

Photodegradation of Scopoletin in Organic Solvents and Aqueous Solutions: Kinetics and Degradation Pathways

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Abstract Scopoletin (hereafter SCO), an excellent candidate of acaricides, was discovered and developed in China. Photolysis kinetics of SCO in organic solvents and different aqueous media were investigated under 500W Xe lamp. Effects of five surfactants, nitrate (NO_3^-), nitrite (NO_2^-), and H_2O_2 on SCO photolysis and photodegradation pathways of SCO in aqueous were also studied. The results indicated that photolysis rate of SCO in organic solvents was in the sequence of acetone > ethyl acetate > methanol, and the corresponding half-lives were 9.63, 36.47, and 49.50 h, respectively. Photolysis rate of SCO in different aqueous media was in the sequence of pure water > river water > natural seawater, and the half-lives were 5.68, 6.66, and 7.79 h, respectively. The five kinds of surfactants, NO_3^- , and NO_2^- had significant photoquenching effects on photolysis of SCO, and H_2O_2 had photosensitization effects on photolysis of SCO. By separation and identification of photoproducts using LC/ESI-MS, it could be concluded that SCO was photolyzed through photorearrangement, photohydrolysis, and photo-oxidation of the molecule itself.

Keywords Scopoletin · Photolysis kinetics · Photodegradation pathway · HPLC/ESI-MS

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1 Introduction

Scopoletin (SCO) (6-methoxy-7-hydroxycoumarin) is a phenolic coumarin and has been isolated from several plant species, such as *Erycibe obtusifolia* Benth (Pan et al. 2011), *Aster tataricus* (Ng et al. 2003), *Foeniculum vulgare* (Kwon et al. 2002), *Artemisia annua* L. (Tzeng et al. 2007), *Sinomonium acutum* (Shaw et al. 2003), and *Melia azedarach* L. fruits (Carpinella et al. 2005). Studies have shown that SCO has a wide spectrum of biological activities, such as pronounced acaricidal (Liang et al. 2011), insecticidal (Tripathi et al. 2011), antifungal (Prats et al. 2006), allelopathic (Pérez and Ormeño-Nuñez 1991), antitumoral (Cassady et al. 1979), antioxidative (Shaw et al. 2003), hepatoprotective (Kang et al. 1998), and anti-inflammatory (Ding et al. 2008). Our research group has long been studying the acaricidal activity of SCO against mites in the lab and field (Qin et al. 2012; Yang et al. 2012; Yang et al. 2013; Zhang et al. 2016), including sublethal effects of SCO on the experimental population of the carmine spider mite, *T. cinnabarinus* (Biosduvals) (Acari: Tetranychidae) (Yong et al. 2011), the resistance evaluation of *T. cinnabarinus* against SCO (Zhang et al. 2011a), acaricidal action mechanism of SCO against *T. cinnabarinus* (Biosduvals) (Yong et al. 2012, Hou et al. 2017), preparation of suspension concentrate of SCO (Yang 2013), and the extracted technique of SCO from *A. annua* L. residues (Ding et al. 2013). These results have been submitted to National Standardization Technical Committee and the approved pesticide name of SCO has been authorized in 2012. However, to obtain a SCO

registration certificate, investigations need to be done, including the environmental fate of SCO.

One of the major agricultural challenges is increasing food production to meet the worldwide demand, while simultaneously decreasing the environmental impact associated with pesticide crop treatments (Trivella et al. 2015). Recently, plant-derived biopesticides have been developed and become attractive alternative pest management tools because most are environmentally friendly (Wu and Gao 2004). To prevent the underestimation of the consequences of pesticide use, each pesticide should be investigated for its environmental fate through intensive simulated environmental conditions in laboratories before field application (Lu et al. 2010; Trivella et al. 2015). Once applied in the field, these compounds are subjected to transferable and degradative processes that can lead to their complete mineralization into inorganic end products, such as CO_2 , H_2O , NH_4^+ , and NO_3^- (Sevilla-Morán et al. 2014). Phototransformation is among potential degradation pathways for pesticides that absorb solar radiations, particularly its ultraviolet component (Trivella et al. 2015; Chianese et al. 2017). Simulated photolysis of pesticides on plant surfaces or in natural waters have been widely investigated (Yang et al. 1999; Chen et al. 2010; Shen et al. 2013; Abramovic et al. 2010; Chelme-Ayala et al. 2010; Baranda et al. 2012; Souza et al. 2013). To systematically study the photochemical reactivity of pesticides on plant surfaces, methanol, ethyl acetate, acetone, and other organic solvents have been used as simulation substances for the plant cuticle constituents (Nag and Dureja 1997; Ou et al. 2005; Lu et al. 2010). Pesticides may enter natural bodies of water during production or after field application through a variety of ways (Silva et al. 2014). To investigate pesticide photolysis in water environment, natural waters were directly collected (Yang et al. 2005; Wu et al. 2006). Different intermediate photoproducts could be formed during photolysis. In many cases, these compounds possess unknown physico-chemical properties, bioactivities, toxicities, and environmental behaviors that differ significantly from their parent compounds (Hildebrandt et al. 2008; Hladik et al. 2008; Kruawal et al. 2005; Marín et al. 2006; Osano et al. 2002). Therefore, it is also important to identify and investigate some stable intermediate photoproducts of pesticides.

To the best of our knowledge, except for few previous study, such as the photostability and fluorescence of SCO in aprotic solvents (Smith et al. 2010), photoproducts of

SCO in aqueous solution under near-UV irradiation (Smith et al. 2012), and photolytic characteristics of SCO in aquatic solutions (Tang et al. 2014), there have been no other study concerning the kinetics of SCO in organic solvents such as methanol, ethyl acetate and acetone, and different aqueous media, as well as the photoproducts and degradation pathway for the photodegradation of SCO in aqueous media under simulated sunlight irradiation. The main purposes of this study are (1) to study the photodegradation of SCO in various solvents, including methanol, ethyl acetate, and acetone; (2) to study the photochemical degradation of SCO in different aqueous media, including pure water, river water, and natural seawater; (3) to study the effects of substances dissolved in water, including surfactants, NO_3^- , NO_2^- , and H_2O_2 , on photolysis of SCO; and (4) to identify the main intermediates of photoproducts and propose the possible photodegradation pathways of SCO in aqueous solutions.

2 Experimental

2.1 Chemicals and Materials

SCO was purchased from Shanghai Yuanye Bio-Technology Co., Ltd. (99% purity, China), and its stock solution (1000 mg/L) was prepared in HPLC grade methanol and stored in the dark at 4 °C. Methanol, ethyl acetate, acetone, sodium dodecyl sulfate (SDS), calcium dodecyl benzenesulfonate (agricultural emulsifier no. 500, No.500), hexadecyl trimethyl ammonium bromide (CTAB), Tween-80, styrylphenol polyoxyethylene ether (agricultural emulsifier no. 600, No.600), sodium nitrate, sodium nitrite, and H_2O_2 (30%, w/w) were analytical grade and provided by ChengDu Kelong Chemical Co., Ltd. (China). HPLC grade methanol and phosphoric acid were supplied by Thermo Fisher Scientific (China) Co., Ltd. and Tianjin Kemiou Chemical Reagent Co. Ltd., respectively. All chemical materials were used without further purification. Reverse osmosis-purified water (RO, with electrical conductivity $20.04 \mu\text{s cm}^{-1}$, 25 °C) and ultra-pure water (with the resistivity $18.25 \text{ M}\Omega \text{ cm}$, 25 °C) were obtained from an ATSmole 1820AC water purification system and used after sterilization. Natural seawater was taken in the western part of the Qingdao Bay, the Yellow Sea. River water was collected in the Jialing river, Beibei, Chongqing, China. Natural seawater and river water were

filtered through a 0.22- μm microporous filter membrane and sterilized before the experiment.

2.2 Methods

2.2.1 Photolysis Experiments

All photolysis experiments were carried out in a BL-GHX-V photochemical reactor (Shanghai Bilon Instruments Co., Ltd., China) equipped with a 500W Xe lamp. In each experiment, an amount 40 mL of reaction solution was taken in a quartz tube with a magnetic stirrer for constant stirring. A DC-0506 chiller was used to maintain a mean internal temperature of 25 ± 1 °C.

Ten milligrams per liter organic solution of SCO was prepared in methanol, ethyl acetate, and acetone. Ten milligrams per liter aqueous solutions of SCO was prepared by adding the corresponding amounts of stock solution in pure water, river water, and natural seawater. For the effect of five surfactants, NO_3^- , NO_2^- , and H_2O_2 on the photodegradation of SCO studies, different amounts of five surfactants, sodium nitrate, sodium nitrite, and H_2O_2 were added into pure water solution of SCO (10 mg/L) to reach 0, 10, and 50 mg/L (five surfactants); 0, 5, and 50 mg/L (sodium nitrate, sodium nitrite); and 0, 20, 50 mg/L (H_2O_2), respectively, before the irradiation. Aliquots of samples (2 mL) were withdrawn after irradiation for 0, 1, 3, 5, 7, 9, 11, and 14 h, and substrate decay was measured by HPLC.

A higher concentration of pure water solution of SCO (80 mg/L) was prepared by adding the corresponding amounts of stock solution in pure water, and an aliquot was removed for HPLC/ESI-MS analysis to identify photoproducts after irradiation for 10 days.

Dark controls were conducted under the same conditions without irradiation. All the photolysis experiments were performed in triplicate.

2.2.2 Analytical Methods

Quantification of SCO in solutions was determined using an Agilent 1260 HPLC (Agilent Technologies, USA) with a variable wavelength detector set at 345 nm and an Agela-Venusil XBP C_{18} column (4.6×250 mm, $5 \mu\text{m}$). The mobile phase used was methanol/0.05% phosphoric acid (40:60, V/V) at a flow rate of 1 mL/min, with a column temperature of 30 °C and injection volume of 10 μL . Under these conditions, the retention time for SCO was about 8.37 min.

A Shimadzu LCMS-8030 system was used to identify the photoproducts of SCO. The column was an Agilent-ZORBAX SB-Aq (4.6×250 mm, $5 \mu\text{m}$). A linear elution gradient program was performed from 30% methanol in ultra-pure water with 0.01% formate, to 38% in 10 min, and then retained for 20 min at a flow rate of 1 mL/min. The analyses were done in positive ion mode under the following conditions: drying gas temperature of 350 °C, capillary voltage of 4.5 kV, nebulizer gas (N_2) flow of 3.00 L min^{-1} , and drying gas (N_2) flow of 15.00 L min^{-1} . Full-scan spectra were recorded from 100 to 220 m/z at a scan time of 1875 u/s.

Photodegradation kinetics equation of scopoletin was fitted by Marquardt method and its half-life was calculated using the following equations (General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China 2014):

$$C_t = C_0 \cdot e^{-kt} \quad (1)$$

$$t_{1/2} = \ln 2/k = 0.693/k \quad (2)$$

where C_t and C_0 are the concentrations of SCO at t and time zero, respectively, and k (h^{-1}) is the photodegradation rate constant. $t_{1/2}$ (h) is the photolysis half-life.

Data were statistically analyzed using Excel 2003 and SPSS 17.0 for Windows (SPSS Inc., Chicago, Illinois).

Effects of surfactant, sodium nitrate, sodium nitrite, and H_2O_2 on photodegradation of SCO were calculated using the following equations:

$$\begin{aligned} &\text{Promotion(inhibition)ratio}(\%) \\ &= (ki - k_0)/k_0 \times 100 \end{aligned} \quad (3)$$

Where k_0 is the photolysis rate constant of SCO in pure water, ki is the photolysis rate constant of the mixture of scopoletin with surfactants, NO_3^- , NO_2^- , and H_2O_2 , respectively. The additive could accelerate SCO photodegradation when the value of promotion (inhibition) ratio (%) was positive; on the contrary, when it was negative, the additive could inhibit photodegradation of SCO.

3 Results and Discussion

3.1 Photolysis Kinetics of SCO in Organic Solvents

The time-concentration profiles of SCO in different organic solvents during the irradiation are shown in Fig. 1. It can be seen that SCO degradation in acetone

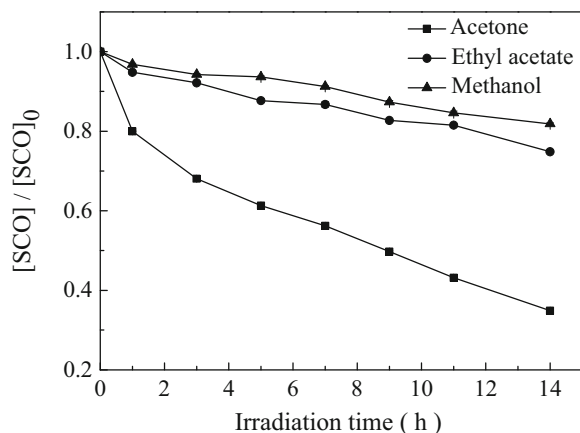


Fig. 1 Photolysis of SCO in organic solvents under 500W xenon lamp (25 °C)

was rapid, while it was slow in ethyl acetate and methanol; the SCO removal was 65.12, 25.15, and 18.15%, respectively, after irradiation for 14 h.

Table 1 shows the photolysis kinetic parameters of SCO in different organic solvents. Their photolysis rates showed the following sequence: acetone > ethyl acetate > methanol, and the corresponding half-lives were 9.63, 36.47, and 49.50 h, respectively.

Wavelength and energy distribution of xenon lamp are similar to those of sunlight; therefore, xenon lamps could simulate sunlight irradiation and is widely used in investigating the photolysis dynamics of organic molecules (Periša et al. 2013; Zhang et al. 2009; Pu et al. 2002). It is a common research method to use organic solvents with selected functionalities as substitutes for components of plant tissues for photodegradation of pesticides (Jia et al. 2011; Ou et al. 2005). Normally, organic solvents, such as hexane, methanol, and acetone, are used as representative model substances for plant cuticle constituents (Yang et al. 2005; Nag and Dureja 1997). In the present paper, the photodegradation of SCO in hexane was not investigated because very

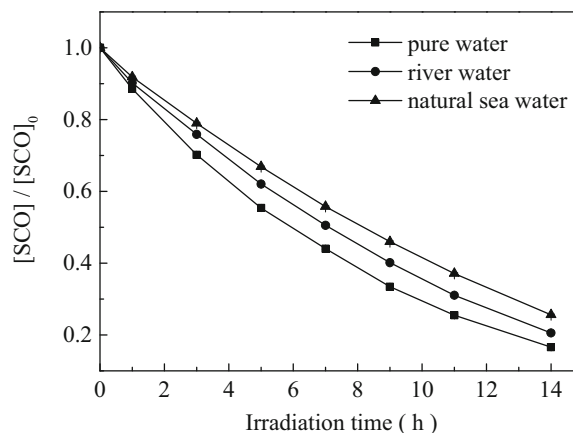


Fig. 2 Photolysis of SCO in different aqueous media under 500W xenon lamp (25 °C)

little SCO was dissolved in hexane. The correlation between photodegradation efficiency of SCO in three solvents and corresponding solvent polarities could not be observed, which concurred with the previous study result (Zhao et al. 2012; Jia et al. 2011; Ou et al. 2005). Effects of acetone on the photolysis of different pesticides are diverse, and acetone, in some photoreaction systems, exhibited marked photosensitive effects that promote photolysis, in some other photoreaction systems, showed marked photoquenching effects that retard photolysis (Cao et al. 2011; Chen et al. 2010). In our study, acetone acted as a triple sensitizer and promoted SCO photolysis by energy-transfer mechanism, which was consistent with the effect of acetone on the photolysis of herbicide ZJ0273 and avermectin (Shen et al. 2013; Wu et al. 2006). There are differences among the SCO photolysis rates in ethyl acetate and methanol and their reaction rates were slower, which might be attributed to the properties of ethyl acetate and methanol and molecular interaction of ethyl acetate and methanol with

Table 1 Photolysis kinetic parameters of SCO in different organic solvents under the 500W xenon lamp (25 °C)

Solvents	Co	R ²	k (h ⁻¹)	t _{1/2} (h)
Acetone	8.918 ± 0.174	0.952	0.072 ± 0.004	9.63
Ethyl acetate	9.569 ± 0.050	0.967	0.019 ± 0.001	36.47
Methanol	9.529 ± 0.033	0.974	0.014 ± 0.0001	49.50

Table 2 Photolysis kinetic parameters of SCO in different aqueous media under the 500W xenon lamp (25 °C)

Waters	Co	R ²	k (h ⁻¹)	t _{1/2} (h)
Natural seawater	9.908 ± 0.073	0.995	0.089 ± 0.002	7.79
River water	10.006 ± 0.076	0.996	0.104 ± 0.002	6.66
Pure water	9.717 ± 0.041	0.999	0.122 ± 0.001	5.68

Table 3 The physical and chemical properties of the water samples in experiment (after sterilization)

Waters	pH	Conductance ($\mu\text{s}\cdot\text{cm}^{-1}$)	COD _{Cr} ($\text{mg}\cdot\text{L}^{-1}$)
Natural seawater	8.22	18,120	49.42
River water	8.05	321	92.25
Pure water	6.81	20.04	–

SCO, respectively. These results were consistent with the effects of ethyl acetate and methanol on pyridaphenthione photolysis (Zhao et al. 2012).

3.2 Photolysis of SCO in Different Aqueous Media

SCO concentrations decreased as irradiation time increased in different aqueous media, wherein the

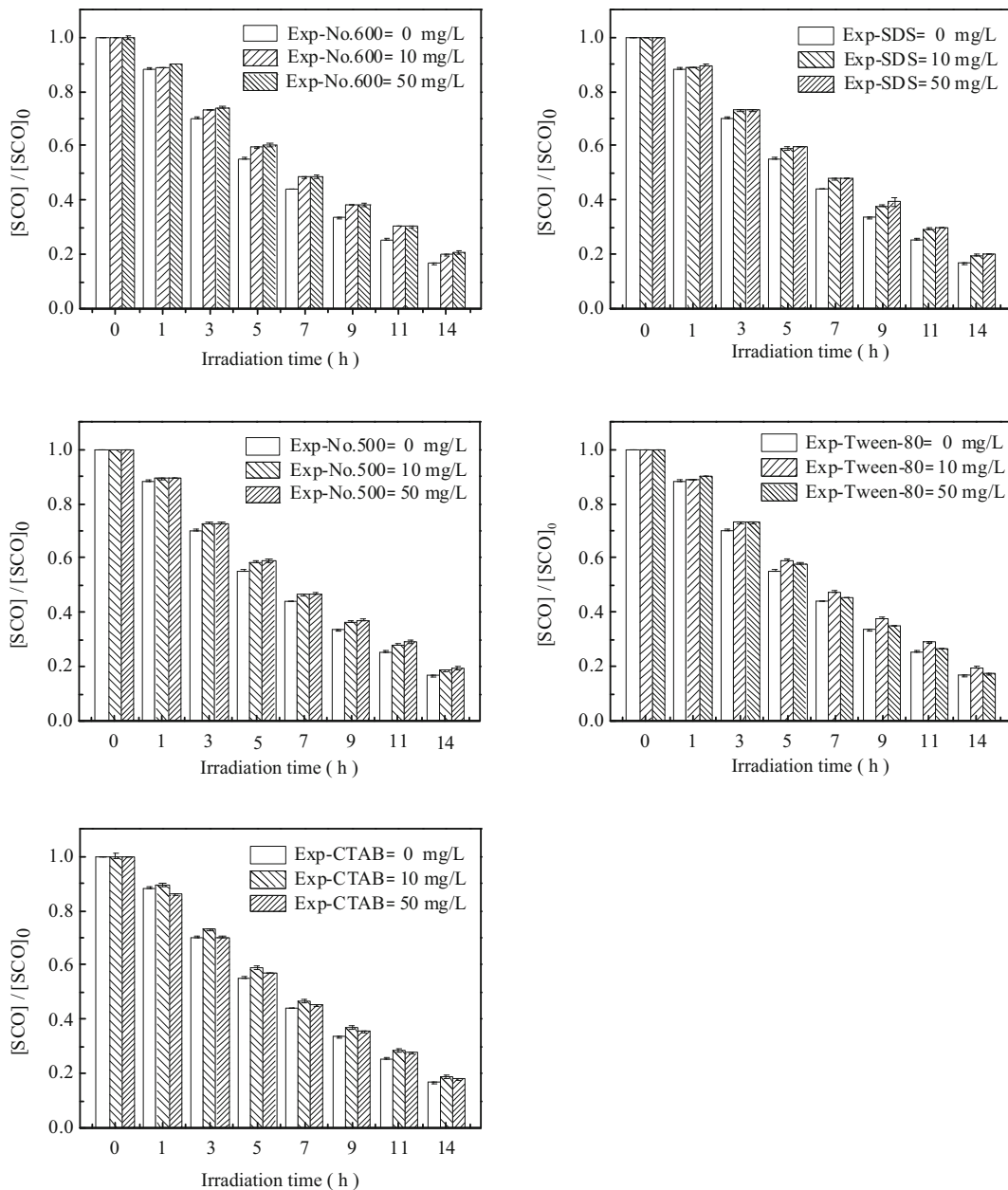


Fig. 3 The effect of surfactants on the photolysis of SCO under 500W xenon lamp (25 °C)

Table 4 Photolytic kinetic parameters of SCO in the solutions containing surfactants under 500W xenon lamp (25 °C)

Surfactants	Conc. (mg/L)	Co	R ²	k (h ⁻¹)	t _{1/2} (h)	Inhibiting ratio (%)
	0	9.717 ± 0.041	0.999	0.122 ± 0.001	5.68	0.00
No.600	10	9.860 ± 0.050	0.998	0.108 ± 0.001	6.42	-11.48
	50	9.935 ± 0.057	0.998	0.107 ± 0.001	6.48	-12.30
SDS	10	10.009 ± 0.051	0.998	0.109 ± 0.001	6.36	-10.66
	50	9.982 ± 0.058	0.998	0.108 ± 0.001	6.42	-11.48
No.500	10	9.860 ± 0.051	0.998	0.113 ± 0.001	6.13	-7.38
	50	9.977 ± 0.047	0.998	0.111 ± 0.001	6.24	-9.02
Tween-80	10	9.887 ± 0.050	0.998	0.110 ± 0.001	6.30	-9.84
	50	9.831 ± 0.060	0.998	0.118 ± 0.002	5.87	-3.28
CTAB	10	10.134 ± 0.065	0.997	0.112 ± 0.002	6.19	-8.20
	50	9.811 ± 0.057	0.998	0.115 ± 0.001	6.03	-5.74

degradation of SCO in pure water was rapid (Fig. 2.). The SCO removal were more than 74.00% and reached 83.43, 79.44, and 74.39% in the pure water, river water, and natural seawater, respectively, after irradiation for 14 h.

The photolysis kinetic parameters of SCO in different aqueous media are listed in Table 2. Their photolysis rates showed the following sequence: pure water > river water > natural seawater, and the corresponding half-lives were 5.68, 6.66, and 7.78 h, respectively.

In this study, SCO photolysis efficiency varied in different bodies of water. The reason probably lies in the different structures of humic substances as the major components of dissolved organic matter, pH, and contents of dissolved inorganic ions in different bodies of water (Table 3). The riverine humic substances, mostly

derived from lignin, retain almost completely its aromatic structure (Wilson et al. 1981), which not only have pronounced quenching effects but also competed with the SCO photolysis for the energy necessary to promote photochemical processes, while the structure of marine humic substances is largely aliphatic (Harvey et al. 1983) and only has quenching effects. The dissolved inorganic ions in natural seawater also inhibited the photodegradation of SCO. Considering the compositional difference between riverine and natural seawater, mostly Na⁺, Cl⁻, Mg²⁺, and HCO₃⁻ could be responsible for the observed quenching effects (Boberic et al. 1998). The natural seawater had significant photoquenching effects on photodegradation of SCO due to its dissolved organic matter, higher content of dissolved inorganic ions, and higher pH which was

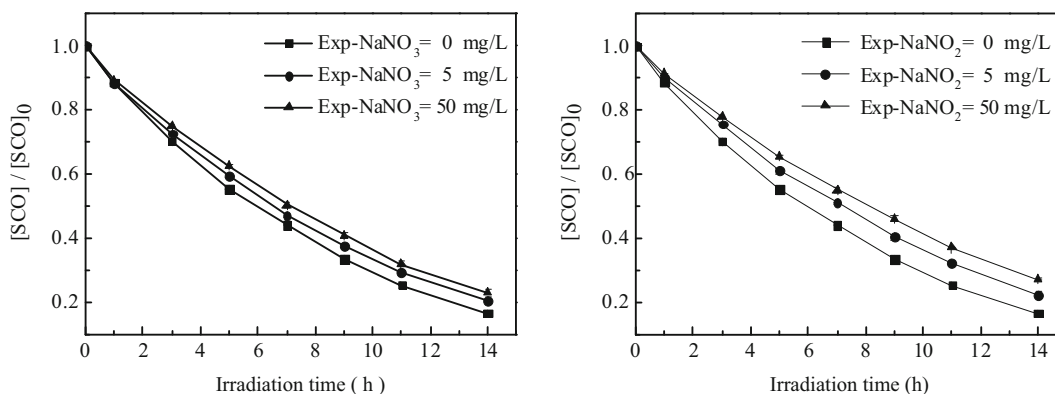
**Fig. 4** The effect of NO₃⁻ and NO₂⁻ on the photolysis of SCO under 500W xenon lamp (25 °C)

Table 5 Photolytic kinetic parameters of SCO in the solutions containing NO_3^- and NO_2^- under 500W xenon lamp (25 °C)

Ion type	Conc. (mg/L)	Co	R^2	k (h^{-1})	$t_{1/2}$ (h)	Inhibiting ratio (%)
Control	0	9.717 ± 0.041	0.999	0.122 ± 0.001	5.68	0.00
NO_3^-	5	9.878 ± 0.052	0.998	0.109 ± 0.001	6.36	-11.94
	50	9.850 ± 0.068	0.996	0.101 ± 0.002	6.86	-20.79
NO_2^-	5	9.939 ± 0.065	0.997	0.102 ± 0.001	6.79	-19.61
	50	10.015 ± 0.058	0.997	0.089 ± 0.001	7.79	-37.10

consistent with the effects of natural seawater on diuron, carbendazim, and triadimefon photolysis (Durand et al. 1990; Zhou et al. 2008; Sun et al. 2009).

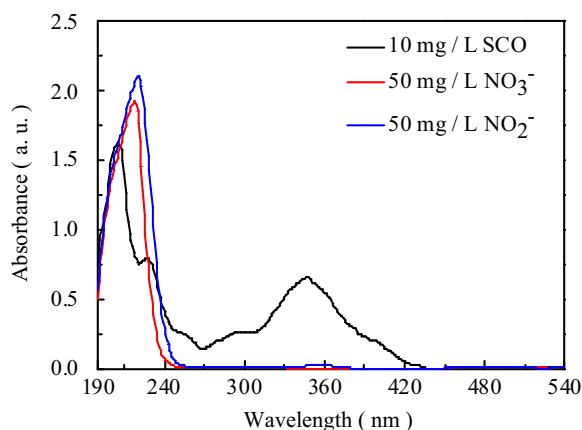
3.3 Effect of Five Surfactants on Photolysis of SCO in Aqueous Solution

Surfactants have been widely applied in detergents, processed foods, and pesticides, and these could enter the natural environment by waste water discharge or other ways. To explore effects of five selected surfactants on SCO removal, two concentrations were tested: 10 and 50 mg/L. All the five surfactants have significant quenching effects on SCO photolysis (Fig. 3). SCO concentrations decreased as the increasing of the irradiation time in the presence of No.600, No.500, SDS, Tween-80, and CTAB. Among them, SCO removal decreased as No.600, SDS, and No.500 concentrations increased, and the SCO removal decreased from 83.43% without No.600, SDS, and No.500 to 79.32, 79.94, and 80.45% with a concentration of No.600, SDS, and

No.500 50 mg/L, respectively, after irradiation for 14 h. SCO removal initially decreased rapidly with increasing addition of Tween-80 and CTAB 10 mg/L. However, SCO removal decreased slowly with increased Tween-80 and CTAB concentrations to 50 mg/L, and the SCO removal decreased from 83.43% without Tween-80 and CTAB to 80.44 and 81.33% with a concentration of Tween-80 and CTAB 50 mg/L, respectively, after irradiation for 14 h.

Table 4. lists the kinetic parameters of the SCO photodegradation reactions in the presence of these five surfactants. In the table, the increase in No.600, SDS, and No.500 concentrations decreased the rate constants. Therefore, the half-lives of photodegradation were increased. Inhibiting ratios of No.600, SDS, and No.500 were 12.30, 11.48, and 9.02% at concentrations of 50 mg/L, respectively. The increase in Tween-80 and CTAB concentrations to 10 mg/L decreased the rate constants. However, an increase in Tween-80 and CTAB concentrations to 50 mg/L slightly increased the rate constants. Inhibiting ratios of Tween-80 and CTAB were 9.84 and 8.20%, respectively, at concentrations of 10 mg/L.

No.600 and No.500 only played competitive roles on SCO photolysis because they could become predominant in absorbing light at their high concentrations;

**Fig. 5** The UV-Vis spectra of SCO, NO_3^- , and NO_2^- **Table 6** Photolytic kinetic parameters of SCO in the solutions containing H_2O_2 under 500W xenon lamp (25 °C)

Conc. (mg/L)	Co	R^2	k (h^{-1})	$t_{1/2}$ (h)	Promoting ratio (%)
0	9.717 ± 0.041	0.999	0.122 ± 0.001	5.68	0.00
20	9.873 ± 0.068	0.997	0.125 ± 0.002	5.54	2.39
50	9.897 ± 0.060	0.998	0.130 ± 0.002	5.33	6.14

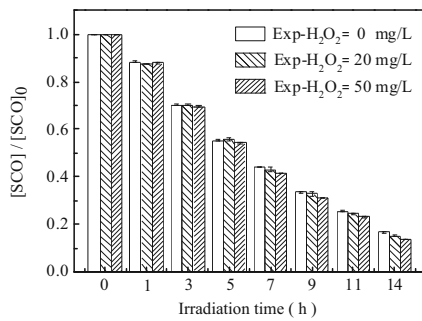


Fig. 6 The effects of H₂O₂ on the photolysis of SCO under 500W xenon lamp (25 °C)

moreover, the quenching effect of No.600 on scopoletin photolysis was higher than No.500. Photodegradation of SCO has been speculated to belong to direct photolysis in the presence of No.600 and No.500. SDS had a stronger quenching effect on the photodegradation of SCO, which may be attributed to a process that competes with the SCO photolysis and an interaction between SDS and SCO for their unique structures. The

significant quenching effects of Tween-80 and CTAB on SCO photolysis depended on optimal concentration. This may be due to the fact that there are special interaction models of these two surfactants with scopoletin or effects of critical micelle concentration (Xiao et al. 2013; Tanaka et al. 1979). Moreover, some surfactants have been reported to have quenching effects on photodegradation of methyl-arathion and vinclozolin in aqueous solutions (Yue et al. 2000; Deng et al. 2006).

3.4 Effect of NO₃⁻ and NO₂⁻ on Photolysis of SCO in Aqueous Solution

The increase in fertilizer application in recent decades has led to diverse inorganic nitrogen entering natural environments. NO₃⁻ and NO₂⁻ are ubiquitous in surface waters and are crucial for compound photolysis in aquatic environments. To explore effects of NO₃⁻ and NO₂⁻ on SCO removal, two concentrations were tested: 5 and 50 mg/L. SCO

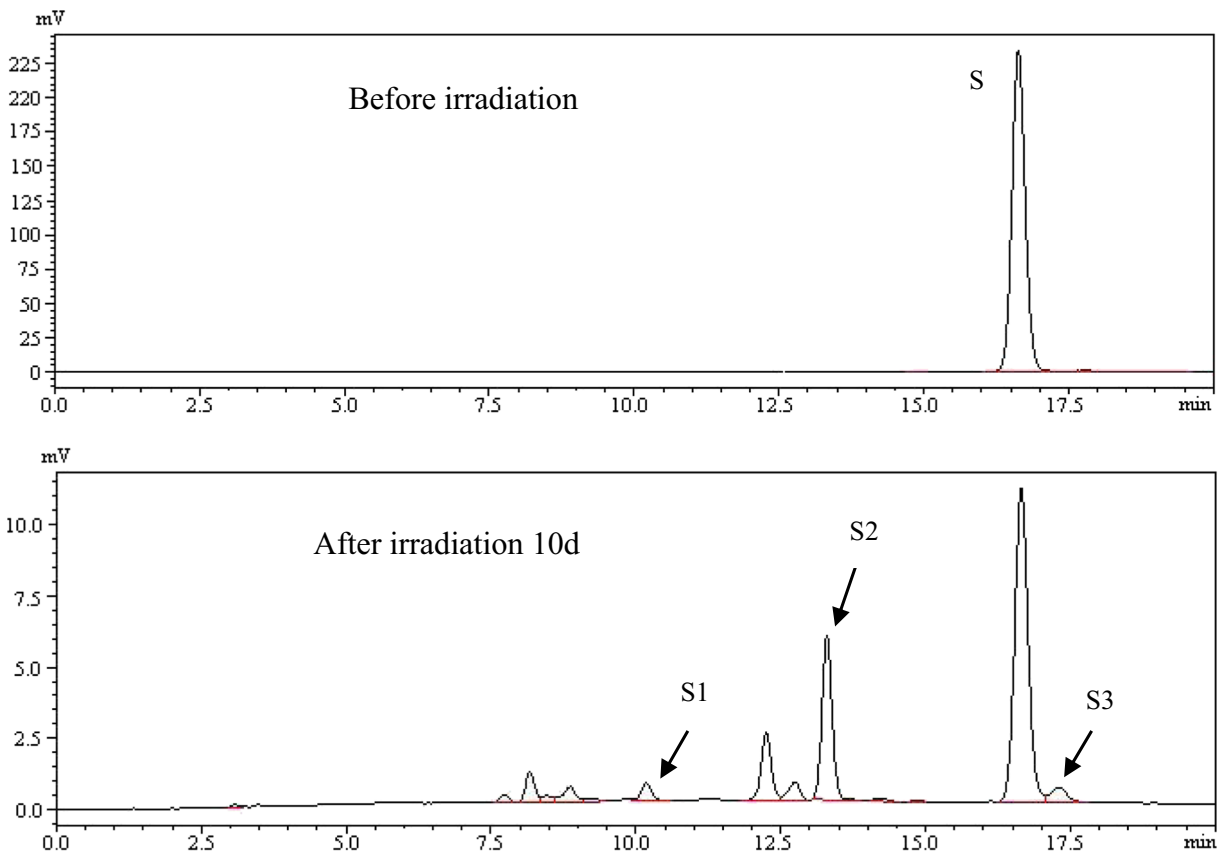


Fig. 7 Chromatogram of SCO before and after irradiation for 10 days under 500W xenon lamp (25 °C) (S: SCO; S1, S2, S3: photoproducts)

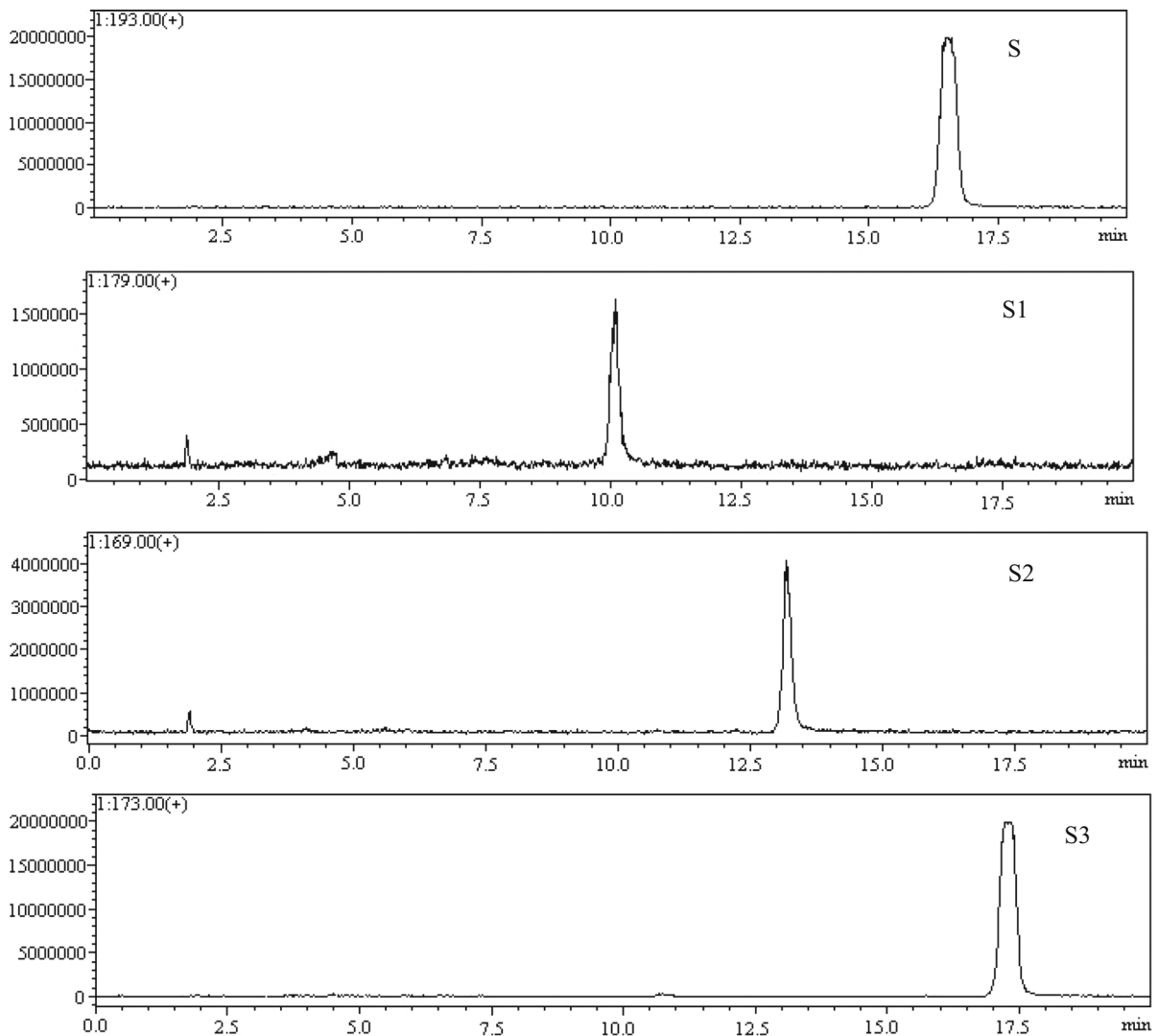


Fig. 8 EIC of SCO irradiated for 10 days under 500W xenon lamp in aqueous solution (positive ion pattern)

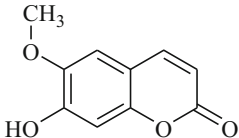
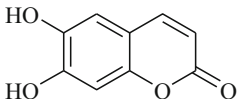
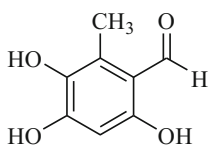
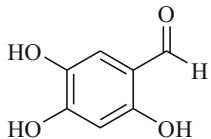
concentrations decreased as irradiation time increased in the presence of NO_3^- and NO_2^- ; however, SCO removal decreased as NO_3^- and NO_2^- concentrations increased (Fig. 4). After irradiation for 14 h, SCO removal decreased from 83.43% without NO_3^- and NO_2^- to 77.02 and 72.80% with a concentration of NO_3^- and NO_2^- 50 mg/L, respectively.

Table 5 lists the kinetic parameters of SCO photodegradation reactions in the presence of NO_3^- and NO_2^- . In the table, with increasing of NO_3^- and NO_2^- concentrations, the photolysis rate constants decreased. Therefore, the half-lives of photodegradation were increased. NO_3^- and NO_2^- had quenching effects on the SCO photodegradation; moreover, the inhibitive

effects on SCO photodegradation by NO_2^- appeared to be more efficient than with NO_3^- . The maximal inhibiting ratios were 20.79 and 37.10% at their highest concentration of 50 mg/L.

NO_3^- and NO_2^- have intensive absorption bands at 190–260 nm; moreover, the photoabsorption band of NO_2^- is higher than that of NO_3^- at the same concentration. Furthermore, SCO has a stronger photoabsorption band within the same range (Fig. 5). NO_3^- and NO_2^- play competitive roles on SCO photolysis for NO_3^- and NO_2^- by absorbing more UV than SCO, leading to the decrease of SCO photolysis. Photodegradation of SCO may belong to direct photolysis in the presence of NO_3^- and NO_2^- . In our study,

Table 7 Degradation products of SCO in aqueous media detected in ESI-MS

Substance	Names and structures	Retention time(min)	Molecular weight	ESI-MS m/z
6-methoxy-7-hydroxycoumarin				
S		16.65	192	193[M+H] ⁺
6,7-dihydroxy-2H-chromen-2-one				
S1		10.18	178	179[M+H] ⁺
3,4,6-trihydroxy-2-methylbenzaldehyde				
S2		13.30	168	169[M+H] ⁺
2,4,5-trihydroxybenzaldehyde				
S3		17.29	154	173[M+H ₂ O+H] ⁺

SCO photolysis was quenched with the addition of NO_3^- and NO_2^- , which coincided with the effect of NO_3^- and NO_2^- on the photolysis of chlorantraniliprole (Zhang et al. 2011b).

3.5 Effects of H_2O_2 on SCO Photolysis in Aqueous Solution

To explore the effects of H_2O_2 on SCO removal, two concentrations were tested: 20 and 50 mg/L. As shown in Fig. 5, SCO concentrations decreased as the irradiation time increased in the presence of H_2O_2 ; moreover,

the SCO removal increased as H_2O_2 concentration increased. After irradiation for 14 h, SCO removal increased from 83.43% without H_2O_2 to 84.96 and 86.24% with a concentration of H_2O_2 20 and 50 mg/L, respectively.

The kinetic parameters of the SCO photodegradation reactions in the presence of H_2O_2 are listed in Table 6. The photolysis rate constants increased as H_2O_2 concentration increased. Therefore, the half-lives of photodegradation were decreased. The photolysis rate constants of SCO were 0.122, 0.125, and 0.130 h^{-1} in the presence of 0, 20, and 50 mg/L of H_2O_2 ,

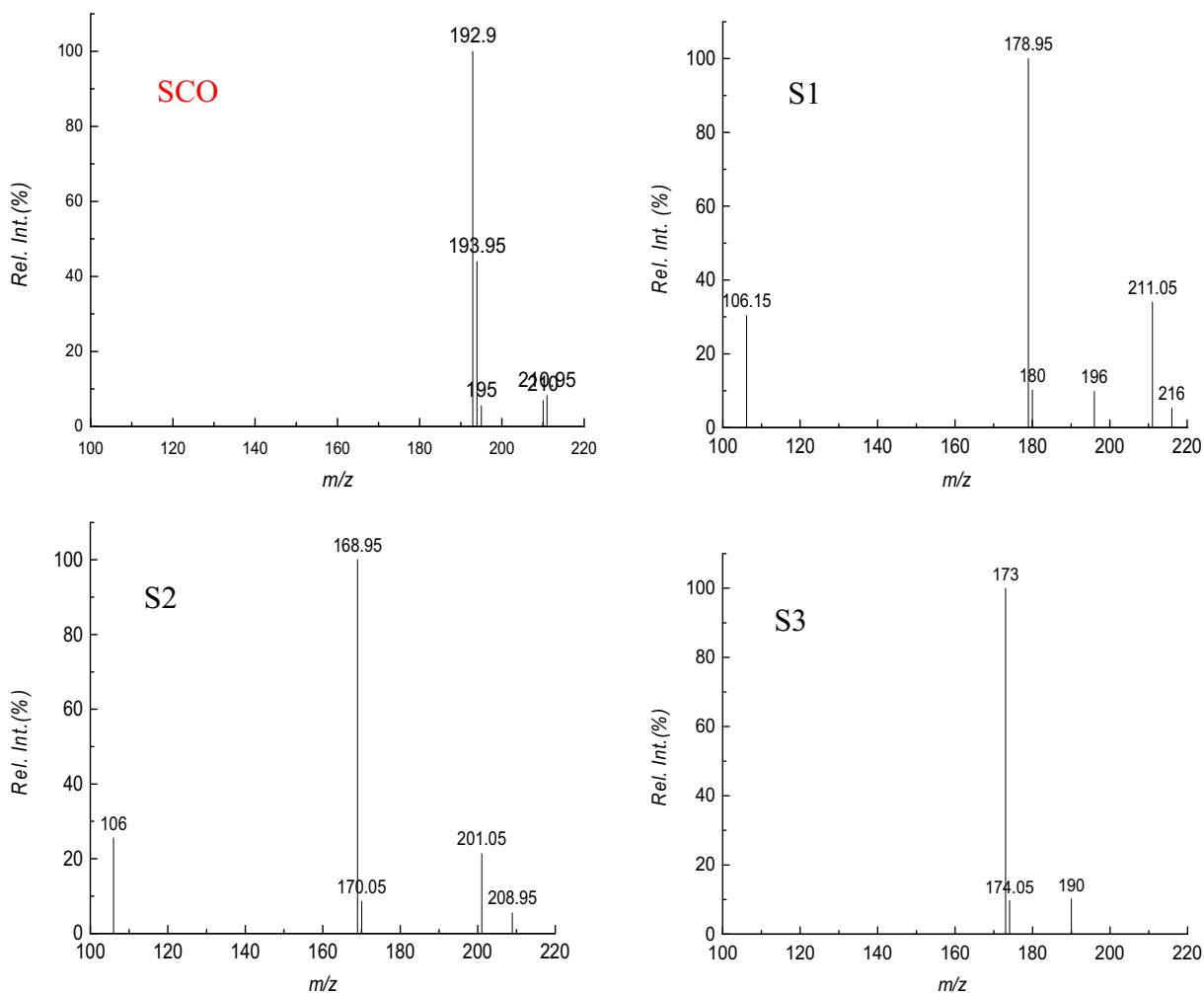


Fig. 9 Mass spectra of SCO and its main photodegradation products

respectively. The maximal promotion ratio was 6.14% at the highest H_2O_2 concentration of 50 mg/L.

H_2O_2 could produce hydroxyl radicals after irradiation, as shown in Eq. (4) (He et al. 2012). As concentrations of H_2O_2 increased, the rate of generation of hydroxyl radicals increased because more light was absorbed by H_2O_2 . Hydroxyl radicals are powerful oxidizing species and could react with the SCO molecules to generate intermediates that could cause the photolysis of the original solutions. As a result, a higher concentration of hydroxyl radicals leads to a higher SCO decomposition rate. Therefore, the enhancement of the SCO degradation is due to the reaction of hydroxyl radicals produced by H_2O_2 in solutions upon irradiation (Liu et al. 2015). In our study, SCO photolysis was enhanced by the addition of H_2O_2 and was consistent with the effect of H_2O_2 on photolysis of parathion and

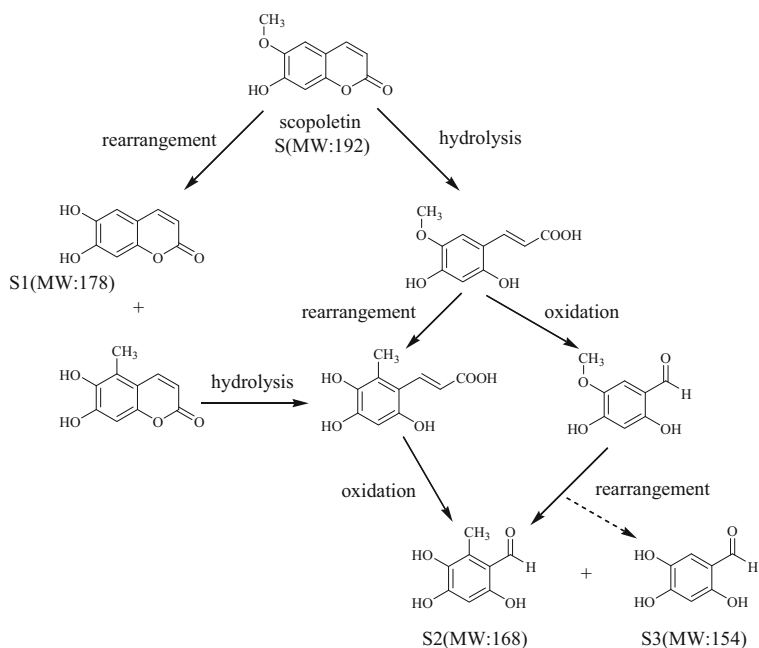
sulfamethoxazole (Wu and Linden 2008; Niu et al. 2013).



3.6 Identification of Photoproducts and Possible Photodegradation Pathways in Aqueous Solution

To obtain detectable stable photoproducts, a high concentration of SCO (80 mg/L) was used for irradiation (Tang et al. 2014). Figure 6 lists chromatogram of SCO before and after 10-day irradiation. At least eight new peaks can be observed from the irradiation sample, which probably corresponds to the new photoproducts. Among them, seven appeared earlier than their parent compound in the HPLC chromatogram, indicating that they were

Fig. 10 Proposed photodegradation pathways of SCO in aqueous solution as induced by 500W xenon lamp



more polarized or had lower molecular weight than SCO, and three were identified. The extracted-ion chromatogram and the corresponding mass spectrum (Figs. 7 and 8) were used to confirm the structures of these three photoproducts due to the lack of standard chemicals for reference. The SCO and its main photoproducts molecular ion plus proton $[M + H]^+$ and corresponding molecular structure are summarized in Table 7.

SCO has different photolysis pathways under different irradiation conditions. Different photoproducts could be obtained at different irradiation time. Previous study reported that near-UV irradiation of aqueous solutions of SCO resulted in the formation of dimmers (Smith et al. 2012). However, in our preliminary identification of photoproducts experiment, no valuable peaks could be obtained as the LC/ESI-MS scan above 220 m/z after 10-day irradiation. Therefore, possible photolysis pathways of SCO in aqueous solution are proposed, based on the determined LC/ESI-MS photoproducts (Fig. 9). There are three types of reaction in SCO photodegradation including photorearrangement, photohydrolysis, and photooxidation (Fig. 10). The molecular ion plus proton $[M + H]^+$ with m/z 179 was identified as an intermediate product (S1) 6,7-dihydroxy-chromen-2-one and proven to be a rearrangement product of the ether methyl side chain from SCO (Gao 1979). The m/z 169 molecular ion was labeled a photo-intermediate product (S2) 3,4,6-trihydroxy-2-methyl-benzaldehyde and was produced by

three reaction pathways from SCO simultaneously: (1) Rearrangement occurred on ether methyl side chain of SCO to produce photoproduct S1 and 6,7-dihydroxy-5-methyl-2H-chromen-2-one, firstly. Hydrolysis then occurred on cyclic ester of intermediate 6,7-dihydroxy-5-methyl-2H-chromen-2-one, and finally oxidation occurred on the acrylic acid side chain of intermediate (E)-3-(3,4,6-trihydroxy-2-methylphenyl) to yield photoproduct S2. (2) First, hydrolysis occurred on the cyclic ester of SCO to produce intermediate (E)-3-(2,4-dihydroxy-5-methoxyphenyl). Then, rearrangement was observed on the ether methyl side chain of intermediate (E)-3-(2,4-dihydroxy-5-methoxyphenyl). Finally, oxidation was observed on the acrylic acid side chain of intermediate (E)-3-(3,4,6-trihydroxy-2-methylphenyl) to yield photoproduct S2. (3) First, hydrolysis was conducted on cyclic ester of SCO to produce intermediate (E)-3-(2,4-dihydroxy-5-methoxyphenyl). Then, oxidation occurred on the acrylic acid side chain of intermediate (E)-3-(2,4-dihydroxy-5-methoxyphenyl) to yield photoproduct 2,4-dihydroxy-5-methoxybenzaldehyde. Finally, rearrangement occurred on the ether methyl side chain of intermediate 2,4-dihydroxy-5-methoxybenzaldehyde to yield S2 and S3. The m/z 173 molecular ion was labeled as photo-intermediate product (S3) 2,4,5-trihydroxy-benzaldehyde that was obtained from the same reaction pathway (3) of S2. The three identified photoproducts should have lower toxicity and fewer environmental risks (Choi et al. 2016; Netzeva

and Schultz 2005). The other photoproducts were not identified for their low detection sensitivity or short existence time, which needed further investigation.

4 Conclusions

Photodegradation of SCO in the organic solvents under 500W Xe lamp radiation was investigated, and the degradation rate was in a sequence of acetone > ethyl acetate > methanol. The half-lives of photodegradation were 9.63, 36.47, and 49.50 h, respectively. Photodegradation rate of SCO in different aqueous media was in the sequence of pure water > river water > natural seawater, and the half-lives were 5.68, 6.66, and 7.79 h, respectively. The five kinds of surfactants, NO_3^- , and NO_2^- had significant photoquenching effects on SCO photodegradation, and H_2O_2 had photosensitization effects on SCO photodegradation.

The major pathways of SCO photodegradation were photorearrangement, photohydrolysis, and photooxidation. Three main photodegradation products of SCO including 6,7-dihydroxy-2H-chromen-2-one, 3,4,6-trihydroxy-2-methyl-benzaldehyde, and 2,4,5-trihydroxy-benzaldehyde were identified by HPLC/ESI-MS techniques. Other photoproducts were not identified for their low detection sensitivity or short existence time, which need further investigation.

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Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

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