Photodegradation of etridiazole by UV radiation during drinking water treatment

Chao Liu, Zhimin Qiang*, Fang Tian, Tao Zhang

State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences (RCEES), Chinese Academy of Sciences, Beijing 100085, China

A R T I C L E  I N F O

Article history:
Received 31 October 2008
Accepted 23 April 2009
Available online 23 May 2009

Keywords:
Etridiazole fungicide
UV radiation
Photodegradation
Quantum yield
Byproducts

A B S T R A C T

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 ± 0.02 mol E−1 at pH 7.0. H2O2 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.

© 2009 Elsevier Ltd. All rights reserved.

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 μg 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/O3 and UV/H2O2 (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...
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 × 0.25 mm × 0.25 μm 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 μM, 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 ± 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, generally used to express the photodegradation of a micropollutant, denoted as C herein, in a vanishing absorption solution (Hessler et al., 1993),

\[ \frac{d[C]}{dt} = 2.3 \frac{\Phi \epsilon I L C}{V} \]

where \( \epsilon \) 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., \( \epsilon L C \)) should be below 0.02. The \( \epsilon \) 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 μM considering an effective optical path length of 4.0 cm. The corresponding first-order rate constants (\( k_1 \)) for \( C_0 = 5 \) μM were deduced, as shown in Table 1. When \( C_0 \) increased above 6.9 μM, 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 μM.

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.
According to this method, the following equation applies:

\[ \frac{\Phi_{E}}{\Phi_{A}} = \frac{C_{E}}{C_{A}} \]

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

\[ \ln \frac{C_{E0}}{C_{E}} = \ln \frac{C_{A0}}{C_{A}} + \frac{1}{\alpha} \int \frac{dC_{E}}{C_{E}} \]

where \( C_{E0} \) and \( C_{A0} \) are the initial ETZ and ATZ concentrations, and \( \alpha = \frac{\Phi_{E}}{\Phi_{A}} \).

The plot of \( \ln \left( \frac{C_{E0}/C_{E}}{C_{A0}/C_{A}} \right) \) vs. \( \ln \left( \frac{C_{A0}/C_{A}}{C_{A0}/C_{A}} \right) \) was shown in Fig. 2. The \( \alpha \) value obtained was 2.76. The \( \Phi \) and \( \epsilon \) values of ATZ are 0.033 mol E\(^{-1}\) and 3683 M\(^{-1}\) cm\(^{-1}\), respectively (Bolton and Stefan, 2002). Thus, the \( \Phi \) value for ETZ was calculated to be 0.46 ± 0.02 mol E\(^{-1}\) at pH 7.0. This high \( \Phi \) 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\(_2\)O\(_2\), hydroxyl radical and superoxide radical. H\(_2\)O\(_2\) can be generated in photochemical processes (Qiang et al., 2002), and its concentration up to 50 \( \mu \)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\(_2\)O\(_2\) 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 \( \mu \)M). It was also reported by Beltrán et al. (1993) that the presence of bicarbonate had no notable effect on H\(_2\)O\(_2\) formation during ATZ photodegradation.

### Table 1

<table>
<thead>
<tr>
<th>Run</th>
<th>( C_0 ) (( \mu )M)</th>
<th>pH</th>
<th>Foreign substance</th>
<th>( k_1 \times 10^5 ) (s(^{-1}))</th>
<th>( R^2 )</th>
<th>( t_{1/2} ) (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>7.0</td>
<td>None</td>
<td>4.3</td>
<td>0.990</td>
<td>2.7</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>7.0</td>
<td>None</td>
<td>3.4(^a)</td>
<td>0.998</td>
<td>3.4</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>7.0</td>
<td>None</td>
<td>2.6(^a)</td>
<td>0.997</td>
<td>4.5</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>6.0</td>
<td>None</td>
<td>4.5</td>
<td>0.999</td>
<td>2.6</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>8.0</td>
<td>None</td>
<td>4.3</td>
<td>0.998</td>
<td>2.7</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>7.0</td>
<td>Bicarbonate</td>
<td>4.3</td>
<td>0.983</td>
<td>2.7</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>7.0</td>
<td>Nitrogen</td>
<td>4.1</td>
<td>0.995</td>
<td>2.8</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>7.0</td>
<td>Oxygen</td>
<td>4.0</td>
<td>0.998</td>
<td>2.9</td>
</tr>
</tbody>
</table>

\(^a\) Initial ETZ concentration.

\(^b\) First-order rate constant.

\(^c\) Pseudo-first-order rate constant.

(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 \( \Phi \) value of a given organic compound (Benitez et al., 2004). According to this method, the \( \Phi \) value of ETZ can be determined from the simultaneous photodegradation of a mixture of ETZ and ATZ. ATZ, whose \( \Phi \) is known, was used as a reference compound in this study. Therefore, the following equation applies:

\[ \frac{dC_{E}}{dC_{A}} = \frac{\Phi_{E}C_{E}}{\Phi_{A}C_{A}} \]

\[ \ln \frac{C_{E0}}{C_{E}} = \alpha \ln \frac{C_{A0}}{C_{A}} \]

The plot of \( \ln \left( \frac{C_{E0}/C_{E}}{C_{A0}/C_{A}} \right) \) vs. \( \ln \left( \frac{C_{A0}/C_{A}}{C_{A0}/C_{A}} \right) \) was shown in Fig. 2. The slope value was 2.76. The \( \Phi \) and \( \epsilon \) values of ATZ are 0.033 mol E\(^{-1}\) and 3683 M\(^{-1}\) cm\(^{-1}\), respectively (Bolton and Stefan, 2002). Thus, the \( \Phi \) value for ETZ was calculated to be 0.46 ± 0.02 mol E\(^{-1}\) at pH 7.0. This high \( \Phi \) indicates that ETZ undergoes a fast photodegradation process.

### Fig. 2

Plot of \( \ln \left( \frac{C_{E0}/C_{E}}{C_{A0}/C_{A}} \right) \) vs. \( \ln \left( \frac{C_{A0}/C_{A}}{C_{A0}/C_{A}} \right) \). Experimental conditions: pH = 7.0, \([ETZ]_0 = 5 \mu M, [ATZ]_0 = 5 \mu M\). The subscripts E and A represent ETZ and ATZ, respectively. The standard deviation of duplicate analyses was below 5%.
The generated H₂O₂ 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 O₂ saturated solution, compared to that in N₂ saturated solution. However, Fig. 3B clearly shows that the ETZ photodegradation rates were very similar in the two reaction solutions respectively saturated with O₂ and N₂, 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 extract 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 ³⁷Cl atom at m/z 248, and an abundant ion at m/z 211 resulting from the loss of one ³⁵Cl 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 ³⁷Cl atom at m/z 214 and an abundant ion at m/z 184 with the loss of CH₂ 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 CH₃ to give the ion at m/z 231 which would lose CH₄ 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 bioransformation 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-hydroxy-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 CH₂ to give an ion at m/z 203. Further loss of C₂H₄ in the ethoxyl group could produce an ion at m/z 175. It is noted that 5-ethoxy-3-hydroxy-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 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 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 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 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).
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. 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.
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 \(\mu\)M, 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\(_2\)O\(_2\) 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\(_2\)O\(_2\) 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 \(10^{10}\) M\(^{-1}\) s\(^{-1}\) (Buxton et al., 1988).

Fig. 5. Proposed mechanism for photodegradation of ETZ. The Arabic numbers are assigned to identify the compounds.
independent of the solution pH within the range of 6.0 to 8.0. The analyses.


4. Conclusions

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.

Acknowledgements

We are grateful to Professor C.P. Huang at the Department of Civil and Environmental Engineering, University of Delaware, USA, for his comments and suggestions on this manuscript. The work was funded by National Natural Science Foundation of China (20677071) and Key Technology R&D Program, Ministry of Science and Technology of China (2006BAJ08B02, 2006BAJ08B10).

References


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 pH value of ETZ was determined to be 0.46 ± 0.02 mol E/C\(_0\) which was typically applied for drinking water disinfection.

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.

Acknowledgements

We are grateful to Professor C.P. Huang at the Department of Civil and Environmental Engineering, University of Delaware, USA, for his comments and suggestions on this manuscript. The work was funded by National Natural Science Foundation of China (20677071) and Key Technology R&D Program, Ministry of Science and Technology of China (2006BAJ08B02, 2006BAJ08B10).

References


4. Conclusions

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.

Acknowledgements

We are grateful to Professor C.P. Huang at the Department of Civil and Environmental Engineering, University of Delaware, USA, for his comments and suggestions on this manuscript. The work was funded by National Natural Science Foundation of China (20677071) and Key Technology R&D Program, Ministry of Science and Technology of China (2006BAJ08B02, 2006BAJ08B10).

References


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 pH value of ETZ was determined to be 0.46 ± 0.02 mol E/C\(_0\) which was typically applied for drinking water disinfection.

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.

Acknowledgements

We are grateful to Professor C.P. Huang at the Department of Civil and Environmental Engineering, University of Delaware, USA, for his comments and suggestions on this manuscript. The work was funded by National Natural Science Foundation of China (20677071) and Key Technology R&D Program, Ministry of Science and Technology of China (2006BAJ08B02, 2006BAJ08B10).

References