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Photochemical degradation of typical herbicides simazine by UV/H_2O_2 in aqueous solution

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ABSTRACT

Aqueous solutions of simazine (SIM, 1-chloro-3,5-bisethylamino-2,4,6-triazine; 2,4-bis(ethylamino)-6-chloro-s-triazine) were photolyzed (λ = 254 nm) under a variety of solution conditions. The initial SIM concentration ranged from 69 to 315 μg/L to approach the typical concentration found in contaminated surface waters. The effects of the initial concentration of hydrogen peroxide (H_2O_2), initial concentration of SIM, pH values, light intensity and different water quality to the degradation of SIM were investigated in the study. The most favorable reaction conditions appear to be a moderate concentration of 120 mg/L H_2O_2 for the highest removal of simazine. In addition, the experimental results show the initial concentration of SIM has little effect on the removal of SIM. The time-dependent degradation profiles of SIM were successfully modeled using an approximation of the pseudo first-order equation and the kinetic parameters were determined.

Keywords: Simazine; Photodegradation; Hydrogen peroxide (H_2O_2); pH; UV-irradiation

1. Introduction

Pesticides are widely used in different forms such as insecticides, herbicides and fungicides as to increase agricultural productivity. However, the wide use of these chemicals may pollute water resources and thus raise human health concern due to their known human toxicity [1]. Simazine (SIM, 1-chloro-3,5-bisethylamino-2,4,6-triazine; 2,4-bis(ethylamino)-6-chloro-s-triazine) is a common triazine herbicides used for protecting crops, which is used to control broad-leaf and grassy weeds in crop fields and on noncrop areas by inhibiting the normal photosynthesis of plants [2]. SIM is suspected as a possible endocrine disrupter and human carcinogen and is believed to have adverse effects on algae flora in soil and water [3]. In Europe, the maximum contaminant level for simazine has been set at 0.1 μg/L in drinking water. Furthermore, simazine is totally banned in some European countries such as Norway [4]. SIM's chemical structure is shown in Fig. 1. Its physical and chemical properties are shown in Table 1 [3].

It is seen from Fig. 1 and Table 1 that SIM contains a chlorine and two ethylamine groups attached to the ring. Moreover, it is slightly soluble in water (5 mg/L at 20°C), has low adsorption in soil and consequently migrates easily towards the underground waters presenting thus a potential danger for public health [5]. In Europe, the maximum contaminant level (MCL) for SIM has been set at 0.1 μg/L in drinking water.

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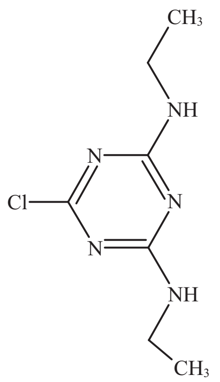

Fig. 1. Structural formula of simazine.

Moreover, simazine is totally banned in some European countries such as Norway [4]. Therefore, there is a need to develop technological approaches for rapidly destroying SIM in water.

Some techniques to eliminate pesticides have been so far considered, like ozonation [6–10], adsorption by granular activated carbon [11–13], but only a few applications specifically about SIM involving photolytic degradation modes have been envisioned and implemented [14–18] and photochemical oxidation methods have shown promise.

When UV light is absorbed directly by H_2O_2, $HO^\bullet$ radicals that attack the organic molecules are generated by photolysis of the –O–O– peroxidic bond [19]

$$H_2O_2 + h\nu \rightarrow 2HO^\bullet \quad (1)$$

Hydrogen peroxide absorbs light (depending on its concentration) in the range of 185–300 nm; the highest hydroxyl radical yields are obtained when short-wave ultraviolet radiations (200–280 nm) are used. Low pressure lamps having an irradiation at 254 nm have been found very effective for the degradation of recalcitrant organic pollutants in UV/H_2O_2 mediated processes [20–24]. As hydroxyl radicals can oxidize organic compounds and attack organic molecules by abstracting a hydrogen atom, adding hydroxyl groups, and transferring electrons, UV/H_2O_2 processes are effective in the degradation of various water contaminants [15–21].

Table 1
Physical and chemical properties of simazine [1]

Parameter	Value
Physical state	Crystalline
Colour	Colourless
Melting point	225–227
Specific gravity	1.302 (20°C)
Vapour pressure	0.000810 mPa at 20°C
Solubility in water	5 mg/l (20°C)
Octanol-water partitioning coefficient (Log Kow)	1.9600
CAS number	122-34-9
Adsorption coefficient	130
Molecular weight	201.70

The objective of this study was to investigate the degradation of SIM during treatment with H_2O_2 and UV at a wavelength of 254 nm. In addition, the effects of light intensity, different water quality including tap water and distilled water, H_2O_2 concentration, initial concentration of SIM, on the decay rate of SIM were also investigated.

2. Materials and methods

2.1. Chemicals and reagents

SIM was purchased from Sigma-Aldrich. H_2O_2 (30%, w/w) was obtained from Sinopharm Chemical Reagent Co. Ltd., China. The mobile phase acetonitrile (HPLC grade) was also purchased from Sigma Chemical Company. Other chemicals used in this study were are at least of analytical grade and used without further purification.

During experimentation, the SIM solution is prepared by the different water. One is the ultra-pure water which was obtained by Milli-Q water purification system. The other is tap water. The characteristics of tap water and distilled water are given in Table 2.

2.2. Experimental procedure

All experiments were carried out in a 20 L double cylindrical stainless reactor. A schematic diagram of the annular photocatalytic reactor system is shown in Fig. 2, which equipped with the immersible low-pressure mercury lamps with the prominent emission at 254 nm. The lamps were introduced into the reactor and kept separated from the aqueous solution by a quartz cooling jacket. In the experiments, light intensity was decided by UV lamps and measured by ferrioxalate actinometry [25]. The points measured are the top center of the reactor. The number of UV lamps and corresponding light intensity are shown in Table 3.

Several series of experiments were carried out in the reactor by varying the initial SIM concentration, pH, H_2O_2 concentration, and light intensity. Distilled water and tap water of Shanghai were selected to examine the effect of water quality on the photodegradation of SIM under similar treatment conditions. The initial SIM concentration was varied in the range from 69 to 315 μg/L. In addition, whenever necessary the pH

Table 2
Characteristics of the experimental water

Water	pH	DOC (mg/L)	Turbidity (NTU)	Conductivity (μs/cm)	UV_{254} (cm^{-1})
Distilled water	7.13–7.56	1.37–1.67	0	<20	<0.006
Tap water	6.95–7.43	4.60–7.02	0.15–0.45	606–720	0.09–0.12

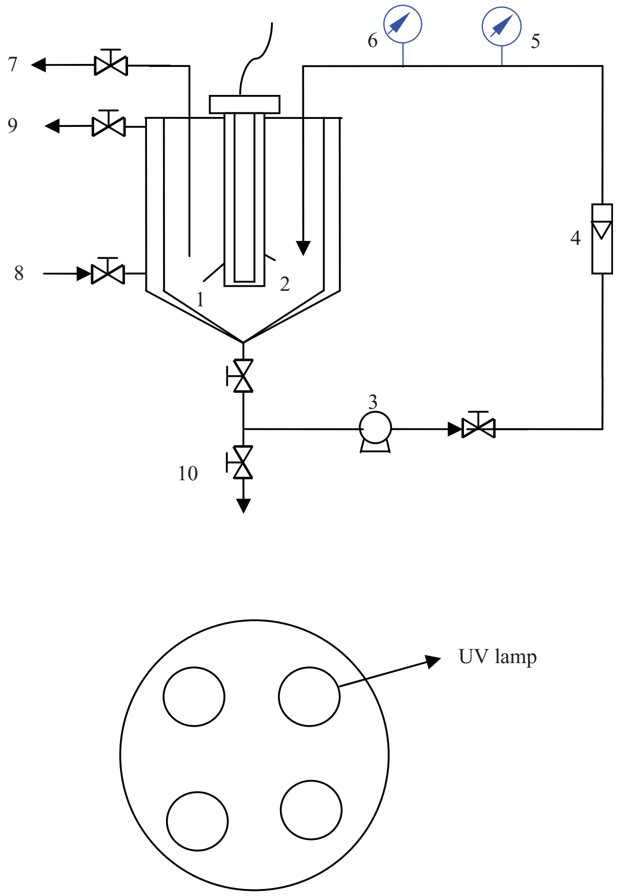

Fig. 2. Schematic diagram of the annular reactor system (1: quartz jacket; 2: UV lamp; 3: circulating pump; 4: flow meter; 5: pressure meter; 6: temperature meter; 7: sample collection; 8: cooling water inlet; 9: cooling water outlet; 10: drain valve).

solution was initially fixed by the addition of H_2SO_4 (H_2SO_4: water = 1:5) or NaOH 1 mol L^{-1} solution.

2.3. Analytical methods

SIM was analyzed by a Shimadzu LC-2010 AHT HPLC (high performance liquid chromatography) equipped with a VP-ODS column (150 mm × 4.6 mm) and ultraviolet detector setting wavelength of 220 nm. Elution was performed with a mobile phase composed of acetonitrile/water (50/50 v/v) at a flow rate of 0.8 ml min^{-1}.

3. Results and discussion

3.1. UV light intensity

In the experiments, SIM solution was prepared by tap water and the concentration of SIM is about 100 μg/L. The concentration of H_2O_2 is 20 mg/L. The effect of light intensity to SIM degradation was studied. The results are shown in Fig. 3.

It is seen from Fig. 3 that the removal of SIM increases with light intensity increases. With different UV intensity radiation for 30 min from one lamp to four lamps, the removal rate of SIM is 72%, 92%, 98%, 100% separately. Therefore, with the UV light intensity increases, the removal of SIM also increases. In addition, the degradation kinetics of SIM was studied. The first-order kinetic model ($dC/dt = -kC$) was used to fit the experimental degradation data and the fitted results are shown in Fig. 4.

It can be seen from Fig. 4 that the first-order reaction model fitted the experimental degradation data closely ($R^2 = 0.995$–0.999). Thus, the results indicated that the modeling can adequately describe both the kinetics of SIM degradation in aqueous solution and the rate increase with UV light intensity increase.

3.2. H_2O_2 concentration

SIM solution was degraded with the UV light intensity of 2.4×10^{-6} Einstein l^{-1} s^{-1} (two UV lamps) and initial H_2O_2 concentration is 0, 10, 20, 40, 60, 80, 100, 120, 150, and 180 mg/L (T = 17 ± 1°C). The effect of H_2O_2 concentration to SIM degradation was studied. SIM solution was prepared by tap water. The kinetic constants of SIM degradation with different H_2O_2 concentration are shown in Fig. 5.

It is seen from Fig. 5 that the kinetic constants increase with H_2O_2 concentration increase when the H_2O_2 concentration is below 120 mg/L. The increase is that H_2O_2 produces highly reactive hydroxyl radical $HO^{\bullet}$ when H_2O_2 directly absorbed UV light. When the concentration of H_2O_2 is at 120 mg/L, the kinetic constant could reach the maximum value 0.1701 min^{-1}. When the H_2O_2 concentration is over 120 mg/L, the kinetic constants decrease with H_2O_2 concentration increase. The decrease is that hydrogen peroxide

Table 3
The number of UV lamps and corresponding light intensity

The number of UV lamps	1	2	3	4
Light intensity in tap water (Einstein l^{-1} s^{-1})	1.1×10^{-6}	2.4×10^{-6}	3.5×10^{-6}	4.6×10^{-6}
Light intensity in distilled water (Einstein l^{-1} s^{-1})	10×10^{-6}	23×10^{-6}	36×10^{-6}	45×10^{-6}

combines hydroxyl radicals to form less reactive hydroperoxyl radicals [19]. Hydrogen peroxide has been found to consume hydroxyl radicals according to the following equations.

$$OH^{\bullet}+H_2O_2 \rightarrow HO_2^{\bullet}+H_2O \quad (2)$$

3.3. Different SIM concentration

Different SIM concentration solution was prepared by tap water. With UV light intensity of 2.4×10^{-6} Einstein l^{-1} s^{-1} (two lamps) and H_2O_2 concentration of 20 mg/L, the effect of different SIM concentration to SIM degradation is studied. The results are shown in Fig. 6.

It is seen from Fig. 6 that three fitting curves are almost parallel and the reaction rates are 0.0775, 0.0784 and 0.0770 min^{-1} separately when the initial SIM concentration is 315, 190 and 69 μg/L. Therefore, the effect of initial SIM concentration to reaction rate of SIM degradation by UV/H_2O_2 process could be ignored.

3.4. Different water quality

Different SIM solutions were prepared by tap water and distilled water. The effect of the different water quality to the degradation of SIM is investigated. The reaction conditions are with the light intensity of 2.4×10^{-6} Einstein l^{-1} s^{-1}, $T = 15 \pm 1°C$, and the H_2O_2 concentration of 20 mg/L. The experimental data are shown in Fig. 7.

It is seen from Fig. 7 that the degradation rate of SIM in the distilled water is greater than the rate in the tap water. Based on the ferrioxalate actinometry results of tap water and distilled water in Table 3, the photon flux in distilled water is higher than that in tap water. Moreover, the presence of organic chemicals and other anions such as bicarbonate and carbonate are the capture of reactive hydroxyl radical in tap water. It is consistent with previous work [26]. It will strongly control the production of reactive hydroxyl radicals. Therefore, the degradation rate of SIM is greater than the rate in the tap water.

4. Conclusions

In this study, SIM rapidly decomposed under UV/H_2O_2 treatment. The most favorable reaction conditions appear to be the concentration of H_2O_2 at 120 mg/L in tap water. In this study, the combination of UV/H_2O_2 leads to a substantial improvement over either treatment by itself under almost all conditions investigated including different UV light intensity, H_2O_2 concentration, different SIM concentration, and different water quality. With the UV light intensity

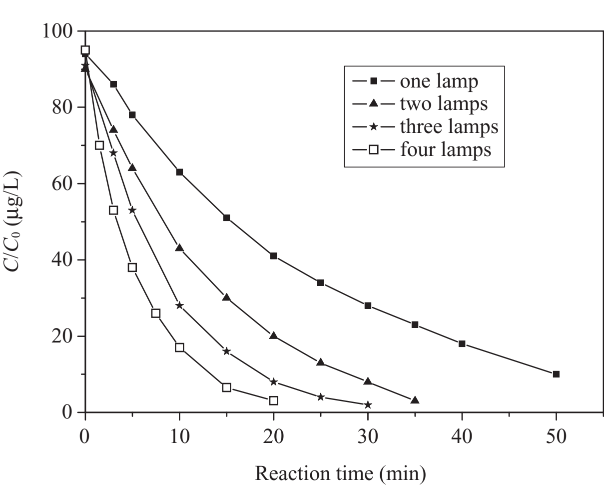

Fig. 3. Degradation curves of simazine under different UV light intensity.

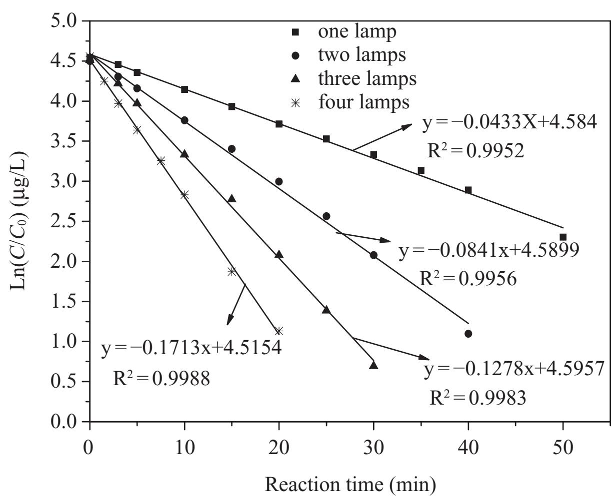

Fig. 4. Fitting the experimental data of SIM degradation by the first order model.

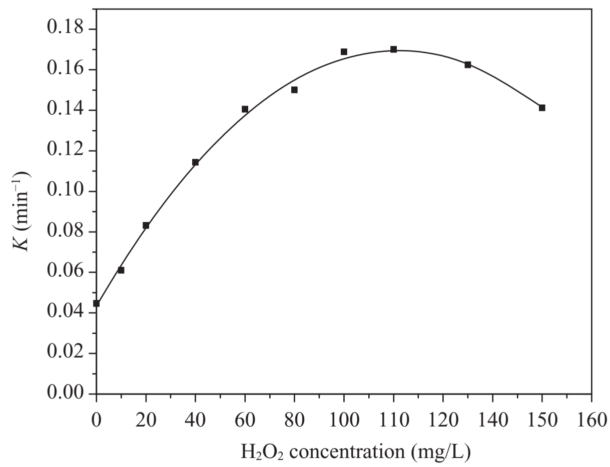

Fig. 5. The relationship curve of the kinetic constants of simazine degradation and H_2O_2 concentration.

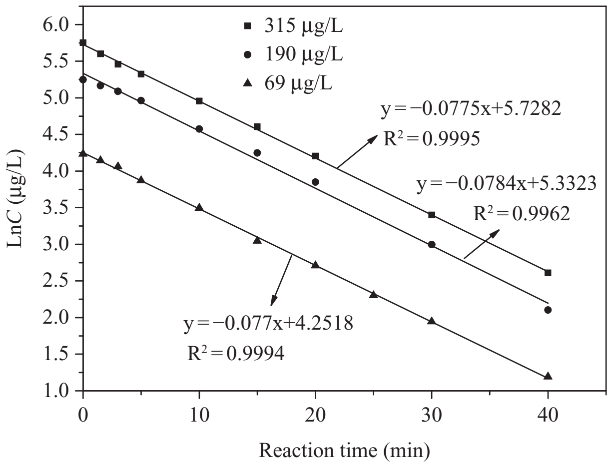

Fig. 6. Fitting the experimental data of SIM degradation by the first order model with different initial SIM concentration.

increases, the removal of SIM increases. Moreover, the effect of initial SIM concentration to reaction rate of SIM degradation could be ignored. In addition, the experimental results showed that the water quality of tap water had a negative impact on the UV/H_2O_2 treatment due to scavenging effects.

Acknowledgements

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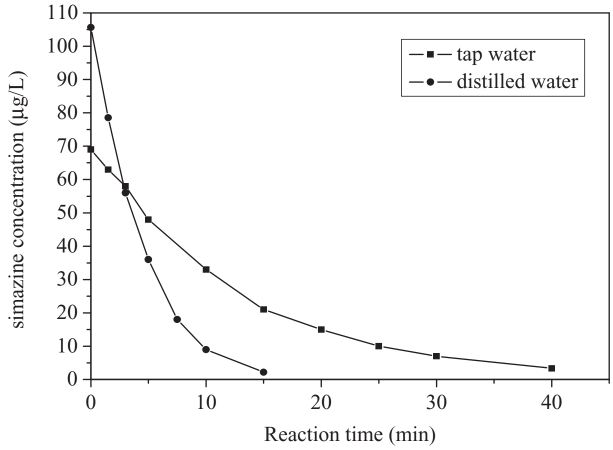

Fig. 7. Degradation curves of simazine prepared with different water quality.

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