temperature, 30 °C; irradiation flux, 2.0 × 10^5 Lx; and reaction for 1 h.

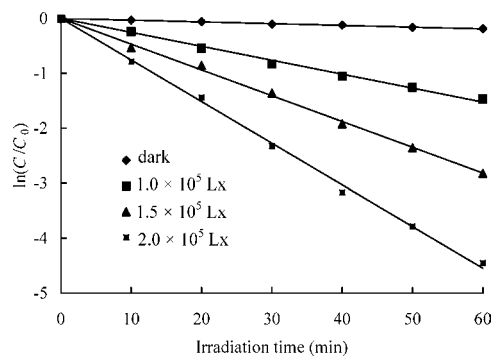**Figure 6.** Relationship of ln(C/C_0) and irradiation time for triazophos degradation with the dark-Fenton and UV-Fenton process at 30 °C.

had been optimized. The maximum triazophos removal was obtained at pH 3.0 (**Figure 5**). At pH 3.0, an about equal amount of Fe^{3+} ion and Fe(OH)$^{2+}$ ions was presented in the reaction solution as Fe(III) oxidized from Fe(II) (*22*). Below pH 3.0, the concentration of the photoactive species Fe(OH)$^{2+}$ declined, resulting in a lower removal rate. According to the pE−pH diagram of iron species (*23*), at a pH higher than 3.0, the Fe(III) precipitated as oxyhydroxides and reduced the photodegradation activity. The optimal pH value of the reaction solution was set at 3.0 at which a large amount of Fe(OH)$^{2+}$ was formed.

Effect of Irradiation Flux. The optimal parameters from the above experiments were selected for the reaction at 30 °C in dark and with UV irradiation luminance to investigate the influence of irradiation flux on the degradation of triazophos with the UV-Fenton process. It was found that the degradation of triazophos with the UV-Fenton process could be treated as a first-order reaction. Thus, the following equation might be applied

$$dC/dt = -k_{obsd}C \qquad (3)$$

or

$$\ln(C/C_0) = -k_{obsd}t \qquad (4)$$

where C_0 and C are the triazophos concentrations in the initial solutions and the samples collected at a designed reaction time, respectively, and k_{obsd} is the observed rate constant for the photodegradation reaction. When the plot of ln(C/C_0) vs reaction time is derived, k_{obsd} is equal to the slope. **Figure 6** shows such plots for triazophos photodegradation using dark-Fenton and UV-Fenton with various irradiation fluxes. The corresponding kinetic data are listed in **Table 1**.

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Table 1. Kinetic Data of Triazophos Photodegradation with Dark and UV-Fenton Processes at 30 °C

| irradiation flux ($\times 10^5$ Lx)	k_{obsd} (min^{-1})	$t_{1/2}{}^a$ (min)	r ($n = 7$)
dark	0.00320	217	0.9971
1.0	0.0254	27.3	0.9968
1.5	0.0470	14.7	0.9987
2.0	0.0758	9.1	0.9988

^{a} Half-life was calculated as $t_{1/2} = (\ln 2)/k_{obsd}$.
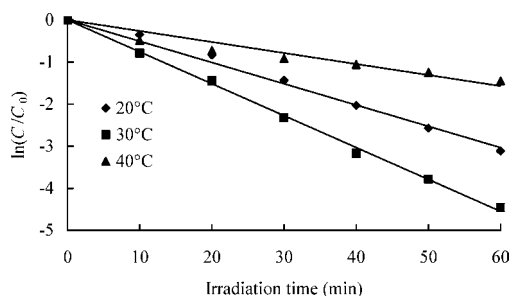
Figure 7. Relationship of $\ln(C/C_0)$ and irradiation time for triazophos degradation with the UV-Fenton process at different temperatures.

Table 2. Kinetic Data of Triazophos Photodegradation with UV-Fenton Processes at Different Temperatures

| T (°C)	k_{obsd} (min^{-1})	$t_{1/2}{}^a$ (min)	r ($n = 7$)
20	0.0505	13.7	0.9955
30	0.0758	9.1	0.9985
40	0.0262	26.5	0.9552

^{a} Half-life was calculated as $t_{1/2} = (\ln 2)/k_{obsd}$.
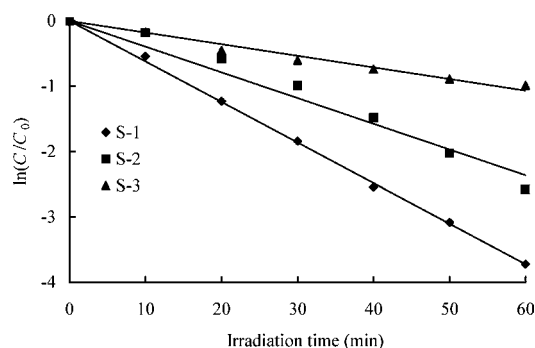
Figure 8. Relationship of $\ln(C/C_0)$ and irradiation time for triazophos degradation with the solar-Fenton process. S-1: Time during 12:00–13:00, $T = 35$ °C, irradiation luminance $= 1.0$–1.2×10^5 Lx. S-2: Time during 9:00–10:00, $T = 30$ °C, irradiation luminance $= 7.1$–8.6×10^4 Lx. S-3: Time during 16:00–17:00, $T = 31.5$ °C, irradiation luminance $= 3.4$–7.2×10^4 Lx.

Table 3. Kinetic Data of Triazophos Photodegradation with the Solar-Fenton Process

irradiation luminance ($\times 10^5$ Lx)	T (°C)	k_{obsd} (min^{-1})	$t_{1/2}{}^a$ (min)	r ($n = 7$)
1.0–1.2	35	0.0620	11.2	0.9990
0.71–0.86	30	0.0394	17.6	0.9666
0.34–0.72	31.5	0.0178	38.9	0.9742

^{a} Half-life was calculated as $t_{1/2} = (\ln 2)/k_{obsd}$.

The results indicated that the photodegradation of triazophos by dark Fenton and UV-Fenton processes was well-described by a first-order reaction model. From the photodegradation half-lives of triazophos in the dark-Fenton and UV-Fenton processes
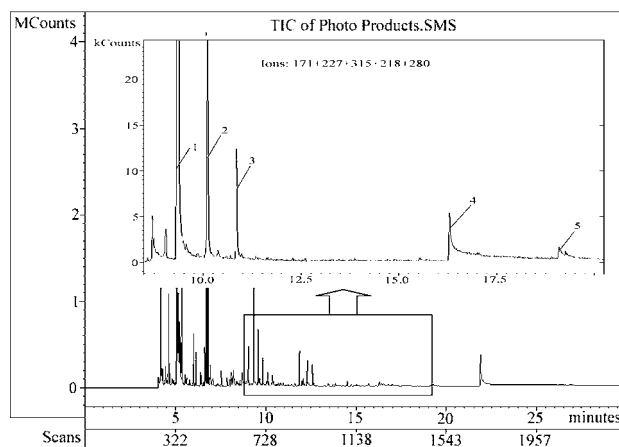
Figure 9. TIC chromatogram in the full-scan mode for trimethylsilyl derivatives of triazophos degradation products in the UV-Fenton process.
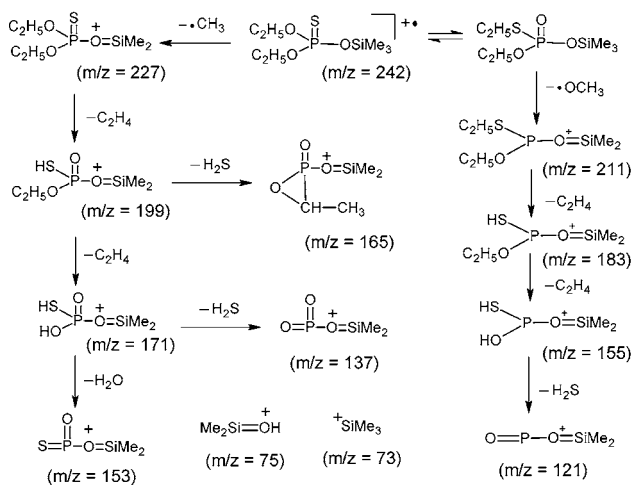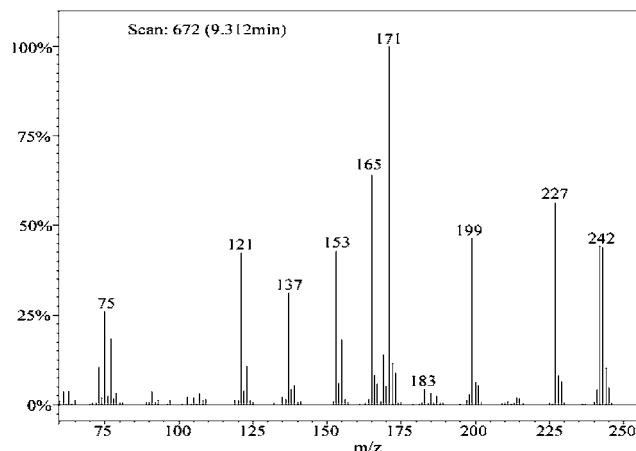
Figure 10. Mass spectrum of peak 1 and its interpretation.

with different irradiation fluxes, it could be concluded that the degradation was accelerated by the UV light. The relationship of k_{obsd} vs irradiation flux indicated that the k_{obsd} was proportional to the irradiation luminance. A linear equation was derived as $k_{obsd} = 0.0504 \, I - 0.0262$, where I was the irradiation luminance, $n = 3$, and $r = 0.9966$.

Effect of Temperature. To study the influence of temperature on the photodegradation rate, k_{obsd} values at 20, 30, and 40 °C were determined with other parameters kept optimized. The results are illustrated in **Figure 7**, and the corresponding kinetic data are listed in **Table 2**. It had been shown that triazophos degradation using the UV-Fenton process at 20 and
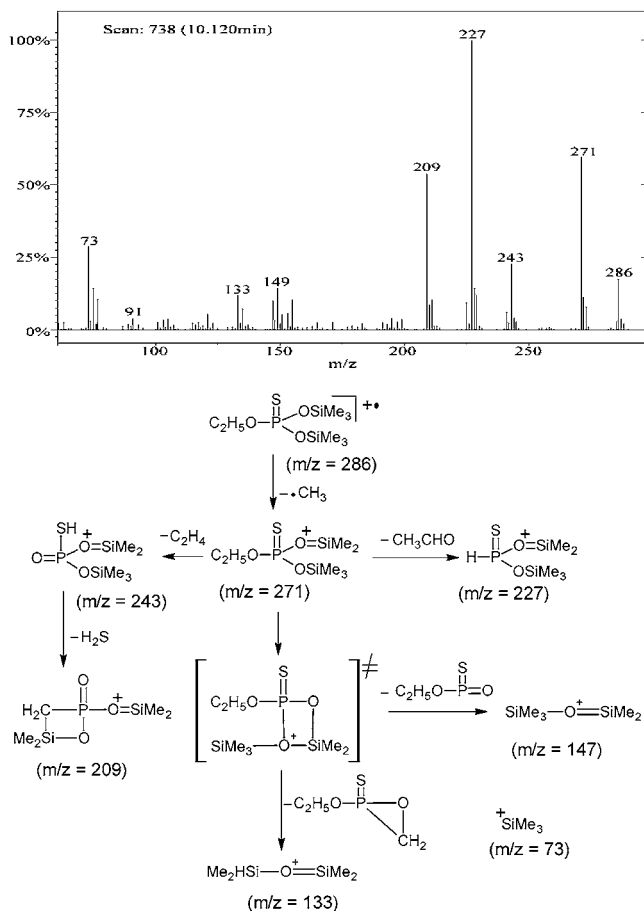
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Figure 11. Mass spectrum of peak 2 and its interpretation.

Figure 12. Mass spectrum of peak 3 and its interpretation.

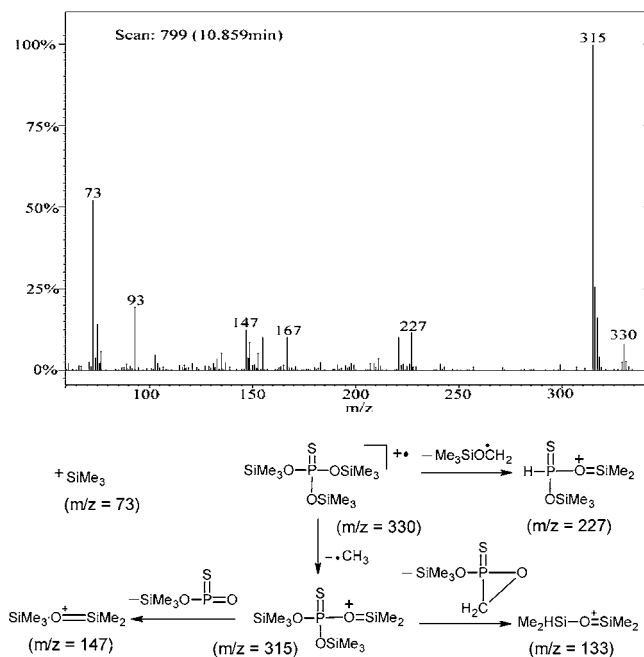**Figure 13.** Mass spectrum of peak 4 and its interpretation.
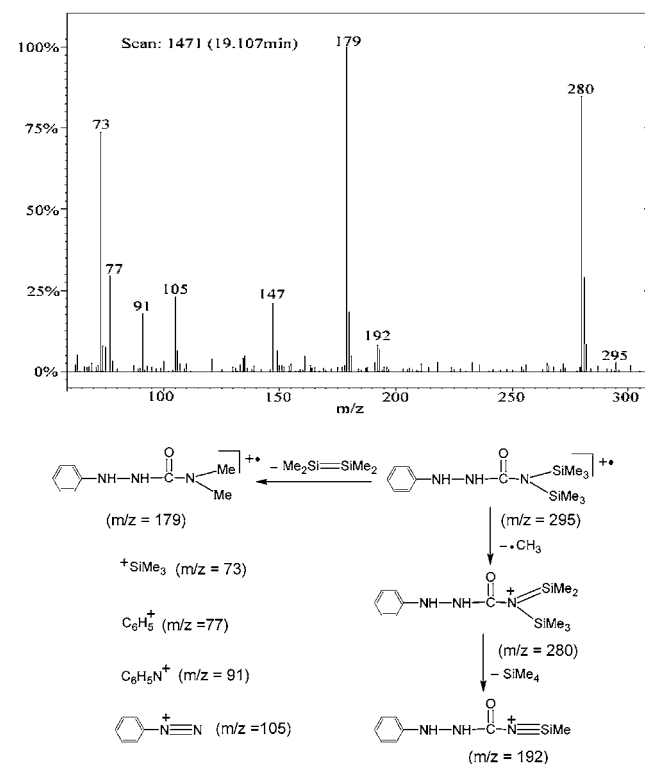
Figure 14. Mass spectrum and interpretation of peak 5.

30 °C fit very well with the first-order reaction ($r > 0.99$), while a somewhat poorer fit at 40 °C ($r = 0.9552$) was observed. The result also showed that the k_{obsd} increased when the reaction temperature increased from 20 to 30 °C; however, it decreased when the reaction temperature increased to 40 °C. The decrease of the linearity and k_{obsd} may be due to the decomposition of H_2O_2 and the formation of brown precipitation. Brown precipi-
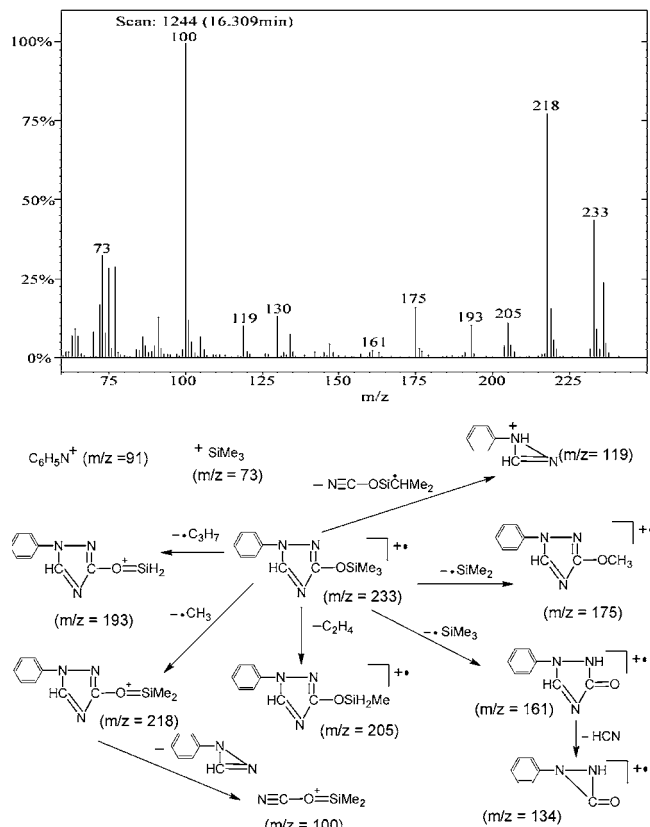
tation did not occur at 20 and 30 °C and began to appear when the temperature was increased to 40 °C.

Degradation with Solar-Fenton Process. Photodegradation of triazophos with the solar-Fenton process was conducted to investigate the feasibility of utilizing sunlight as an irradiation source. Using the optimal parameters, the degradations were
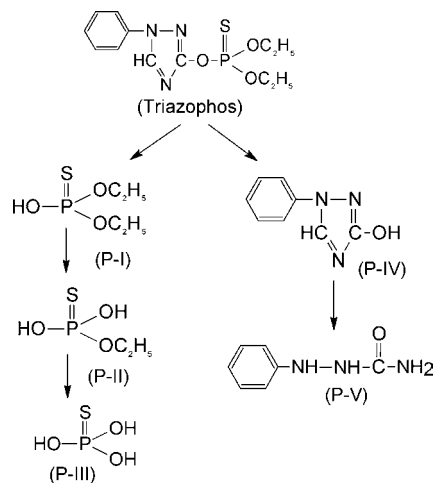
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Figure 15. Proposed degradation pathway of triazophos with the UV-Fenton process.

carried out during three different time intervals in one day. **Figure 8** shows the results, and **Table 3** lists the corresponding kinetic data. From **Figure 8** and **Table 3**, it can be concluded that the photolysis of triazophos with the solar-Fenton process was also described by a first-order equation, although the correlation coefficients (r) of S-2 and S-3 were not very close to the value of 1, because of the fluctuation of the solar irradiation flux. The half-life of triazophos by solar-Fenton photodegradation was only 11.2 min at $1.0-2 \times 10^5$ Lx and a temperature of 35 °C. The half-life for UV-Fenton degradation of triazophos at 30 °C and 1.0×10^5 Lx was 27.3 min (**Table 1**), while it was 17.6 min for solar-Fenton degradation at 30 °C and $0.71-0.86 \times 10^5$ Lx (**Table 3**). Thus, it can be inferred that the solar-Fenton process is more effective than the UV-Fenton process when operated under the same conditions. The reason may be that some wavelengths present in sunlight but absent in the lamp light (**Figure 2**) are more effective for photo-Fenton reaction. This indicated that solar irradiation is a desirable light source for photo-Fenton degradation of triazophos, which shows a good potential for treating wastewater containing triazophos.

Degradation Products and Proposed Pathway. Because the operation parameters in the solar-Fenton process were difficult to control due to the fluctuation of irradiation and temperature, the photochemical oxidation products of triazophos were examined using the UV-Fenton process, and the total ion current (TIC) chromatogram of GC-MS is presented in **Figure 9**. The mass spectra of peaks 1−5 in **Figure 9** and their corresponding interpretations are shown in **Figures 10−14**, respectively. Peaks 1−5 in **Figure 9** could be tentatively identified as the corresponding trimethylsilyl derivatives of *O,O*-diethyl phosphorothioic acid (P-I), monoethyl phosphorothioic acid (P-II), phosphorothioic acid (P-III), 1-phenyl-3-hydroxy-1,2,4-triazole (P-IV), and phenylsemicarbazine (P-V), respectively. All of the compounds except P-V were also found to be the hydrolytic products in our previous study (*24*). On the basis of products detected, a possible degradation pathway of triazophos with the UV-Fenton process is proposed in **Figure 15**.

In conclusion, the investigation results showed that triazophos in aqueous solution was relative stable to irradiation from the sun and the mercury lamp. However, the photo-Fenton process can degrade triazophos effectively. Optimal parameters for UV-Fenton degradation of triazophos were 50 mmol/L H_2O_2, 0.3 mmol/L $FeSO_4$, and pH 3.0. With the optimized parameters, the degradation of triazophos using UV-Fenton and solar-Fenton

processes followed the first-order reaction model. The solar-Fenton process offers a promising method to remove triazophos in water.

LITERATURE CITED

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