Photodegradation of etridiazole by UV radiation during drinking water treatment

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ABSTRACT

The photodegradation of etridiazole (ETZ) in water by UV radiation at 254 nm was investigated. Results indicate that the simulated first-order rate constants decreased with the increase of initial ETZ concentration (i.e., 5, 20 and 30 μM), and did not show any pH dependence within the range from 6.0 to 8.0. The quantum yield was $0.46 \pm 0.02 \text{ mol E}^{-1}$ at pH 7.0. H_2O_2 was generated at trace levels in the range from 0 to 1.0 μM during photodegradation of ETZ. Direct photodegradation was responsible for the decomposition of ETZ in distilled water by UV radiation. Three organic byproducts were identified: 5-ethoxy-3-dichloromethyl-1,2,4-thiadiazole, 5-ethoxy-1,2,4-thiadiazole-3-carboxylic acid and 5-ethoxy-3-hydroxyl-1,2,4-thiadiazole. About 90% of chloro mass in the initial ETZ was released as Cl^- at the end of photodegradation. In contrast, the formation of sulfate and nitrate was insignificant. In general, ETZ decayed more quickly in groundwater than in sand-filtered or surface water. It is reasonably deduced that ETZ may not get removed effectively under a typical UV dose of 40 mJ cm^{-2} at most water treatment plants that employ UV radiation for disinfection.

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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 (Dalvi and Howell, 1977). Etridiazole (ETZ, 5-ethoxy-3-trichloromethyl-1,2,4-thiadiazole) is one of the most extensively used fungicides for controlling phycomycetous fungi in plants, tomatoes, turf, and cotton as described by US Environmental Protection Agency (US EPA, 2000). Literature data about its distribution in aqueous environment are very scarce, but the reported maximum concentration of 0.23 ng m^{-3} of ETZ in Iowa air and its wide usage may predict its occurrence in natural waters (Peck and Hornbuckle, 2005). Based on the generic estimated exposure concentration model, the chronic and acute ETZ concentrations resulting from turf use in related water resources were 32.3 and $230 \mu\text{g L}^{-1}$, respectively (US EPA, 2000).

ETZ is a toxic chemical that can inhibit the hepatic drug metabolizing enzyme system (Dalvi and Howell, 1977). Potential exposure to ETZ from drinking water may engender the chronic dietary risk as it has been classified as a B2 carcinogen (US EPA, 2000). To avoid the potential threat of ETZ to human beings, drinking water standards have regulated a maximum contaminant level (MCL) in treated waters. For example, Australian drinking water guidelines set an MCL for ETZ at 0.1 mg L^{-1} (National Health and Medical Research Council of Australia, 2004). The European Union

(EU) drinking water standards more strictly regulate a level for any particular pesticide at 0.0001 mg L^{-1} and the sum of all pesticides at 0.0005 mg L^{-1} (EU, 2007).

Once ETZ occurs in raw waters at a concerned level, appropriate treatment processes have to be applied to comply with the drinking water standards. At water treatment plants, UV radiation is regarded as a promising disinfection means due to its effectiveness in bacteria inactivation and leading to a low concentration of disinfection byproducts (Sharpless and Linden, 2001; Meunier et al., 2006). Moreover, direct photolysis was also reported to be responsible for the degradation of some organic compounds in advanced oxidation processes such as UV/O_3 and $\text{UV/H}_2\text{O}_2$ (Adams and Randtke, 1992).

Even until now literatures about ETZ degradation, UV photodegradation included, are very limited. With this context in mind, this study was focused on the elimination of ETZ using UV radiation under conditions simulating those applied at water treatment plants. Furthermore, the reaction mechanism was proposed through identification of photodegradation byproducts. The detailed experimental scheme included: (1) study the photodegradation kinetics; (2) determine the quantum yield (Φ); (3) identify photodegradation byproducts; and (4) examine the feasibility of UV radiation for ETZ removal in natural waters.

2. Materials and methods

2.1. Standards and reagents

ETZ (99.5% purity), N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane and peroxidase from horseradish (lyophilized, 5KU) were purchased from

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Sigma–Aldrich. Atrazine (ATZ, 99% purity) was obtained from the National Research Center for Certified Reference, China. Other chemicals used in this study were at least of analytical grade and used without further purification.

2.2. Analytical methods

ETZ and ATZ were determined with gas chromatograph/mass spectrometer (GC/MS) (7890 GC and 5975 MSD, Agilent) equipped with an HP-5 MS column (30 m $\times$ 0.25 mm $\times$ 0.25 μ m film thickness). Helium gas was used as carrier gas at a flow rate of 1 mL min⁻¹. The oven temperature started at 60 °C and ramped linearly to 280 °C at 30 °C min⁻¹. The MS detector was operated in the electron ionization mode at 70 eV. The retention time for ETZ and ATZ was determined to be 7.5 and 8.6 min, respectively. The quantification and confirmation ions used in the selected ion monitoring mode were 213, 211 and 183 for ETZ, and 215 and 200 for ATZ. The detection limits for ETZ and ATZ were 0.1 and 0.3 μ M, respectively.

The concentration of H₂O₂ was determined by the peroxidase-DPD method (Bader et al., 1988). The concentrations of chloride, sulfate and nitrate were measured by a Metrohm 861 ion chromatograph. Total organic carbon (TOC) was analyzed with a Tekmar–Dohrmann Phoenix 8000 TOC analyzer.

2.3. Experimental

2.3.1. Photodegradation kinetics in distilled water

Photodegradation experiments were conducted in a 1-L cylindrical glass reactor filled with 1 L of fresh ETZ aqueous solution at 25 $\pm$ 2 °C. A low-pressure mercury vapor lamp primarily emitting radiation at 254 nm (nominal power 5 W, produced by Beijing Electric Light Source Institute) was placed vertically in a quartz sleeve at the center of the reactor. Iodide/iodate actinometry, which was originally proposed by Rahn (1997) and further developed by Goldstein and Rabani (2008), was employed to determine the incident radiation flux of the UV lamp (7.4 $\times$ 10⁻⁷ E s⁻¹, equivalent to a power output of 350 mW). The effective optical path length was thus calculated to be 4.0 cm.

Several series of experiments were first carried out in distilled water by varying the initial ETZ concentration, pH, and foreign substances. The initial ETZ concentration was varied in the range from 5 to 35 μ M. The pH was adjusted with 10 mM phosphate buffer (different ratios of H₂PO₄⁻ to HPO₄²⁻) to 6.0, 7.0 and 8.0, individually. Selected foreign substances, namely bicarbonate (1 mM), oxygen gas (flow rate = 1 L min⁻¹) and nitrogen gas (flow rate = 1 L min⁻¹) were introduced into the reaction system if required. At the onset of experiments, the lamp was allowed to warm up for 10 min. Samples were withdrawn at preselected intervals, and each 5 mL of aqueous sample was extracted with 2 mL of methyl tert-butyl ether (MTBE) immediately after sampling. The extraction mixture was agitated for at least 2 min to ensure adequate contact between the water and MTBE layers. The MTBE layer was analyzed with GC/MS. H₂O₂, anions and TOC were also analyzed if required. All experiments were conducted in duplicate.

2.3.2. Byproducts identification

Solid-phase extraction (SPE) was applied to samples prior to the analysis and identification of photodegradation byproducts. Each reaction sample of 250 mL was extracted using a 500-mg Waters Oasis HLB extraction cartridge. The cartridge was conditioned in sequence with 5 mL of methanol and 5 mL of distilled water. After passage of the sample, the cartridge was vacuum-dried. The analytes were then eluted with 4 mL of dichloromethane and 4 mL of methanol successively into a glass tube. The eluate was evaporated to dryness under a gentle stream of nitrogen gas and then

50 μ L of BSTFA and 50 μ L of pyridine were added. The glass tube was capped, vortexed for about 20 s, and placed in 60 °C water bath for 30 min to allow the derivatization reaction to complete. The mixture was allowed to cool down to room temperature and the residual BSTFA and pyridine were blown off under a gentle stream of nitrogen gas. Finally, the derivatives were dissolved in 250 μ L of hexane and analyzed by GC/MS. The GC oven temperature started at 40 °C and held for 2 min, ramped at 3 °C min⁻¹ to 100 °C and held for 5 min, ramped at 5 °C min⁻¹ to 150 °C, and further ramped at 20 °C min⁻¹ to 290 °C. The total analysis time for each sample was 46 min.

2.3.3. Photodegradation of etridiazole in natural waters

Three natural waters in Beijing area were selected to examine the effect of water matrix on the photodegradation of ETZ under otherwise similar water treatment conditions: (1) groundwater collected from Changping District; (2) sand-filtered water prior to disinfection collected from the No. 9 Waterworks; and (3) surface water collected from Jingmi Trench. These waters were filtered through a 0.45- μ m cellulose filter and stored at 4 °C until use. The dissolved organic carbon (DOC) value was 1.2, 2.6 and 9.7 mg L⁻¹ and the absorbance at 254 nm was 0.016, 0.032 and 0.048 for the groundwater, sand-filtered and surface water, respectively. ETZ was spiked at a low concentration of 1.4 μ M, and the solution pH value was adjusted to 7.0. Samples were withdrawn at preselected time intervals, and the ETZ concentration was measured. The effective UV fluence rates of the reactor were calculated to be 2.95, 2.87 and 2.81 mW cm⁻² for the groundwater, sand-filtered and surface water, respectively, based on the absorbance of the water samples and the reactor geometry using the point source summation method (White, 1999; Macauley et al., 2006).

3. Results and discussion

3.1. Effects of initial etridiazole concentration and pH

Fig. 1A shows that increasing the initial ETZ concentration would decrease its degradation efficiency. First-order kinetics is generally used to express the photodegradation of a micropollutant, denoted as C herein, in a vanishing absorption solution (Hessler et al., 1993),

$$-\frac{d[C]}{dt} = 2.3 \frac{\Phi \epsilon I_0 L [C]}{V} \quad (1)$$

where ϵ is the molar extinction coefficient; I_0 and L denote the incident radiation flux and optical path length in the UV reactor, respectively; and V represents the volume of reaction solution. As proposed by Nicole et al. (1990), in this case the optical density of the solution (i.e., ϵLC) should be below 0.02. The ϵ value for ETZ was determined to be 720 M⁻¹ cm⁻¹ in this work. Therefore, Eq. (1) was valid only when C_0 was less than 6.9 μ M considering an effective optical path length of 4.0 cm. The corresponding first-order rate constants (k_1) for $C_0 = 5 \mu$ M were deduced, as shown in Table 1. When C_0 increased above 6.9 μ M, the kinetics of photodegradation would deviate from the first-order rate law and start to approach the zero-order rate law (Hessler et al., 1993). Then, if the photodegradation of ETZ was approximated by the pseudo-first-order kinetics, the resulting rate constant would decrease as C_0 increased from 5 to 30 μ M.

Fig. 1B shows the change of normalized residual ETZ concentration with reaction time at different pH values ranging from 6.0 to 8.0, which represents the typical condition in drinking water treatment plants. The similar first-order rate constants in Table 1 indicate the negligible pH dependence of ETZ photodegradation. In the neutral pH range, deprotonated ETZ is the primary form in water

Fig. 1. Photodegradation of ETZ: (A) effect of initial ETZ concentration, pH = 7.0 and (B) effect of pH, $[ETZ]_0 = 5 \mu\text{M}$. The standard deviation of all data points was below 5%.

Table 1

First-order and pseudo-first-order rate constants of ETZ photodegradation under different experimental conditions in distilled water. Experimental conditions: incident radiation flux of UV lamp = $7.4 \times 10^{-7} \text{ E s}^{-1}$, $T = 25 \pm 2^\circ\text{C}$, $[\text{bicarbonate}] = 1 \text{ mM}$, nitrogen gas flow rate = 1 L min^{-1} , oxygen gas flow rate = 1 L min^{-1} .

Run	C_0 (μM) ^a	pH	Foreign substance	$k_1 \times 10^3$ (s^{-1}) ^b	R^2	$t_{1/2}$ (min)
1	5	7.0	None	4.3	0.990	2.7
2	20	7.0	None	3.4 ^c	0.998	3.4
3	30	7.0	None	2.6 ^c	0.997	4.5
4	5	6.0	None	4.5	0.999	2.6
5	5	8.0	None	4.3	0.998	2.7
6	5	7.0	Bicarbonate	4.3	0.983	2.7
7	5	7.0	Nitrogen	4.1	0.995	2.8
8	5	7.0	Oxygen	4.0	0.998	2.9

^a Initial ETZ concentration.

^b First-order rate constant.

^c Pseudo-first-order rate constant.

($\text{pK}_a = 2.77$, Tomlin, 2003). The insignificant pH influence on UV photodegradation rate of neutral propachlor was also reported by Benitez et al. (2004). Thus, no pH adjustment is required for eliminating ETZ by UV radiation in drinking water treatment.

3.2. Determination of quantum yield

A competition kinetic model has been previously used to determine the Φ value of a given organic compound (Benitez et al., 2004). According to this method, the Φ value of ETZ can be determined from the simultaneous photodegradation of a mixture of ETZ and ATZ. ATZ, whose Φ is known, was used as a reference compound in this study. Therefore, the following equation applies:

$$\frac{dC_E}{dC_A} = \frac{\Phi_E \epsilon_E C_E}{\Phi_A \epsilon_A C_A} \quad (2)$$

where E and A are referred to ETZ and ATZ, respectively. By rearrangement and upon integration of Eq. (2) we have:

$$\ln \frac{C_{E0}}{C_E} = \alpha \ln \frac{C_{A0}}{C_A} \quad (3)$$

where C_{E0} and C_{A0} are the initial ETZ and ATZ concentrations, and

$$\alpha = \frac{\Phi_E \epsilon_E}{\Phi_A \epsilon_A} \quad (4)$$

The plot of $\ln(C_{E0}/C_E)$ vs. $\ln(C_{A0}/C_A)$ was shown in Fig. 2. The α value obtained was 2.76. The Φ and ϵ values of ATZ are 0.033 mol E^{-1} and $3683 \text{ M}^{-1} \text{ cm}^{-1}$, respectively (Bolton and Stefan, 2002). Thus, the Φ value for ETZ was calculated to be $0.46 \pm 0.02 \text{ mol E}^{-1}$ at pH 7.0. This high Φ indicates that ETZ undergoes a fast photodegradation process.

3.3. Effect of foreign substances

The decomposition of an organic compound in photochemical processes may proceed via two pathways: (1) direct photodegradation in which the organic compound absorbs photons to get decomposed; (2) indirect photodegradation in which reactive intermediates generated from UV photolysis of the target compound and/or other co-existing substrates further react with the target compound (Lam and Mabury, 2005). The most common reactive intermediates formed in aquatic photochemical processes are reactive oxygen species (ROS) such as H_2O_2 , hydroxyl radical and superoxide radical. H_2O_2 can be generated in photochemical processes (Qiang et al., 2002), and its concentration up to $50 \mu\text{M}$ was detected during the UV degradation of ATZ (Beltrán et al., 1993). To investigate the influence of the ROS formed on the ETZ photodegradation, several foreign substances (i.e., bicarbonate, dissolved oxygen and nitrogen) were introduced to the reaction system.

Fig. 3A shows that although H_2O_2 was generated at somewhat varied rates in the presence of different foreign substances, all its concentrations were at trace levels (i.e., from 0 to $1.0 \mu\text{M}$). It was also reported by Beltrán et al. (1993) that the presence of bicarbonate had no notable effect on H_2O_2 formation during ATZ photodegradation.

Fig. 2. Plot of $\ln(C_{E0}/C_E)$ vs. $\ln(C_{A0}/C_A)$. Experimental conditions: pH = 7.0, $[ETZ]_0 = 5 \mu\text{M}$, $[ATZ]_0 = 5 \mu\text{M}$. The subscripts E and A represent ETZ and ATZ, respectively. The standard deviation of duplicate analyses was below 5%.

The generated H_2O_2 can undergo rapid photolysis under UV radiation (Nicole et al., 1990), yielding a photolysis product, namely hydroxyl radical. Since bicarbonate is a well-known hydroxyl radical scavenger, experiments were conducted to study the effect of bicarbonate on the degradation of ETZ. Fig. 3B shows that the ETZ degradation was not affected by the addition of bicarbonate, indicating a negligible hydroxyl radical contribution to ETZ degradation. Although bicarbonate is ubiquitous in natural waters, the results indicate that UV radiation is applicable to ETZ removal in natural waters when bicarbonate is present.

Lee et al. (2005) reported that due to the formation of superoxide radicals, a notable increase in photodegradation rate of N-nitrosodimethylamine was found in O_2 saturated solution, compared to that in N_2 saturated solution. However, Fig. 3B clearly shows that the ETZ photodegradation rates were very similar in the two reaction solutions respectively saturated with O_2 and N_2 , implying the negligible ROS involvement. Therefore, it is concluded that the decomposition of ETZ by UV radiation occurred predominantly via direct photodegradation in distilled water in our reaction system.

3.4. Proposed photodegradation mechanism

Fig. 4 shows the identification of organic byproducts, mass balance on chlorine atom and removal of TOC. By analyzing the ex-

tract from reaction solution with GC/MS, several pertinent peaks were tentatively identified as presented in Fig. 4A.

Comparing with the standard mass spectrum of ETZ, the probability of compound **1** being ETZ was 99%. ETZ has a molecular ion at m/z 246, an isotopic molecular ion containing one ^{37}Cl atom at m/z 248, and an abundant ion at m/z 211 resulting from the loss of one ^{35}Cl atom in the trichloromethyl group.

Compound **2** with a molecular ion at m/z 212 could correspond to 5-ethoxy-3-dichloromethyl-1,2,4-thiadiazole. It has an isotopic molecular ion containing one ^{37}Cl atom at m/z 214 and an abundant ion at m/z 184 with the loss of C_2H_4 in the ethoxyl group. The fragments agreed well with the mass spectrum previously reported by Van Welie et al. (1991).

Compound **3** with a molecular ion at m/z 246 may correspond to the silanized derivative of 5-ethoxy-1,2,4-thiadiazole-3-carboxylic acid. The molecular ion could lose CH_3 to give the ion at m/z 231 which would lose C_2H_4 in the ethoxyl group to give the ion at m/z 203. The molecular ion at m/z 246 could also lose the silane group to yield an ion at m/z 173. 5-Ethoxy-1,2,4-thiadiazole-3-carboxylic acid was identified as a biotransformation metabolite in the urine of rat and man (Van Welie et al., 1991).

Compound **4** with a molecular ion at m/z 218 (M) may correspond to the silanized derivative of 5-ethoxy-3-hydroxyl-1,2,4-thiadiazole. It has two isotopic molecular ions at m/z 219 (M+1) and at m/z 220 (M+2). The normalized intensities of M, M+1 and M+2 were 100, 13.4 and 7.7, which were very similar to the values of 100, 14.6, and 9.1, respectively, based on the isotopic calculation. The molecular ion could lose CH_3 to give an ion at m/z 203. Further loss of C_2H_4 in the ethoxyl group could produce an ion at m/z 175. It is noted that 5-ethoxy-3-hydroxyl-1,2,4-thiadiazole has never been reported before.

Fig. 4B shows chloride ion release and TOC removal as a function of reaction time. It should be mentioned that no notable formation of nitrate and sulfate ions were observed even when ETZ was completely degraded. Nitrogen and sulfur atoms remained in the thiadiazole ring. Chloride ion was the major anionic byproduct which accounted for about 90% with respect to chlorine mass at 60 min. Most chloro initially present in ETZ was released as chloride ion to the solution eventually, indicating that compound **2** was a minor species. The low removal efficiency of TOC indicates that ETZ could not be mineralized by UV radiation.

Fig. 5 illustrates the proposed mechanism for ETZ photodegradation. In this study, dechlorination of the trichloromethyl moiety and substitution of the trichloromethyl group by OH group occurred during photodegradation of ETZ in water by UV radiation. The homolysis of C–Cl bond was found to be the major step of photodegradation of captan and butachlor (Schwack and Flößer-Müller, 1990; Zheng and Ye, 2001). The homolytic cleavage of C–Cl bond would lead to the replacement of chloro by OH group and H atom (Burrows et al., 2002). Compound **2** could form via the latter pathway if sufficient hydrogen donors were present (Schwack and Flößer-Müller, 1990). In aqueous solution, however, this substitution is generally not favored. Therefore, the degree of formation of compound **2** was insignificant, which agrees well with results shown in Fig. 4B. Once the replacement of chloro by OH group advanced completely, 5-ethoxy-1,2,4-thiadiazole-3-carboxylic acid (compound **5**) would be generated. Its formation was also favored by the decrease of pH during the photodegradation of ETZ when phosphate buffer was absent. The cleavage of C–C bond which connects the trichloromethyl moiety with the thiadiazole ring could probably occur under UV radiation. Then, the replacement of the trichloromethyl moiety with OH group would yield 5-ethoxy-3-hydroxyl-1,2,4-thiadiazole (compound **6**).

Besides the identification of organic byproducts, their toxicity should also be concerned because the organic byproducts can sometimes be more toxic than the parent compound (Verstraeten

Fig. 3. Effects of foreign substances on: (A) H_2O_2 formation, $[\text{ETZ}]_0 = 35 \mu\text{M}$ and (B) ETZ degradation, $[\text{ETZ}]_0 = 5 \mu\text{M}$. Experimental conditions: pH = 7.0, [bicarbonate] = 1 mM, nitrogen gas flow rate = 1 L min^{-1} , oxygen gas flow rate = 1 L min^{-1} . The standard deviation of all data points was below 5%.

Fig. 4. Byproducts identification and TOC removal: (A) GC/MS spectra of organic byproducts and (B) chloride ion release and TOC removal. Experimental conditions: pH = 7.0, [ETZ]₀ = 30 μM . The Arabic numbers are assigned to identify the compounds. Error bars represent the standard deviation of duplicate analyses.

et al., 2002). Compound 2 was found to be highly toxic on an acute basis (US EPA, 2000). The toxicity of compounds 5 and 6 was unknown, but their fungitoxicity can be expected to be lower due

to the lack of trichloromethyl moiety which leads to the fungitoxicity of captan (Lukens, 1966). From safe-guarding the drinking water quality point of view, additional research about the chronic

Fig. 5. Proposed mechanism for photodegradation of ETZ. The Arabic numbers are assigned to identify the compounds.

dietary risk of ETZ degradation byproducts to human health should be addressed in the future.

3.5. Photodegradation of etridiazole in natural waters

To assess the effectiveness of ETZ removal by UV radiation in water treatment plants, additional experiments were carried out in natural waters including groundwater, sand-filtered water and surface water. Fig. 6 shows the change of normalized residual ETZ concentration as a function of UV fluence (UV dose, the product of UV fluence rate and irradiation time) in the three water media. The removal efficiency of ETZ was about 10 and 90% at the UV dose of 40 and 1375 mJ cm^{-2} , respectively. The UV dose of 40 mJ cm^{-2} is typically applied at water treatment plants (Meunier et al., 2006). As indicated above, the photodegradation of ETZ with a low concentration can be expressed by the first-order kinetics. As a result, the photodegradation rate constant of ETZ is independent of its initial concentration. By analogy, even if ETZ is present in water resource at a concentration of less than 1.4 μM , an ineffective removal can be reasonably deduced at the typical UV dose of 40 mJ cm^{-2} .

Results also indicate that among the three water media, the comparatively fastest ETZ removal was observed in the groundwater, followed by those in the sand-filtered water and surface water. Natural organic matter (NOM) is ubiquitously present in natural waters. NOM can impede the photodegradation of target compound through competitive absorption of UV radiation (Benitez et al., 2004). The groundwater had the lowest DOC concentration (i.e., 1.2 mg L^{-1}), which tends to account for the fastest photodegradation of ETZ. The indirect photodegradation was insignificant in natural waters in this study; otherwise the fastest photodegradation of ETZ would have occurred in the surface water which had the highest TOC concentration of 9.7 mg L^{-1} .

UV in combination with O_3 or H_2O_2 could enhance the destruction of micropollutants compared to UV alone (Hessler et al., 1993; Benitez et al., 2004). In order to meet the drinking water regulations for pesticides, ETZ included, UV/ O_3 or UV/ H_2O_2 which produces abundant hydroxyl radicals is expected to be more effective in pesticide degradation. Hydroxyl radicals can react very quickly towards pesticides with second-order rate constants generally ranging from 10^8 to $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (Buxton et al., 1988).

Fig. 6. Photodegradation of ETZ in natural waters. Experimental conditions: pH = 7.0, [ETZ]₀ = 1.4 μM. Error bars represent the standard deviation of duplicate analyses.

4. Conclusions

The simulated first-order rate constants decreased with the increase of initial ETZ concentration (i.e., 5, 20 and 30 μM), and was independent of the solution pH within the range of 6.0 to 8.0. The Φ value of ETZ was determined to be $0.46 \pm 0.02 \text{ mol E}^{-1}$. H₂O₂ was generated at trace levels and had little influence on photodegradation of ETZ. Direct photodegradation was the major mechanism for the decomposition of ETZ in distilled water by UV radiation.

Three organic byproducts, namely, 5-ethoxy-3-dichloromethyl-1,2,4-thiadiazole, 5-ethoxy-1,2,4-thiadiazole-3-carboxylic acid, and 5-ethoxy-3-hydroxyl-1,2,4-thiadiazole, were identified. The degree of dechlorination of ETZ reached about 90% at the end of reaction, while nitrate and sulfate were not detectable. The degree of mineralization was insignificant as indicated by the removal efficiency of TOC.

The fastest ETZ degradation was observed in groundwater, compared to sand-filtered water and surface water, probably due to the competitive absorption of UV radiation by NOM. Based on the results obtained, it could be expected that ETZ would not be removed effectively at the UV dose of 40 mJ cm^{-2} which was typically applied for drinking water disinfection.

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