



Article Photodegradation Behavior of Agricultural Antibiotic Oxytetracycline in Water

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Abstract: Due to their overuse in agriculture, antibiotics are discharged into the aquatic environment, which poses a threat to human health and aquatic organisms. The agricultural antibiotic oxytetracycline (OTC) persists in aquatic media for a long time due to its resistance to biological degradation. Photolysis is a main pathway for its degradation in the natural environment and wastewater treatment, and thus, the photolysis of OTC should be investigated. In this study, the effects of reaction conditions such as the irradiation conditions, the initial OTC concentration, and the water matrix on OTC photolysis were investigated. The most efficient degradation was observed when UV-C was used as the irradiation source ($k = 0.0148 \pm 0.0008 \text{ min}^{-1}$), and the removal ratio increased with higher light intensity. A lower initial OTC concentration and higher solution temperature were advantageous for the degradation of OTC. The presence of humic acid or inorganic ions negatively affected the degradation rate of OTC. In addition to the effects of the reaction conditions, the degradation kinetics of OTC in actual agricultural water and the photolysis of various antibiotics such as streptomycin, validamycin A, and oxolinic acid were further studied. This work proved that various factors could decrease the photodegradation of OTC, which raises the potential risks that are associated with the persistent use of antibiotics in the water environment. Therefore, the results of the present study can help to provide an understanding of the effects of various reaction conditions on the degradation of agricultural antibiotics.

Keywords: agricultural antibiotics; oxytetracycline; photodegradation; coexisting ions; actual agricultural water

1. Introduction

Agricultural antibiotics are widely used in modern agriculture for crop production and animal husbandry. Due to their high stability, agricultural antibiotics are incompletely removed by wastewater treatment and animal metabolism processes; thus, these substances are continually being transported to aquatic environments [1]. Therefore, the overuse of agricultural antibiotics can pose a threat to aquatic ecosystems (e.g., toxic effects on algae) and human health (e.g., as a cause of hypouricemia and hypokalemia) [2–4]. Due to their widespread occurrence and potential risks to humans and aquatic organisms, the detection of antibiotics in aquatic environments such as surface water and drinking water has been extensively studied in many regions [5]. For example, 13 antibiotics were detected (3.1–109 ng/L) in the surface water and sediments of a river in China [6]. The widespread presence of 14 antibiotics in the surface water (below 82.5 ng/L) in Singapore was also reported [7].

Oxytetracycline (OTC), a tetracycline-class antibiotic, is commonly used as an animal feed additive, but it is poorly absorbed, with 30–90% of the parent compound being



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). excreted [8]. Due to its resistance to biological degradation, conventional wastewater treatment is ineffective to remove OTC, and it is therefore emitted into the natural aquatic environment [9]. Therefore, OTC is commonly detected in the effluent wastewater treatment plant (564.30 ng/L) [10] and environmental water samples (10 to 388 μ g/L) [11]. Once it is discharged, OTC remains in the water for a long time before undergoing complex reactions. Among the various reactions in natural aqueous media, photodegradation is the predominant mechanism in determining the environmental fate of antibiotics in water [12,13]. Furthermore, understanding the photodegradation behavior of OTC in water is meaningful for wastewater treatment as photo-based advanced oxidation processes (AOPs) such as direct photolysis [14], UV/H₂O₂ [15], and UV/persulfate [16] treatments are efficient approaches for the degradation of OTC.

During the photodegradation of OTC, various parameters of the water matrix, such as the solution temperature and coexistence of inorganic ions or natural organic matter (NOM), are important factors that directly affect the elimination efficiency of OTC. For example, the thermodynamic collision model and direct photolysis kinetics of OTC at different temperatures indicate that the direct photolysis of OTC is accelerated at higher temperatures [14]. NOM, such as humic acid (HA) and fulvic acid (FA), can exhibit both positive and negative effects; the excited triplet states of NOM can generate reactive species (e.g., $O_2^{\bullet-}$, 1O_2) to promote degradation [17], but NOM can also inhibit photolysis by screening the light and/or scavenging the reactive species [18,19]. Similarly, inorganic ions can affect the degradation efficiency during UV photolysis [20].

Therefore, the aim of this study is to observe the effects of the water matrix on the degradation kinetics of OTC. Specifically, the effects of the solution temperature, the initial OTC concentration, the light intensity, and the coexistence of inorganic ions or NOM were investigated. Furthermore, the degradation kinetics of OTC in real agricultural water, as well as those of other commonly used antibiotics (streptomycin (SM), validamycin (VM), and oxolinic acid (OA)) were also investigated.

2. Materials and Methods

2.1. Chemicals

OTC ($C_{22}H_{24}N_2O_9$, $\geq 95\%$) and SM ($C_{21}H_{39}N_7O_{12}$, $\geq 95\%$) were purchased from Tokyo Chemical Industry Co., Ltd. (Toshima Kita-gu, Japan). OA ($C_{13}H_{11}NO_5 \geq 95\%$), formic acid (CH_2O_2 , $\geq 99\%$), and VM ($C_{20}H_{35}NO_{13}$) were purchased from Sigma-Aldrich Co., Ltd. (St. Louis, MO, USA). Sodium chloride (NaCl, $\geq 99\%$), sodium sulfate (Na $_2SO_4$, $\geq 98.5\%$), methyl alcohol (CH_3OH , $\geq 99.5\%$), and sodium hydroxide (NaOH, $\geq 99\%$) were purchased from Samchun Pure Chemical Co. Ltd. (Pyeong-taek, Korea). HA ($C_{187}H_{186}O_{89}N_9S_1$), sodium nitrate (NaNO₃, $\geq 99\%$), and sodium carbonate (Na $_2CO_3$, $\geq 99\%$) were purchased from Daejung Chemicals & Metals Co. Ltd. (Si-hueng, Korea). Acetonitrile (C_2H_3N , $\geq 99.9\%$) was purchased from Avantor Performance Materials, LLC (Radnor, PA, USA). All of the solutions were prepared with deionized water (18.2 M Ω /cm) using a Direct-Q 3 UV system (Millipore, Burlington, MA, USA).

2.2. Photodegradation Experiments

The photolysis experiments were conducted in a black acrylic box equipped with 4 W lamps. A quartz beaker containing 50 mL of the reaction solution was placed in the center of the acrylic box. The initial concentrations were adjusted to 100 mg/L for OTC, SM, and VM and 15 mg/L for OA. All of the photolysis experiments were conducted in duplicate. To investigate the factors affecting OTC photodegradation, photolysis experiments were conducted under various reaction conditions: (1) light irradiation sources: UV-C, UV-A, or visible light; (2) a different number of lamps: 2, 4, or 6 lamps; (3) initial OTC concentrations: 50, 100, or 150 mg/L; (4) solution temperatures: 15, 25, or 35 °C; (5) coexistence NOM

or the ions Cl^- , SO_4^{2-} , NO_3^- , and HA. To compare the degradation rate by photolysis, pseudo-first-order kinetics model was used as follows [21,22]:

$$K_{\rm obs} = -\frac{d\left[\ln\left(\frac{C}{C_0}\right)\right]}{dt}$$

2.3. Analytical Methods

The concentration of OTC in a sample was determined using a YL 9100 HPLC system (Youngin Chromass, Anyang-si, Korea) using a vacuum degasser unit, quaternary pump, column compartment with a SunFire[®] column ($4.61 \times 50 \text{ mm}$, 5 µm particle size), UV/Vis detector, and autosampler (YL 9150). The flow rate of the two mobile phases consisting of ACN and formic acid (0.1%) (15:85) was 1.0 mL/min.

The molar extinction coefficients of the four antibiotics at 254 nm were calculated using the Beer–Lambert Law:

 $A_{254} = \varepsilon_{254} C l$

where A_{254} is the absorbance at 254 nm, ε_{254} is the molar extinction coefficient which was measured at 254 nm (M⁻¹ cm⁻¹), *C* is the concentration (M) of the antibiotic, and *l* is the length of the cell (cm). The absorbance of each sample at 254 nm was determined using a UV-vis spectrophotometer (NEO-S2117, NEOGEN, Seoul, Korea).

3. Results and Discussion

3.1. Effects of Irradiation Source, Light Intensity, Initial OTC Concentration, and Solution *Temperature on OTC Degradation*

To investigate the effects of the light irradiation source on OTC degradation, the OTC solution was irradiated with visible light, UV-A, and UV-C (Figure 1a). Increasing the irradiation time increased the degradation of OTC, which can be attributed to the greater opportunity that is available to absorb photons. The degradation of OTC by all of the irradiation sources followed a pseudo-first-order kinetics procedure ($R^2 > 0.96$), and the observed rate constants (k) for visible light, UV-A, and UV-C were 0.1163 ± 0.0081 , 0.0982 ± 0.0035 , and 0.8915 ± 0.0398 h⁻¹, respectively (Figure 1b). Among the tested light irradiation sources, UV-C exhibited the most efficient OTC degradation. The estimated k value by UV-C irradiation was comparable to that of a previous study (0.0171–0.0321 min⁻¹), which performed OTC UV-C photolysis with different pH conditions [14,23]. The higher degradation rate that was obtained by UV-C than that which was obtained by UV-A or visible light is due to its higher photonic energy and absorption [24]. This result indicates that UV-C irradiation has the potential for its application to the direct photolysis treatment process owing to its fast degradation rate. The effect of light intensity on the degradation of OTC was investigated by changing the number of lamps (Figure 1c,d). The removal ratios of OTC at 120 min using 2, 4, and 6 lamps were 56.63 ± 0.98 , 81.80 ± 1.01 , and $91.33 \pm 0.52\%$, respectively. The increased degradation ratio with the additional lamps indicates the important role of light irradiation in OTC degradation. Subsequently, solutions with initial OTC concentrations of 50, 100, and 150 mg/L were prepared to observe the effect of the initial concentration on the degradation efficiency and k value (Figure 2a,b). The removal ratio of OTC at 120 min decreased from 87.01 \pm 0.87 to 67.55 \pm 0.99% when the initial concentration was increased from 50 to 150 mg/L. This result is similar to those in previous studies [25,26], and the decreasing trend can be attributed to the decreased exposure of OTC to UV irradiation when the initial OTC concentration was increased [27]. The effects of the temperature on the degradation of OTC via photolysis and the associated k value were then studied by adjusting the solution temperature to 15, 25, or 35 °C (Figure 2c,d). The rate of OTC degradation was accelerated with an increasing solution temperature, and the removal ratios after 120 min of UV irradiation at 15, 25, and 35 $^{\circ}$ C were 53.39 \pm 7.98, 74.84 \pm 1.99, and 81.43 \pm 0.96%, respectively, suggesting that temperature has a significant effect on OTC photolysis efficiency [14].



Figure 1. (a) Degradation efficiency and (b) pseudo-first-order kinetic plots of OTC under different light irradiation sources. (c) Effects of light intensity on the OTC degradation efficiency and (d) its pseudo-first-order kinetic plots.



Figure 2. Effects of (**a**) initial concentration and (**c**) reaction temperature on OTC degradation. Pseudofirst-order kinetic plots for different (**b**) initial concentration and (**d**) reaction temperature conditions.

3.2. Effects of HA and Inorganic Ions on OTC Degradation

NOM and inorganic ions are commonly present in natural water environments. Sufficient initial concentrations of inorganic ions (50 mg/L) and HA (10 mg/L) which were added to influence the degradation rate were added [28,29]. Figure 3a shows the effect of HA (10 mg/L) and inorganic ions (50 mg/L) on the OTC degradation efficiency. NOMs such as HA can act as a photosensitizer to produce reactive species (e.g., H_2O_2, O_2^{-1}, OH , and ${}^{1}O_{2}$ [30] or as an inhibitor to decrease the overall photodegradation efficiency of the target organic compound [31]. In the presence of HA, the removal ratio of OTC at 120 min decreased from 81.80 ± 1.01 to $69.31 \pm 0.63\%$, indicating that HA had a negative effect on the photolysis process. The k value decreased from 0.0148 ± 0.0008 to 0.0098 ± 0.0002 min⁻¹ when HA was added (Figure 3b). This can be attributed to the screening of light by HA. The estimated absorbance of the HA that was used in this study was 0.0184 mg/L/cm, and thus, it could inhibit the absorption of light by OTC [18]. Furthermore, HA can also scavenge excited-state organic molecules, resulting in a decreased photodegradation rate [28]. The inorganic ions Cl⁻, SO_4^{2-} , and NO_3^{-} inhibited the photodegradation of OTC, and the k values of the control solution and solutions containing coexisting Cl^{-} , SO_4^{2-} , or NO_3^- were 0.0148 \pm 0.0008, 0.0101 \pm 0.0004, 0.0110 \pm 0.0002, and 0.0106 \pm 0.0003 min⁻¹, respectively. The inhibitory effect of the anions might be due to the decreased transmittance of the UV irradiation, thereby decreasing the absorption of photons by OTC [32].



Figure 3. (**a**) OTC degradation efficiency and (**b**) pseudo-first-order kinetic plots in the presence of HA and inorganic anions.

3.3. Degradation of OTC in Agricultural Water and Photolysis of Other Agricultural Antibiotics

The water matrix of actual agricultural water is more complex than that of pure water as it contains various types of dissolved organic matter and inorganic ions. To fully investigate the effects of the complex water matrix, a photolysis experiment was conducted using OTC that was dissolved in agricultural water (Figure 4a,b). The characteristics of agricultural water are summarized in Table S1. The OTC was moderately degraded in agricultural water ($73.63 \pm 1.80\%$). However, the degradation efficiency was slightly inhibited when it was compared to that in pure water. This result indicates that the dissolved organic matter and inorganic ions that are present in the agricultural water inhibited the UV irradiation, which is consistent with the results that are presented in Section 3.2. In addition to OTC, the degradation kinetics of the common agricultural antibiotics SM, VM, and OA under UV-C irradiation were investigated (Figure S1). The initial concentrations of SM and VM were the same as that which was used for OTC (100 mg/L), while the initial concentration of OA was set at 15 mg/L due to its lower solubility in water (37 mg/L at pH 7.5) [33]. The removal efficiencies of OTC, SM, VM, and OA were 81.80 ± 1.01 , 39.57 ± 4.72 , 68.88 ± 7.47 , and $53.85 \pm 1.32\%$, respectively. Among the four antibiotics, OTC showed the highest degradation efficiency. This result is likely due to its higher molar extinction coefficient at 254 nm (OTC: $11,141 \text{ M}^{-1} \text{ cm}^{-1}$) when it is compared to those of the other antibiotics (SM: $0.000 \text{ M}^{-1} \text{ cm}^{-1}$, VM: $0.000 \text{ M}^{-1} \text{ cm}^{-1}$, and OA: 1328 M⁻¹ cm⁻¹) (Figure S2 and Table S2). The k and half-life $(t_{1/2})$ values that

were determined under various photolysis conditions during this study are summarized in Table 1. These results indicate that various operating conditions and water matrix changed the degradation kinetics of antibiotics during photolysis, and they can contribute to future studies for understanding the removal of antibiotics in the water treatment and natural water environment.



Figure 4. (a) Effect of actual agricultural water on OTC degradation and pseudo-first-order kinetic plots for (b) OTC under actual agricultural water conditions.

Table 1. Observed rate constants (*k*) and half-lives ($t_{1/2}$) determined in the photodegradation of agricultural antibiotics under various reaction conditions.

Parameter								
Irradiation Source	Antibiotic	Number of Lamps	Solution Temperature (°C)	Initial Con- centration (mg/L)	Coexisting Matter	k (min ⁻¹)	R ²	Half-Life, $t_{1/2}$ (min)
Visible light	OTC	4	25	100	-	0.0019 ± 0.0001	0.97	364.7
UV-A	OTC	4	25	100	-	0.0016 ± 0.0001	0.99	433.1
UV-C	OTC	4	25	100	-	0.0148 ± 0.0008	0.99	46.8
UV-C	OTC	2	25	100		0.0070 ± 0.0002	1.00	99.0
UV-C	OTC	6	25	100		0.0207 ± 0.0012	0.98	33.5
UV-C	SM	4	25	100	-	0.0044 ± 0.0003	0.97	157.5
UV-C	VM	4	25	100	-	0.0099 ± 0.0001	1.00	70.0
UV-C	OA	4	25	15	-	0.0065 ± 0.0002	1.00	106.6
UV-C	OTC	4	15	100	-	0.0062 ± 0.0003	0.98	111.8
UV-C	OTC	4	35	100	-	0.0141 ± 0.0001	1.00	49.1
UV-C	OTC	4	25	50	-	0.0172 ± 0.0011	0.97	40.3
UV-C	OTC	4	25	150	-	0.0095 ± 0.0003	1.00	72.9
UV-C	OTC	4	25	100	Cl ⁻	0.0101 ± 0.0004	0.99	68.6
UV-C	OTC	4	25	100	SO_4^{2-}	0.0110 ± 0.0002	1.00	63.0
UV-C	OTC	4	25	100	NO_3^-	0.0106 ± 0.0003	1.00	65.4
UV-C	OTC	4	25	100	HÅ	0.0098 ± 0.0002	1.00	70.7

4. Conclusions

The photodegradation kinetics of OTC were affected by various reaction parameters. UV-C irradiation resulted in the highest degradation rate $(0.891 \pm 0.040 \text{ h}^{-1})$ due to the higher photonic energy and absorption rates. The increased degradation efficiency with higher light intensity indicated the important role of light irradiation in the degradation of OTC. The initial OTC concentration and solution temperature markedly affected the OTC photodegradation kinetics. The presence of coexisting HA or inorganic ions negatively affected the photolysis efficiency due to their light-screening effect. Compared to that in pure water, the degradation rate of OTC in agricultural water was reduced, which was attributed to the existence of NOM and inorganic ions. Among the four agricultural antibiotics that

were tested (OTC, SM, VM, and OA), OTC showed the highest degradation rate due to its higher molar extinction coefficient at 254 nm (11,141 M^{-1} cm⁻¹). As photolysis is a major degradation mechanism of agricultural antibiotics in the natural aquatic environment and wastewater treatment, the results that have been obtained during this study should provide a better understanding of the removal of agricultural antibiotics under various photodegradation conditions.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/w14213379/s1, Figure S1: (a) Comparison of the degradation efficiencies of four agricultural antibiotics and (b) pseudo-first-order kinetic plots for the four agricultural antibiotics; Figure S2: Measured absorbances of the antibiotics at different concentrations for determination of their extinction coefficients; Table S1: Characteristics of actual agricultural water; Table S2: Determined molar extinction coefficients of the four agricultural antibiotics.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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