Photolysis of cyflufenamid in liquid media
Zhangyu Zheng, Chunyan Zhang, Haiyan Shi, Zhiwei Liu, Jinsheng Duan and Minghua Wang

ABSTRACT

The photolysis of cyflufenamid (CFA) in different organic solvents and water under ultraviolet irradiation was investigated. The photolytic rate constant and photolytic half-life were measured for the different solvents. Factors influencing the photolysis of CFA were investigated, including initial concentration, types of solvent, pH, occurrence of catalyst (TiO2), and environmental substances (Fe3+, Fe2+, NO3, NO2). Photolysis of CFA followed first-order kinetics in various systems, and the photolytic rate of CFA decreased with increased initial concentration. Photolytic rates of CFA in different solvents were as follows: n-hexane > methanol > acetonitrile > ultrapure water > ethyl acetate. The pH had a significant effect on the photolysis of CFA, and the photolysis rate reached its peak at pH 9.0. NO2 and TiO2 had positive effects on the photolysis of CFA, while Fe2+ had an adverse effect. NO3 in aqueous solution had no effect on the photolysis of CFA. In addition, the rates of photolysis were accelerated at lower concentrations of Fe2+ (0.5–5 mmol L−1) and decreased at higher concentrations (10 mmol L−1). Moreover, a main photolytic product of CFA was confirmed to be N-cyclopropoxy-2,3-difluoro-6-(trifluoromethyl)benzamide, and cleavage of the amido bond was proposed to be the predicted photolysis pathway in n-hexane.

Key words | cyflufenamid, metabolite, photolysis pathway, photolysis, ultraviolet radiation

INTRODUCTION

The abuse of pesticides in environmental media and poses a great hazard to humans as well as the environment (Liu et al. 2010; Chowdhury et al. 2011). Studies on the environmental behavior of pesticides not only provide accurate data for risk evaluation of pesticides in the environment, but also give a scientific and rational guidance for the application of pesticides. Among the various environmental behaviors, photolysis is a common degradation pathway of pesticides in liquid media (Burrows et al. 2002; Massad et al. 2004; Kiss et al. 2007; Moreira et al. 2017). Pesticide may undergo direct or indirect photolysis through direct photon absorption and indirect photoreaction (Canonica & Tratnyek 2005; Prados-Joya et al. 2011; Pinna & Pusino 2011, 2012). Many factors play a significant role in the photolysis process, such as media (atmosphere, surface of the soil, surface water, and surface of the plant), light sources, physicochemical properties of pesticides, the nature of photocatalysts, and some environmental coexistence substances (Burrows et al. 2002; Chnirheb et al. 2012). Media and environmental coexistence substances can absorb solar radiation to reach an excited state and subsequently generate reactive oxygen species (ROS) such as hydroxyl radicals (OH·), peroxyl radicals (ROO·) and singlet oxygen (1O2). These ROS always play key roles in promoting or inhibiting the process of photodegradation (Filipe et al. 2013; Reddy & Kim 2015). In addition, good water solubility of pesticides can increase the dispersion ability of pesticide molecules and promote their photoorradiation absorption (Nélieu et al. 2004; Sevilla-Morán et al. 2008; Belaidi et al. 2012; Martínez-Zapata et al. 2013).

The products of photolysis may be more toxic and persistent than the parent in ecological systems. Therefore, they may pose a greater threat to non-target organisms in the environment (Sinclair & Boxall 2003; Sakellarides et al. 2005; Zhou et al. 2017). Thus, it is of great importance to understand the degradation pathways of pesticides, identify their degradation products for proper environmental risk assessments (ERA), and the rational use of pesticides.

Cyflufenamid (CFA) developed as a novel amidoximes fungicide by Nippon Soda Co. Ltd was used for the
Photolysis experiments

Photolysis experiments were conducted in a XT5409-XPC xenon-arc photostability test chamber (Xutemp, Hangzhou, China) equipped with vertical UV lamps. The irradiation intensity (3.00 mw cm⁻²) was measured by a UV-A radiometer (365 nm) (Handy, Beijing, China). All experiments were carried out at a temperature of 25 ± 1 °C.

The UV lamps were used as the radiation source to study the photolysis of CFA in liquid media. The quartz tubes contained 20 mL of each sample and were suspended inside the chamber using homemade metallic supports (Figure 1). The samples (2.0 mL) were taken out directly from the organic solvent and aqueous solutions by pipette at different irradiation times and analyzed subsequently. The control experiments were carried out at the same time under identical conditions but in the absence of irradiation.

The stock standard solution of CFA (1,000 mg L⁻¹) was prepared in acetonitrile. The standard working solutions were diluted into 0.5, 1.0, 2.0, 5.0, and 10 mg/L by the mixture of acetonitrile:water (v/v, 80/20). The different concentrations of CFA ranged from 1.0 to 10.0 mg L⁻¹ and were used to study the effect of initial concentrations on the photolysis of CFA. The solutions of CFA were prepared at 5 mg L⁻¹ in n-hexane, ethyl acetate, acetonitrile, methanol and water to evaluate the effect of solvents on the photolysis of CFA. The photolysis experiments were carried out with buffers (20 mL) of pH 4.0, 7.0, and 9.0, with 5.0 mg L⁻¹ CFA to evaluate the effect of pH. Furthermore, all

EXPERIMENT

Chemicals and materials

CFA (99.00% purity) was obtained from Jiangsu Longdeng Co., Ltd (Jiangsu, China). Methanol, acetone, n-hexane, acetonitrile, ethyl acetate, potassium nitrate, sodium nitrite, ferric chloride, ferrous sulfate, and TiO₂ of analytical grade were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd (Beijing, China). Ultrapure water was produced using a Milli-Q water purification system (Millipore, USA). The pH was determined using a PP-50 professional pH meter (Sartorius, Germany). Acetate buffer (pH 4), phosphate buffer (pH 7), and carbonate buffer (pH 9) were prepared according to standard methods (General Administration of Quality Supervision, Inspection and Quarantine of the People’s Republic of China 2014).
experiments were conducted in an aqueous solution (pH = 7) with 5.0 mg L\(^{-1}\) CFA to evaluate the effects of different concentrations of the following substances: Fe\(^{2+}\) and Fe\(^{3+}\) at 0.5, 1, 5, and 10 mmol L\(^{-1}\); NO\(_3\) and NO\(_2\) at 0.5, 5, 25, and 50 mg L\(^{-1}\); and TiO\(_2\) at 0.5, 5, 25, and 50 mg L\(^{-1}\).

**Extraction and analysis for CFA**

The samples (2.0 mL) were taken out directly from acetonitrile, methanol, and aqueous solutions (Fe\(^{3+}\), Fe\(^{2+}\), NO\(_3\), NO\(_2\), and TiO\(_2\)) in triplicate at different times (Table S1, available with the online version of this paper). The sample was analyzed by high-performance liquid chromatography (HPLC) with an Agilent 1260 HPLC-UV (Agilent, USA) equipped with an Eclipse XDB-C18 column (250 mm × 4.6 mm, 5 μm). The mixture of acetonitrile-water 80:20 (v/v) was used as a mobile phase with a flow rate of 1.0 mL min\(^{-1}\) at 30 °C under detector wavelength 220 nm with an injection volume of 20 μL. Under these conditions, the retention time for CFA was approximately 6.2 min. Good linearity was observed for CFA in the range of 0.5–10 mg/kg, and the linear regression equation was 
\[
y = 44.589x - 0.7250 \quad (R^2 = 1).
\]

The samples in n-hexane and ethyl acetate were analyzed using gas chromatography (GC) with an Agilent 7890A GC-ECD equipped with a DB-1701 capillary column (30 m × 250 μm × 0.25 μm). Nitrogen was used as the carrier gas with a constant flow of 2.0 mL min\(^{-1}\). The column temperature was initially 150 °C and was increased subsequently to 280 °C at a rate of 15 °C min\(^{-1}\), and then held for 2 min. The inlet and detector temperatures were 270 °C and 300 °C, respectively. The injection volume was 1.0 μL. Under these conditions, the retention time for CFA was approximately 9.0 min.

The photolysis kinetics of CFA followed the rules of first-order kinetics. The degradation rate constant (k) and half-life (T\(_{1/2}\)) were estimated according to the following equations:

\[
C_t = C_0e^{-kt}
\]
\[
\ln(C/C_0) = -kt
\]
\[
T_{1/2} = \ln 2/k
\]

where \(C_0\) (mg L\(^{-1}\)) and \(C_t\) (mg L\(^{-1}\)) are the concentrations of CFA at times zero and \(t\), respectively; \(t\) is the irradiation time, and \(k\) is the rate constant (min\(^{-1}\)) of the photodegradation.

**Identification of photolytic products**

A sample of 100.0 mg L\(^{-1}\) CFA in n-hexane was photodegraded in a quartz tube under ultraviolet lamp irradiation. The samples were withdrawn after 4 h and detected by GC-MS on an Agilent 6890N gas chromatograph equipped with a 5973N mass-selective detector (Agilent, USA). The separation of CFA from its photolytic products was performed using a HP-5 mass spectrometry (MS) capillary column (30 m × 250 μm × 0.25 μm) with helium as the carrier gas, at a constant flow of 1.0 mL min\(^{-1}\). The column temperature was initially 70 °C and then increased at a rate of 20 °C min\(^{-1}\) to 260 °C and held for 1 min. Next, it was heated up to 300 °C by 10 °C min\(^{-1}\) and held for 10 min. The injector temperature was set at 250 °C and the injection volume was 1.0 μL. The source, quadrupole, and transfer-line temperatures were 230 °C, 150 °C, and 280 °C, respectively. The MS system was operated in electron impact mode at 70 eV with an ion current of 270 μA. Full-scan MS data were acquired over the range of m/z 50–500 to obtain the fragmentation spectra of the photolytic products.

**RESULTS AND DISCUSSION**

**Photolysis kinetics of CFA**

The photolysis kinetics of CFA followed first-order kinetics in all experiments (Table S2, available with the online version of this paper). The rate constants (k) and half-life (T\(_{1/2}\)) depended on the various experimental conditions. The control experiment showed that CFA did not undergo hydrolysis in the dark. Therefore, it was further confirmed that the decreased concentration of CFA during the irradiation process was caused by photolysis reactions.

Subsequent experiments were undertaken to investigate indirect photolysis using the same initial concentration of CFA and different concentrations of pH, NO\(_3\), NO\(_2\), Fe\(^{2+}\), Fe\(^{3+}\), and TiO\(_2\).

**Effect of initial concentration on photolysis**

The effects of the initial concentration of CFA on photolysis are shown in Figure 2.

In the same luminous energy conditions, with the greater number of pesticide molecules, the greater the pesticide dose per unit area. The luminous energy of CFA molecule decreased with an increase of concentration of CFA. In addition, the metabolite was formed and also absorbed the
luminous energy. Therefore, the photodegradation rate of CFA was decreased with an increase of initial concentration (Chowdhury et al. 2014; Chen et al. 2016).

Effects of solvent on photolysis of CFA

According to the degradation efficiency, the photolytic rates in different media followed the order \(n\)-hexane > methanol > acetonitrile > ultrapure water > ethyl acetate, with half-lives of 13.4 to 121.6 min, respectively (Table 1). These half-life values were related mainly to the UV absorption of the organic solvents. The UV absorption wavelengths were less than 210 nm for \(n\)-hexane, methanol, acetonitrile, and water. The maximum UV absorption wavelength was 220 nm for CFA. The ethyl acetate with the maximum absorption of 256 nm competes with CFA for UV, which will reduce the absorption of CFA to UV. In addition, ethyl acetate in the C=O bond will affect the light absorption of CFA, and so the CFA photochemical degradation rate is slowest in ethyl acetate (Ou et al. 2005; Lu et al. 2007).

Effect of pH on the photolysis of CFA

The photolytic rate in buffer solutions of different pH under ultraviolet lamp irradiation followed the order: pH 9.0 > pH 7.0 > pH 4.0 (Figure 3). The half-life of CFA at pH 9.0 was 59.2 min, which was approximately half that of pH 4.0 (119.5 min). It could be inferred that the degradation of CFA occurred more easily in alkaline than neutral and acidic conditions.

There are a large amount of hydroxyl ions (OH\(^{-}\)) in alkaline solution, and hydroxyl radicals (OH\(^{·}\)) are generated under UV irradiation. The presence of hydroxyl radicals caused the cyclization of CFA to accelerate the degradation of CFA. Under acidic conditions, a large amount of H\(^{+}\) inhibited the hydroxylation of CFA in water matrices (Hua et al. 2000; Wang & Shi 2014; Chen et al. 2017).

Effect of ferric and ferrous ions on photolysis of CFA

As shown in Figure 4, when the concentrations of Fe\(^{3+}\) ranged from 0.5 to 5 mmol L\(^{-1}\), the half-life of CFA decreased from 50.6 to 14.4 min; however, it is worth mentioning that the half-life increased to 141.4 min when the concentration of Fe\(^{3+}\) was 10 mmol L\(^{-1}\). The results indicated that Fe\(^{3+}\) played a photocatalyst role when the

### Table 1 | The photolytic kinetics of CFA (at concentration 5 mg L\(^{-1}\)) in liquid media

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Rate constant (min(^{-1}))</th>
<th>Half-life (min)</th>
<th>Determination coefficient (R(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n)-hexane</td>
<td>0.0519</td>
<td>13.4</td>
<td>0.9553</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.0239</td>
<td>28.9</td>
<td>0.9770</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.0130</td>
<td>53.3</td>
<td>0.9548</td>
</tr>
<tr>
<td>Water</td>
<td>0.0090</td>
<td>77.0</td>
<td>0.9381</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>0.0057</td>
<td>121.6</td>
<td>0.9811</td>
</tr>
</tbody>
</table>
concentration was below 5 mmol L\(^{-1}\) during CFA photolysis. In contrast, the presence of Fe\(^{2+}\) had an inhibitory effect. Its half-life increased from 99.0 to 346.5 min as the Fe\(^{2+}\) concentrations increased from 0.5 to 10 mmol L\(^{-1}\).

The Fe\(^{2+}\) (Fe(OH)\(_2\)) solution system, the hydroxyl complex, and other substances competed with CFA for the absorption of light, reducing the fraction of light absorbed by CFA (Sevilla-Morán et al. 2008; He et al. 2011). Meanwhile, with the increase of irradiation time, the color of the turbidity of the aqueous solution increased, and the light absorption shield effect became stronger. For the Fe\(^{3+}\) solution systems, the formation of a large number of hydroxyl radicals and photooxidation in a certain range of concentrations increased the photolytic rates of CFA in water matrices. Additionally, CFA formed a complex with the Fe\(^{3+}\) and underwent direct photolysis (Safarzadeh-Amiri et al. 1999; Mazellier et al. 1997), which accelerated the degradation of CFA.

**Effect of NO\(_3^-\) and NO\(_2^-\) on photolysis of CFA**

When the concentration of nitrate (NO\(_3^-\)) increased from 0.5 to 50 mg L\(^{-1}\), the degradation rate showed no significant differences compared with the control (Table 2). However, nitrite (NO\(_2^-\)) enhanced the photolytic efficiency of CFA. Its half-life decreased from 72.9 to 42.5 min, with the concentration changing from 0.5 to 50 mg/L. The nitrate not only stimulated the photolysis for the formation of hydroxyl radicals but also inhibited the direct photolysis due to its light absorption (Sevilla-Morán et al. 2008). Because those two effects were relatively balanced, the nitrate had no significant effect on the photolysis of CFA. Some researchers found a similarly interesting phenomenon for photolysis of alloxynil and pharmaceuticals in sewage treatment plant effluents (Andreozzi et al. 2003; Sevilla-Morán et al. 2008).

**Effect of TiO\(_2\) on photolysis of CFA**

As shown in Figure 5, when the concentration of TiO\(_2\) was in the range of 0.5–50 mg L\(^{-1}\), the half-life of CFA increased from 32.1 min to 72.9 min compared to the control (77.5 min). TiO\(_2\) promoted the photolysis of CFA, and the improvement decreased as the concentration increased. TiO\(_2\) is a widely used additive for many industries, including food, pharmaceutical, and personal care products, and can easily enter the environmental system after use. TiO\(_2\) can reduce the oxidation–reduction potential of pesticide molecules and improve the utilization of light energy because of its strong oxidation (Wong & Chu 2003; Selli et al. 2008; Bougheloum & Messalhi 2009; Kondrakov et al. 2014). With the formation of hydroxyl radicals and H\(^+\) in the solution, CFA was oxidized and the photolysis of CFA was accelerated. However, the amount of the reaction substrate was constant and the light transmittance of the solution was reduced as the concentration of TiO\(_2\)

Table 2 | Photolytic constants of CFA in different NO\(_3^-\) and NO\(_2^-\) buffer solutions

<table>
<thead>
<tr>
<th>Concentration (mg L(^{-1}))</th>
<th>Rate constant (min(^{-1}))</th>
<th>Half-life (min)</th>
<th>Determination coefficient (R(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NO(_3^-)</td>
<td>NO(_2^-)</td>
<td>NO(_3^-)</td>
</tr>
<tr>
<td>0</td>
<td>0.0090</td>
<td>0.0090</td>
<td>77.0</td>
</tr>
<tr>
<td>0.5</td>
<td>0.0099</td>
<td>0.0095</td>
<td>70.0</td>
</tr>
<tr>
<td>5</td>
<td>0.0095</td>
<td>0.0106</td>
<td>72.9</td>
</tr>
<tr>
<td>25</td>
<td>0.0096</td>
<td>0.0122</td>
<td>72.1</td>
</tr>
<tr>
<td>50</td>
<td>0.0097</td>
<td>0.0163</td>
<td>71.4</td>
</tr>
</tbody>
</table>

Figure 4 | Effects of Fe\(^{3+}\) and Fe\(^{2+}\) on photolysis of CFA. The solution of Fe\(^{2+}\) and Fe\(^{3+}\) is prepared by ultra pure water (pH = 7), and the concentration of CFA is 5 mg L\(^{-1}\).
increased. Therefore, the positive effect of TiO₂ to the photolysis was weakened gradually because the light energy was insufficient.

**Photolytic products and proposed pathways**

The photolytic products of CFA in n-hexane were determined and identified by GC–MS. In comparison with the total ion current (TIC) (Figure 6(a)) of the CFA standard solution, a new peak was observed at 6.05 min (compound A), and the retention time of CFA was 9.53 min. According to the full scan MS information, the molecular ion peak of the parent ion was 412 (m/z), and the molecular ion peak of compound A was 294 (m/z). In the MS spectra of 412, major fragment ions (275, 294, 321) were observed (Figure 6(a)). In the MS spectra of 294, major fragment ions (294, 223, 203) were observed (Figure 6(b)), and in After cleavage of CFA’s amide bond, m/z = 294. Thus, the fracture...
mechanism was proposed to be the cleavage of the amide bond, and the metabolite was N-cyclopropoxy-2,3-difluoro-6-(trifluoromethyl) benzamide (Figure 6(c)).

CONCLUSION

The possible effects of different influences, including initial concentration, organic solvent, pH, and four different inorganic ions on the photolysis of CFA have been investigated. The photolysis of CFA followed the laws of first-order kinetics under UV lamp irradiation. The photolytic rate of CFA decreased with increased initial concentration. The degradation rates of CFA in different solvents showed the following order: n-hexane > methanol > acetonitrile > water > ethyl acetate. CFA was more easily photolyzed under alkaline conditions, reacting 2.0 times faster than under acidic conditions. There is no influence with the presence of NO3⁻, and the photolytic rates were increased by NO₂ and TiO₂. The photolytic rates were inhibited effectively by Fe²⁺. Interestingly, the photolytic rates were increased with lower concentrations of Fe³⁺, and the results were antipodal with higher concentrations (5 mmol L⁻¹). Further, the photolytic products in n-hexane were first identified by GC–MS. These findings are very significant to the photochemical fate of CFA in the environment, which may be helpful for understanding the photolytic behaviors of CFA in surface waters and the surface of plant leaves. The study of the photolysis can provide a scientific basis for CFA's environmental safety and scientific and rational use.

ACKNOWLEDGEMENTS

This work was supported by the National Key Research and Development Program of China (2016YFD0200207).

REFERENCES


European Food Safety Authority (EFSA) 2009 Conclusion regarding the peer review of the pesticide risk assessment of the active substance cyflufenamid. *EFSA Journal* **7**(5), 258r.


Chemosphere 95 (1), 370–378.


