d Collection

보건학석사 학위논문

Degradation Characteristics of Acridine during UV/chlorination Reaction

UV/chlorination 반응에서의 아크리딘
저감 특성에 관한 연구

2017년 2월

서울대학교 보건대학원
환경보건학과 환경보건학 전공
최 대 진

Abstract

Degradation Characteristics of Acridine during UV/chlorination Reaction

Dae-jin Choi

Department of Environmental Health Sciences

Graduate School of Public Health

Seoul National University

Recently, pharmaceuticals, personal care products (PPCPs) and endocrine disrupting compounds (EDCs) have been detected at trace concentrations in water around the world. Even, several trace contaminants were detected in municipal wastewater treatment plant (WWTP) effluent and drinking water treatment plant (DWTP) that people are intake every day. Although these contaminants are present in trace concentrations, the environment and

ecosystem can be negatively affected by continuous exposure. Acridine, a three-ring compound, is group of water contaminants with mutagenic and carcinogenic activity. Acridine has been used as a chemical intermediate in the manufacture of dyes and the synthesis of pharmaceuticals. Also, acridine is generated in diesel exhaust, coal burning, coal tar and coke-oven emissions. Especially, acridine can be formed as a degradation intermediate of carbamazepine (CBZ) using as pharmaceutical by such as biodegradation and UV/H_2O_2 reactions. According to increase of environmental threat by residual contaminants in water treatment processes, many techniques have been developed by previous studies. Advanced oxidation processes (AOPs), the techniques characterized by the generation of radicals, can be applied to water treatment processes. In this study, chlorination, UV photolysis and UV/chlorination reactions were conducted to remove acridine in water. The UV-C light more effectively removed acridine than UV-A and UV-B lights in water. Under the UV/chlorination reaction, acridine was more effectively removed than by UV photolysis and chlorination only reactions. During UV/chlorination reaction, 100 ng/L acridine was removed to 80% within 60 min and completely removed after 240 min. The removal efficiency of acridine was higher at lower pH condition. The chlorine dose was a significant factor in the degradation of acridine in UV/chlorination reaction. DOM can inhibit degradation of acridine in water. By-products of acridine during UV, chlorination and UV/chlorination reactions were confirmed by

using mass spectrometer. Six acridine by-products were identified during UV photolysis reaction. Also, three acridine by-products was identified during chlorination and UV/chlorination reaction, respectively. By-products were generated when OH and Cl radicals degrade acridine during UV/chlorination reaction. Using time profiles of acridine by-products, the degradation pathway of acridine by-products was also proposed during UV photolysis, chlorination and UV/chlorination reaction. The results of our study can provide important information when the UV/chlorination reaction was conducted to remove acridine in WWTP and DWTP. Ultimately, this study is helpful to improvement in the public health though maintaining clean water.

Contents

List of Figures

List of Tables

Ⅰ. Introduction

1. Background

Recently, pharmaceuticals, personal care products (PPCPs) and endocrine disrupting compounds (EDCs) have been detected at trace concentrations (i.e., < 100 ng/L) in water around the world. The sources of pharmaceuticals and PPCPs and EDCs in water are medical waste, industrial activity, landfill leachates, runoff from agricultural fields and urban runoff (Westerhoff et al., 2005; Benotti et al., 2008; Murray et al., 2010; Yoon et al., 2010; Nam et al., 2014; Nakada et al., 2016). In addition, above 80% of pharmaceuticals were detectable in one municipal wastewater treatment plant (WWTP) effluent because of the incomplete removal of pharmaceuticals during a WWTP and receiving water was contaminated (Murray et al., 2010). Previous studies, several trace contaminants were detected in drinking water treatment plant (DWTP) effluent that people are intake every day (Stackelberg et al., 2004; Nam et al., 2014). However, conventional water treatment processes was not designed to remove residual trace contaminants in WWPT and DWTP. Although these contaminants in water are present in trace concentrations, the environment and ecosystem can be negatively affected by continuous exposure (Klavarioti et al., 2009; Murray et al., 2010). Therefore, many

studies have been conducted to confirm fate of trace contaminants and to remove the trace contaminants in water.

2. Information of the study compound

Acridine, a three-ring compound, belongs to azaarenes, an established group of water contaminant with mutagenic and carcinogenic activity (Cooney et al., 1983; Furst and Uetrecht, 1993; Vogna et al., 2004). Acridine was used as a chemical intermediate in the manufacture of dyes and the synthesis of pharmaceuticals. Also, acridine is generated in diesel exhaust, coal burning, coal tar and coke-oven emissions. Especially, acridine can be formed as a degradation intermediate of carbamazepine (CBZ) using as pharmaceutical by such as biodegradation and UV/H_2O_2 reactions in water environment (Kaier at al., 1996; Chiron et al., 2006; Laurentiois et al., 2012; Lekkerkerker and Teunissen et al., 2012). Therefore, it is important to confirm an occurrence of CBZ in water. CBZ widely used as antiepileptic and psychotropic activities has been detected by previous studies in water (Table 3).

The ecotoxicity testing results for acridine was informed in previous studies (Table 4). Also, the toxicity value of human body was studied that no observed effect concentration (NOEC) was 0.4 mg/L (Parkhurst et al., 1981). When human was exposed to acridine during a long time, symptoms appear in human body such as vomiting, respiratory difficulties, hypothermia and cyanosis.
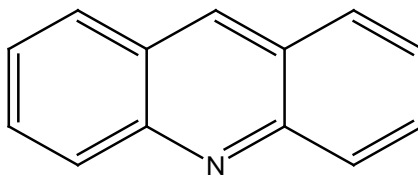
Figure 1. Molecular structure of acridine.

Table 1. Physicochemical properties of acridine.

Parameter	Acridine
CAS number	260-94-6
Molecular formula	$C_{15}H_9N$
Molecular weight (g mol^{-1})	179.22
Solubility (g mL^{-1})	0.1
Log K_{ow}	3.5
pK$_a$	5.45
Melting point (℃)	108
Boiling point (℃)	346

Table 2. Occurrence of acridine in various sample.

Water system	Concentration (ng/L)	Country	Reference
WWPT effluent	5.7 ~ 38	France	Leclercq et al., 2009
Surface soil	0.4 ~ 1.8	China	Wei et al., 2015
Road dust	17.1 ~ 77.8	China	Wei et al., 2015

Table 3. Occurrence of carbamazepine (CBZ) in water.

Water system	Concentration (ng/L)	Country	Reference
WWTP effluent	157.3 ~ 293.4	France	Togola et al., 2008
	155	USA	Gao et al., 2012
	85.1 ~ 90.1	Taiwan	Lai et al., 2016
	442.5 ~ 1007	France	Chiffre et al., 2016
	596.7 ~ 727.7	Australia	Robberts et al., 2016
Surface water	<0.5 ~ 356	South Wales	Kasprzyk-Hordern et al., 2008
	N.D[a] ~ 56	France	Togola et al., 2008
	24.9 ~ 214	Portugal	Paíga et al., 2016
	21 ~ 209	UK	Nakada et al., 2016
DWTP effluent	N.D ~ 43	France	Togola et al., 2008
WWTP effluent	<5 ~ 195		Choi et al., 2008
Mankyung river	N.D ~ 595		Kim et al., 2009
Han river	8.4 ~ 68	South Korea	Yoon et al., 2010
WWTP effluent	40 ~ 74		Behera et al., 2011
DWTP effluent	1.7 ~ 17.7		Nam et al., 2014

a : Not detected.

Table 4. Comparison of ecotoxicity testing results for acridine.

Organism	End point	Concentration (mg/L)	Reference
Daphnia magna	48h LD_{50}	2.3	Parkhurst et al., 1981
Chironomus tentans	48h LD_{50}	1.96	Cushman et al., 1981
Algae spp. (multiple species)	EC_{50}[b]	0.08 ~ 0.79	Dijkman et al., 1997
Algae spp.	EC_{50}	2.1	
Daphnia spp.	EC_{50}	4.6	Eisentraeger et al., 2008
Vibrio fischeri (5, 15, 30 min)	EC_{10} EC_{50}	0.78 ~ 0.98 5.34 ~ 6.90	
Pseudokirchneriella subcapitata	EC_{10} EC_{50}	0.11 0.61	Donner et al., 2013
Daphnia magna	EC_{10} EC_{50}	0.39 0.71	

a : Lethal dose for 50 percent kill.

b : Effective concentration value.

3. Water treatment processes

Pharmaceuticals, PPCPs and EDCs were informed as persistent organic contaminants due to difficulty of removal in conventional water treatment system. Therefore, many techniques have been developed by previous studies.

UV photolysis have been commonly used for removing emerging contaminants in previous study (Pereira et al., 2007). However, UV alone reaction was not effective in removing pharmaceuticals (Vogna et al., 2004; Kim et al., 2009).

Chlorination reaction has also been commonly used in water treatment process due to low cost of chlorine (Acero et al., 2010). Especially, chlorination reaction can degrade the aromatic compounds such as trihalomethanes (THMs) and haloacetic acids (HAAs) which was known as potential carcinogen (Singer et al., 1999). However, chlorination reaction was not designed to removal trace contaminants. Moreover, chlorination reaction was informed to generate by-products of degradation target compound. Generated by-products may be more toxic than original compound. Therefore, more strong treatment has been required to remove the by-products as well as original compound.

Advanced Oxidation Processes (AOPs), the techniques characterized by the generation of radicals, can be applied to the suitable degradation of

pharmaceuticals, PPCPs and EDCs during water treatment processes (Kim et al., 2009; Cruz et al., 2012). AOPs can be conducted in combination with several oxidation techniques (UV/H_2O_2, UV/O_3, UV/Fenton, UV/chlorination) to increase the removal efficiency and reaction velocity of the residual trace contaminants in water treatment processes (Shemer et al., 2006; Kim et al., 2009; Lajeunesse et al., 2013).

Degradation of acridine was studied by using AOPs in previous studies (Table 5). In previous studies, acridine was mainly degraded by using UV/H_2O_2 and biodegradation reactions. However, it has not been completely removed and degradation by-products of acridine was not studied by using AOPs in previous studies. Also, biodegradation was required to reacting a large time and UV/H_2O_2 reaction was expensive to apply removing residual water contaminants.

In this study, therefore, UV/chlorination reaction combined UV photolysis and chlorination was applied to remove acridine in water. Previous studies (Lyon et al., 2012; Nam et al., 2015) reported that removal efficiency during UV/chlorination reaction was higher than UV photolysis and chlorination reactions. Also, we conducted to identify degradation by-products of acridine during UV photolysis, chlorination, UV/chlorination reactions.

Table 5. Previous studies on acridine degradation by AOPs

Compound	Media	Treatment process	Operational condition	Analysis	Findings	Reference
Acridine	Swage sluge, Aquifer materials (contaminated by landfill leachate)	Biodegradation	$[C]_0$: 1 µg/mL	HPLC GC-MS	1 µg/mL of acridine was reduced to 0.05 1 µg/mL after one week of incubation	Knezovich et al., 1990
		Biodegradation	$[C]_0$: 1 to 6 µg/mL		Identify of transformation of acridine and its derivatives	Kaiser et al., 1996
	Water	UV/H$_2$O$_2$	$[CBZ]_0$: 0.5 mM $[H_2O_2]_0$: 100 mM pH 7	GC-MS	0.005 mM of acridine was generated CBZ degradation and was removed under 0.001 mM. during 50 min.	Vogna et al., 2004
		Photolysis, ClO$_2$ oxidation, Biodegradation	$[C]_0$: 50 µg/L UV wavelength : 250 to 190 nm $[ClO_2]_0$: 13.5 mg/L	GC-MS LC-MS	76% acridine removal in photolysis and 38% acridine removal in ClO$_2$ treatment	Kosjek et al., 2009

4. Objectives

In this study, we established the optimal method to analyze acridine with liquid chromatography - tandem mass spectrometry (LC-MS/MS). Laboratory experiments were performed to determine Kinetics of acridine during UV photolysis, chlorination and UV/chlorination reactions in various conditions (UV photolysis condition, pH, chlorine dose, DOM). Next, to identify degradation by-products of acridine, full scanning of samples was conducted with mass spectrometer. Additionally, we confirmed time profiles of acridine by-products with LC-MS/MS and proposed possible degradation pathways during UV photolysis, chlorination and UV/chlorination reactions though using ACD/MS fragmenter software.

Ⅱ. Materials and methods

1. Chemicals

Acridine ($C_{13}H_9N$; ACS regent, 99%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). The stock solution of acridine for analysis was dissolved in 1 g/L of methanol (CH_3OH; Optima grade, Fisher Scientific, Pittsburgh, PA, USA) and diluted from 1 to 100 ng/L before the measurement.

In addition, acridine was carried out in a circulating photolysis chlorination reaction. Sodium hypochlorite solution (NaOCl, $Cl_2 \geq 4\%$, Sigma-Aldrich Co. Ltd., USA) and sodium thiosulfate ($Na_2S_2O_3$, Sigma-Aldrich Co. Ltd., USA) were used as chlorine disinfectant, and its quencher. Humic acid (HA, Sigma-Aldrich Co. Ltd., USA) was used as the dissolved organic matter. Hydrochloric acid (HCl; Sigma-Aldrich Co. Ltd., USA) and Sodium hydroxide (NaOH; Mallinckrodt, St. Louis, MO, USA) were used to adjust the pH condition of solution. Ammonium acetate ($CH_3CO_2NH_4$; Sigma-Aldrich Co. Ltd., USA), ammonium formate (HCO_2NH_4; Sigma-Aldrich Co. Ltd., USA) and formic acid (HCOOH, Fluka, Buchs, Switzerland) were used as buffer solution in the analytical mobile phase during measurement of acridine with LC-MS/MS.

2. Laboratory experiments

The experiments of photolytic degradation of acridine were conducted by a circulating photolytic reactor system. A stirred 2 L glass bottle was used as a reservoir. A peristaltic pump (Cole-Parmer, Vernon Hills, IL, USA) was connected for circulating system. The reactor system was connected with flexible teflon tube. The solution was constantly circulated in the reactor system at a flow rate of 1 L/min. The photolytic reactor system is shown in Figure 2.

The UV chamber consisted of four UV lamps (San-kyo electrics, 20 W) and six quartz columns (10 mm × 650 mm). The UV lamps used at experiment were UV-A lamp (365 nm), UV-B lamp (312 nm) and UV-C lamp (254 nm). The intensity of UV lamps was confirmed by a radiometer (VLX-3W Radiometer 9811-50, Cole-Parmer, Vernon Hills, IL, USA) at a distance of 20 mm. The light intensity of four UV lamp was 3.0 mW/cm^2 (UV-A), 3.3 mW/cm^2 (UV-B) and 4.0 mW/cm^2 (UV-C). The UV chamber and bottle in solution were covered with an aluminum foil in order to minimize UV exposure. The absorbance value of acridine was measured with ultraviolet-visible spectrometer (Biomate 3, Thermo FisherSciece, Icn., Waltham, USA).

Chlorination experiments were conducted at the circulating photolytic reactor system without UV radiation. The chlorine concentration was

determined by a concentration of Cl_2 with the sodium hypochlorite dose (mL). It was determined using the N, N-diethyl-p-phenylenediamine (DPD) powder pillow colorimetric method (USEPA approved HACH 8021 method) with a HACH DR/890 Colorimeter (HACH Company, Loveland, CO, USA). UV/chlorination reaction were also performed using the circulating photolytic reactor system by spiking the hypochlorite in solution.

The degradation kinetics were performed by spiking 200 ng of acridine in 2L of distilled water and NaOCl solution was added into the bottle. To confirm degradation kinetics of acridine at constant time intervals, 200 mL of solution in bottle was withdrawn for solid-phase extraction (SPE). Then, 1 mL of 0.1 M sodium thiosulfate was injected to the collected sample to quench residual chlorine.
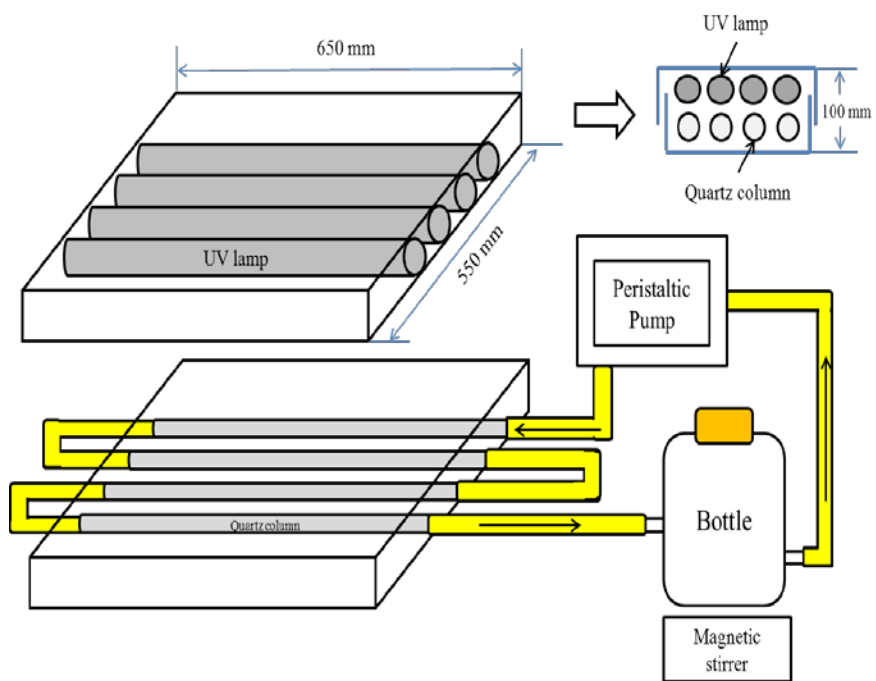
Figure 2. Schematic diagram of a circulating photolytic reactor system.

3. Analytic methods

All Samples were filtered through 0.45-µm GF/C filter (Whatman, UK) to remove impurities. SPE was conducted using a hydrophile–lipophile balance cartridge (Oasis HLB, Waters, USA). Next, the cartridges were conditioned with 5 mL of methanol and distilled water. Then, samples were loaded on the cartridges. After samples loading, the cartridges were dried for 10 min. The cartridges were eluted with 5 mL of methanol in tube. Using a nitrogen evaporator (CVE-3100, EYELA, Japan), the samples were evaporated. Finally, 1 mL of methanol was loaded in tube to dissolve the remaining compound. Samples that was gathered in 2 mL of vial (Agilent technologies, USA) were measured with HPLC (Nexera, Shimadzu, Kyoto, Japan) connected to a triple-quadrupole mass spectrometer (API-4000, Foster City, Canada) with an electron ion spray source working in positive mode. Target compounds were separated with a reverse-phase C_{18} column (Xterra MS 3.5 µm; 2.1×100 mm, Waters, Milford, MA, USA). The isocratic mobile phase was 5:95 water with 10 mM ammonium formate and 0.3% formic acid (v/v): methanol. The flow rate was 0.2 mL/min, the injection volume was 10 µL and the temperature of column oven was 20 ℃.

For degradation product identification, samples were analyzed by a triple quadrupole mass spectrometer using a 1 mL glass syringe (Hamilton Co.,

Reno, NV, USA). The mass spectrometer was performed with an electrospray ion source in positive mode. Identified precursor ions though full scanning of samples were fragmented to confirm product ions using collision with nitrogen gas.

The method detection limits (MDLs) were evaluated in the range 1.00 ~ 1.70 ng/L throughout the experiment. The absorbance of acridine was detected by using UV spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan). By-products of acridine was detected by mass spectrometer full scanning from 30, 60, 120, 240 reaction time, respectively. Then, degradation efficiency of by-products was measured by using LC-MS/MS. The proposed structures and degradation pathways of by-products were identified by using ACD/MS Fragmenter (ACD Labs, Advanced Chemistry Development, Inc., Canada).

Ⅲ. Results and discussion

1. Absorbance spectrum of acridine and removal efficiency by UV photolysis condition

The compound has an inherent absorbance spectrum and the UV photolysis condition caused different removal efficiency of acridine in water. Therefore, it was important to identify a characteristic absorbance spectrum of acridine. Figure 3 shows result in absorbance spectrum of acridine detected by using UV spectrometer. The photosensitivity of acridine was the most sensitive at 248 nm and the second peak of absorbance of acridine is detected at 354 nm.

Degradation process of organic matter using UV photolysis reaction has been widely used for water treatment system (Eq. (1) ~ (4)). The main mechanism of the UV photolysis reaction is the following ones (Legrin et al., 1993).

$$C + h\nu \rightarrow C^* \qquad\qquad (1)$$

$$C^* + O_2 \rightarrow {}^{\bullet}C^+ + {}^{\bullet}O_2{}^- \qquad\qquad (2)$$

$$R - X + h\nu \rightarrow {}^{\bullet}R + {}^{\bullet}X \qquad\qquad (3)$$

$$\cdot R + O_2 \rightarrow RO_2 \qquad\qquad (4)$$
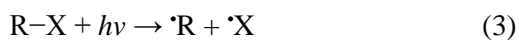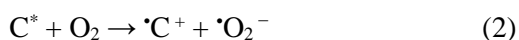
Legrin et al. reported that photo-oxidation reactions upon electronic excitation of the organic substrate imply in most cases an electron transfer from the excited-state (C^*, Eq. (1)) to groundstate molecular oxygen (Eq. (2)), with subsequent recombination of the radical ions or hydrolysis of the radical cation, or homolysis (Eq. (3)) to form radicals which then react with oxygen (Eq. (4)).

Figure 4 shows results of removal efficiency of acridine according to UV photolysis conditions and chlorine. All acridine was removed in UV-C + Cl_2 reaction and the removal efficiency of acridine during UV-A + Cl_2 reaction was higher than that during UV-B + Cl_2 reaction. Due to different detected photosensitivity of acridine, the above result was obtained during the degradation experiments. Therefore, UV-C was appropriate to remove acridine from water.

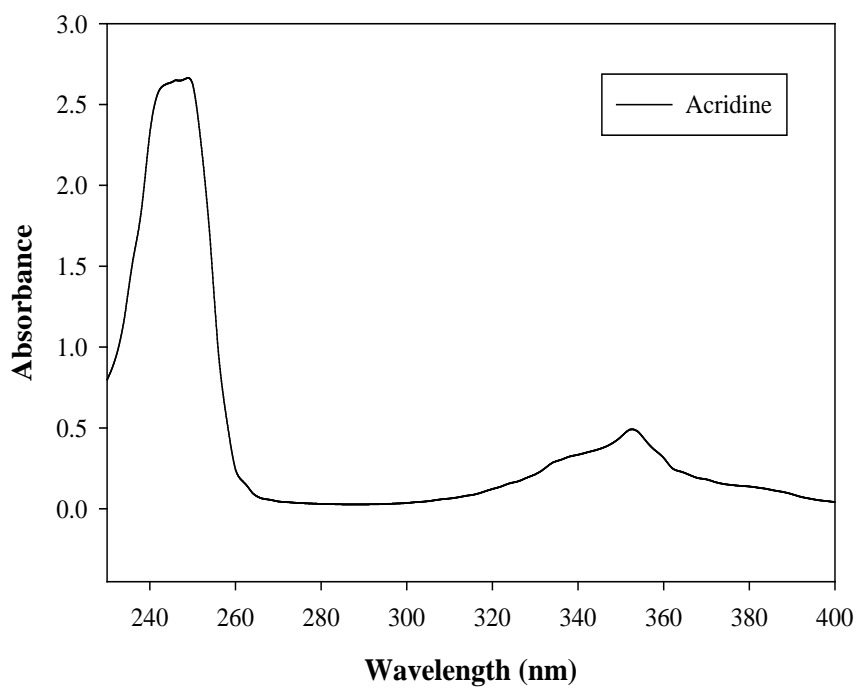**Figure 3.** Absorbance spectrum of acridine based on the UV wavelength ([Acridine]$_0$ = 100 ng/L, pH = 7).

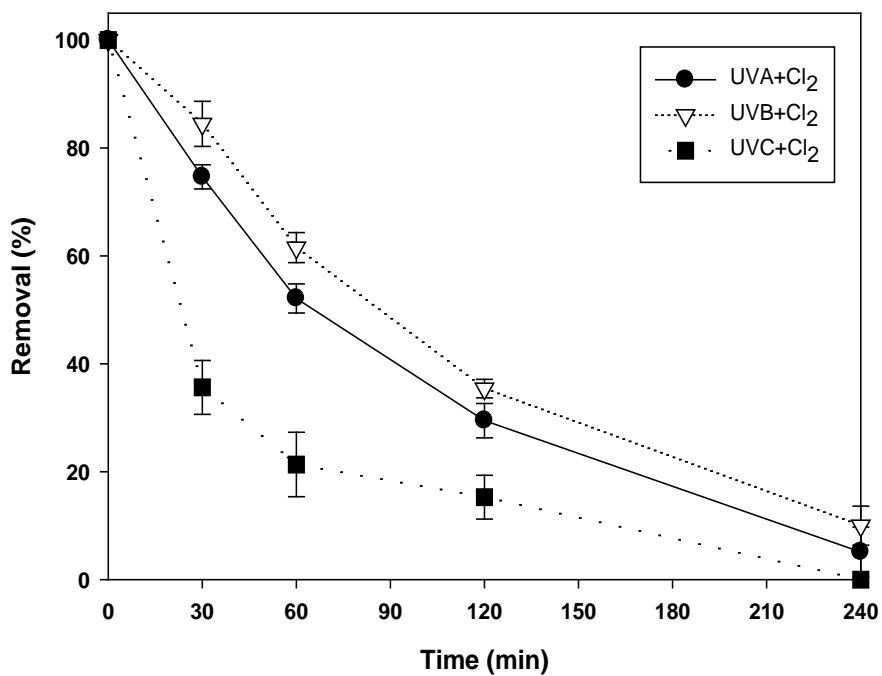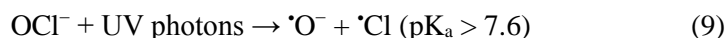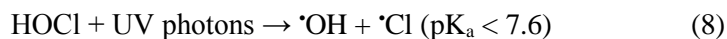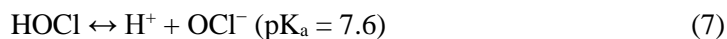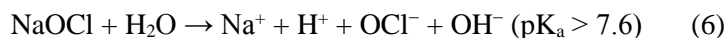**Figure 4.** The removal of acridine in UV-A, UV-B and UV-C combined chlorination reactions (n = 2, $[Acridine]_0 = 100$ ng/L, $[Cl_2]_0 = 5$ mg/L, UV-A $_{intensity} = 2.5$ mW/cm^2, UV-B $_{intensity} = 3.5$ mW/cm^2, UV-C $_{intensity} = 4.0$ mW/cm^2, pH = 7).

2. Kinetics of acridine in UV photolysis, chlorination-only, and UV/chlorination reactions

Figure 5 shows degradation of acridine results during UV photolysis, chlorination-only, and UV/chlorination reactions. The removal efficiency of acridine during UV/chlorination reaction was higher than removal efficiency of the two reactions. Chlorination reaction was used to degrade organic pollutants through the oxidation of free chlorine (Westerhoff et al., 2005; Michael et al., 2007; Nam et al., 2015). However, the predominant active species from the UV/chlorine reaction is OH radical (Nowell et al., 1992). Although the target compound was different in the previous study (Qin et al., 2014), the results of removal aspect was similar (UV/chlorination > UV photolysis > chlorination). The production of OH radicals, when aqueous chlorine solutions are exposed to UV, has enabled the UV/chlorination reaction to become a potential advanced oxidation process (Jing et al., 2011). The mechanisms of UV/chlorination reaction (Emmanuel et al., 2004; Feng et al., 2007; Jing et al., 2011; Qin et al., 2014; Nam et al., 2015) is represented depicted according to the following equations from (5) to (12).

$$NaOCl + H_2O \rightarrow HOCl + NaOH \ (pK_a < 7.6) \qquad (5)$$

$$NaOCl + H_2O \rightarrow Na^+ + H^+ + OCl^- + OH^- \ (pK_a > 7.6) \qquad (6)$$

$$HOCl \leftrightarrow H^+ + OCl^- \ (pK_a = 7.6) \qquad (7)$$

$$HOCl + UV \ photons \rightarrow {}^{\bullet}OH + {}^{\bullet}Cl \ (pK_a < 7.6) \qquad (8)$$

$$OCl^- + UV \ photons \rightarrow {}^{\bullet}O^- + {}^{\bullet}Cl \ (pK_a > 7.6) \qquad (9)$$

$${}^{\bullet}O^- + H_2O \rightarrow {}^{\bullet}OH + OH^- \qquad (10)$$

Scavenging reactions by HOCl, and OCl⁻

$${}^{\bullet}OH + OCl^- \rightarrow {}^{\bullet}OCl + OH^- \qquad (11)$$

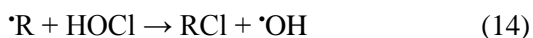$$HOCl + {}^{\bullet}OH \rightarrow {}^{\bullet}OCl + H_2O \qquad (12)$$

Figure 6 shows that removal efficiency of acridine was high during the UV/chlorination reaction under acidic condition (pH = 3). Hypochlorous acid (HOCl) is formed when NaOCl is used as the source of chlorine (Eq. (5), Emmanuel et al., 2004). OH and Cl radicals having strong oxidative power were generated during UV/chlorination reaction under acidic condition (Eq. (8)). Previous studies reported the rate constants of OH radical scavenging by OCl⁻ and HOCl species as 8.8×10^9/M·s (Eq. (11)) and 8.5×10^4/M·s (Eq. (12)), respectively (Watts and Linden., 2007; Nam et al., 2015; Kim et al., 2016). This can be explained that scavenging of OH radicals mainly generate under presence of OCl⁻ ions. Thus, to increase removal efficiency of acridine, we should conduct the UV/chlorination reaction under acidic pH condition.

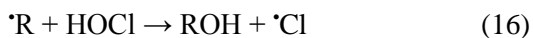Next, we investigated the effect of chlorine dose during UV/chlorination

reaction. Figure 7 showed that the removal efficiency of acridine was higher when the high chlorine dose was used in UV/chlorination reaction.

The result of Figure 8 shows effect of dissolved organic matter (DOM) during UV/chlorination reaction. The removal efficiency of acridine was inhibited when DOM concentration was increased in UV/chlorination reaction. DOM present in natural waters plays an important role about pesticide degradation (Dimou et al., 2004). However, DOM, being the primary light-absorbing species in surface water, can inhibit the rate of photolysis and can efficiently scavenge OH radicals (Dimou et al., 2004; Torrents et al., 1997). In addition, previous studies (Feng et al., 2007; Nam et al., 2015) reported that DOM could influence the two chain reactions by OH and Cl radicals in water during the UV/chlorination reaction (Eq. (13) to (16)).

OH radical chain

$$^{\bullet}OH + RH \rightarrow {^{\bullet}R} + H_2O \qquad (13)$$

$$^{\bullet}R + HOCl \rightarrow RCl + {^{\bullet}OH} \qquad (14)$$

Cl radical chain

$$^{\bullet}Cl + RH \rightarrow {^{\bullet}R} + HCl \qquad (15)$$

$$^{\bullet}R + HOCl \rightarrow ROH + {^{\bullet}Cl} \qquad (16)$$
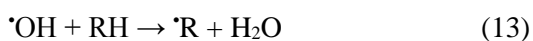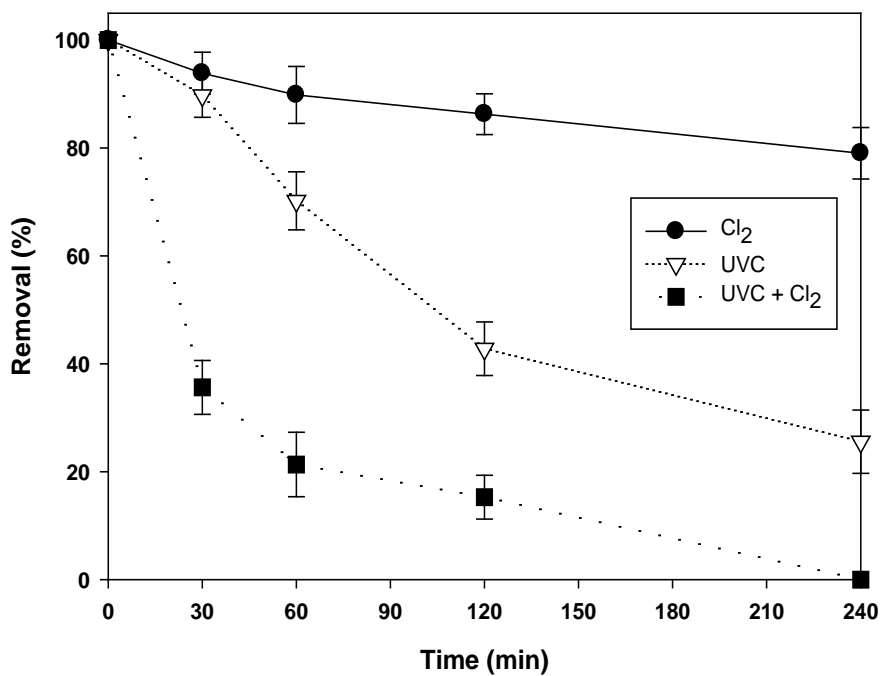
Figure 5. The removal of acridine in UV photolysis, chlorination-only, and UV/chlorination reaction (n = 2, [Acridine]$_0$ = 100 ng/L, [Cl$_2$]$_0$ = 5 mg/L, UV-C $_{intensity}$ = 4.0 mW/cm^2, pH = 7).
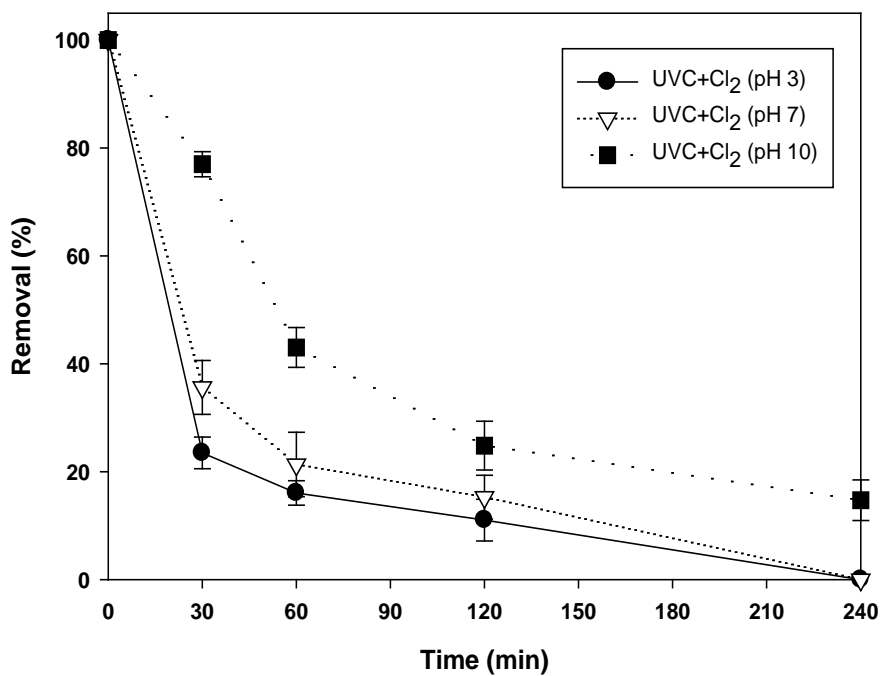
Figure 6. The removal of acridine in pH conditions during UV/chlorination reaction (n = 2, $[Acridine]_0 = 100$ ng/L, $[Cl_2]_0 = 5$ mg/L, UV-C $_{intensity} = 4.0$ mW/cm^2).
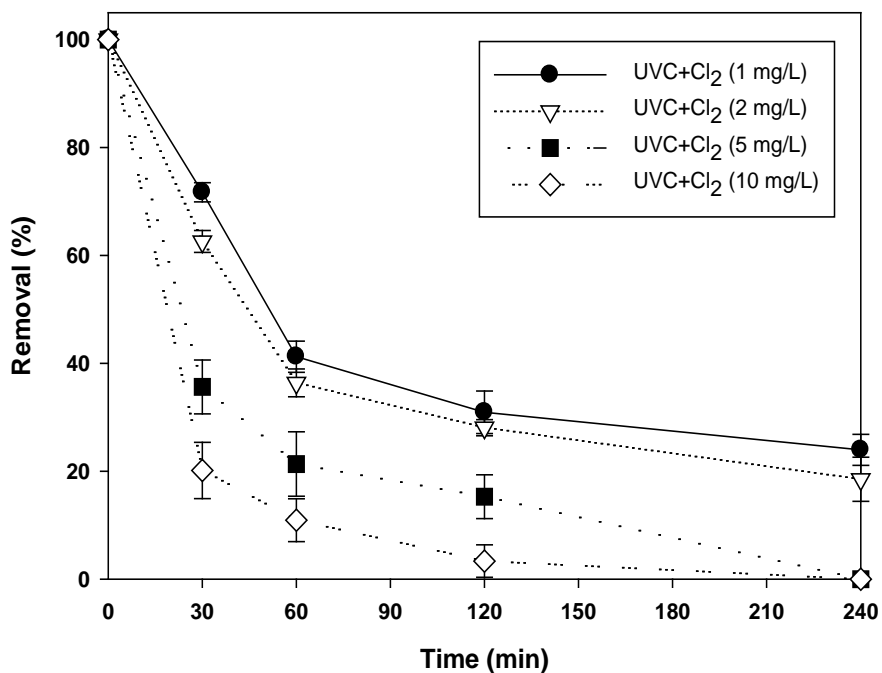
Figure 7. The effect of acridine by chlorine dose during UV/chlorination reaction (n = 2, [Acridine]$_0$ = 100 ng/L, UV-C $_{intensity}$ = 4.0 mW/cm^2, pH = 7).
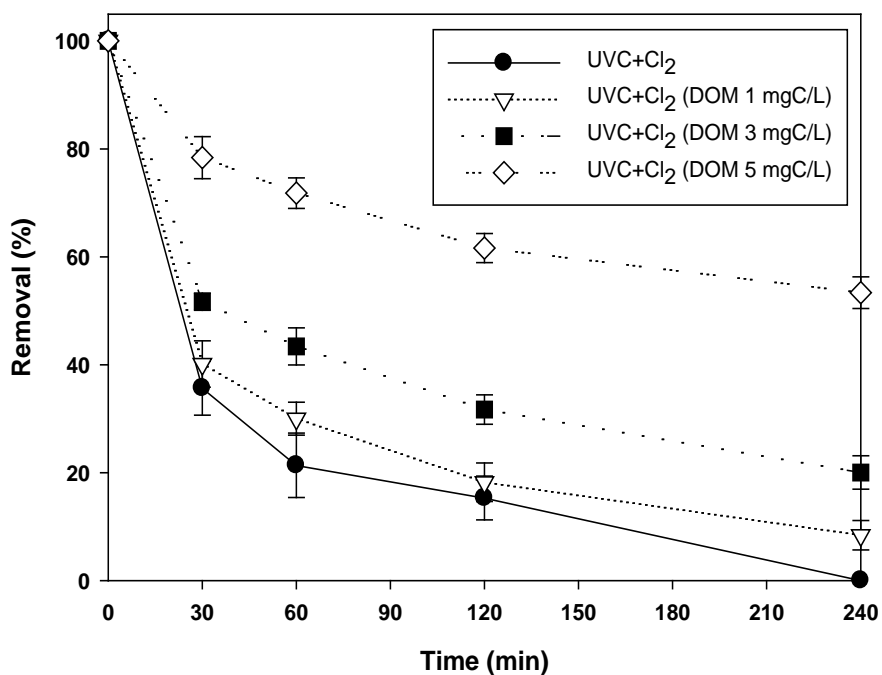
Figure 8. The effect of acridine by DOM concentration during UV/chlorination reaction (n = 2, [Acridine]$_0$ = 100 ng/L, [Cl$_2$]$_0$ = 5 mg/L, UV-C $_{intensity}$ = 4.0 mW/cm^2, pH = 7).

3. By-products identification during reactions

We confirmed the results of acridine removal efficiency during three reactions (UV photolysis, chlorination, UV/chlorination) in various condition. In recently years, many researchers have been interested in generation of degradation by-products during water treatment processes. Therefore, we also conducted experiments to identify generation of degradation by-products and time profiles during three reactions by using LC-MS/MS. Degradation by-products of acridine was selected in the electro spray ionization (ESI) full scan mode using mass spectrometer. Acridine by-products were determined by comparing precursor and product ions detected in the reaction samples. In addition, structures and pathways of degradation by-products of acridine during three reactions was proposed by using ACD/MS fragmenter software.

3.1. By-products in UV photolysis reaction

During UV photolysis reaction, six by-products were identified from the degradation of acridine. Precursor ion of six by-products was m/z 108, 124, 130, 138, 156 and 196 (Table 6). Figure 9 shows the time profiles of acridine by-products. Time profiles of acridine by-products represent generation and degradation aspect of by-products during the reaction. All by-products increased during UV photolysis reaction. Especially, we confirmed that by-product 1 (m/z 108), 2 (m/z 124) and 3 (130) were major by-products during UV photolysis reaction. Although peak area of by-products increased, it may decrease in large time reaction and more strong water treatment process.

Figure 10 shows the proposed degradation pathways of acridine by-products during UV photolysis reaction. Structure and pathway of acridine by-products were proposed by using ACD/MS fragmenter software that predict to fragment of compound in conditions. Equations from (1) to (4) is major mechanism that generate by-products during UV photolysis reaction. Super oxide radical attack to C=C double bonds and nitrogen free electron pair transfer reaction occur during UV photolysis reaction. Proposed degradation by-product 6 (m/z 196) was introduced in previous study degrading CBZ as acridone (Chiron et al., 2006).

Table 6. Information of acridine by-products generated during UV photolysis reaction.

Compound	Chemical Formula	Predicted molecular weight	Precursor ion (m/z)	Product ions (m/z)
Acridine	$C_{13}H_9N$	179	180	152, 151
By-product 1	C_7H_9N	107	108	91, 79
By-product 2	C_7H_9NO	123	124	95, 81
By-product 3	C_9H_7N	129	130	119, 101
By-product 4	$C_8H_{11}NO$	137	138	95, 93
By-product 5	$C_{11}H_9N$	155	156	139, 99
By-product 6	$C_{13}H_9NO$	195	196	165, 99

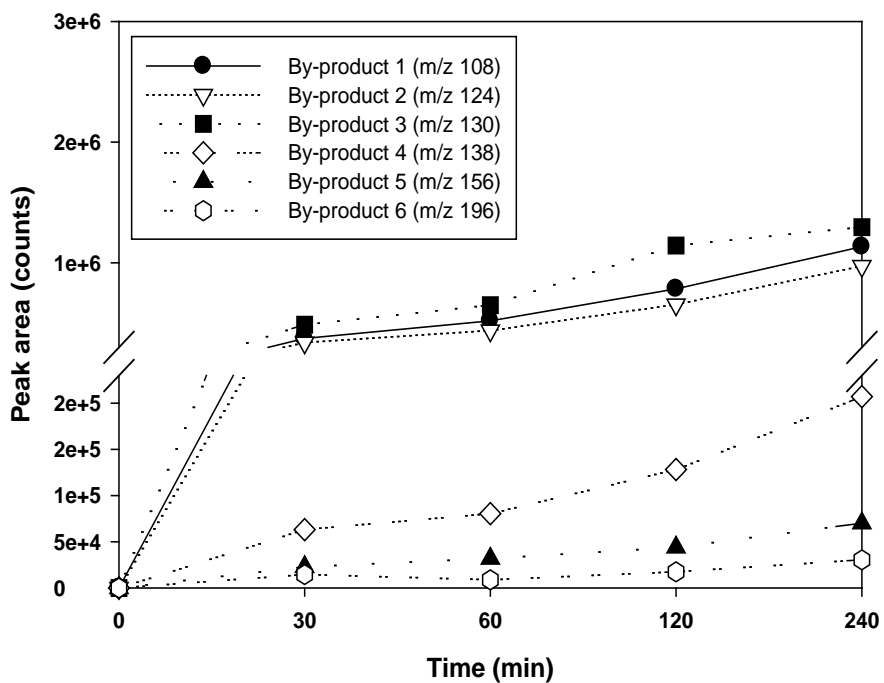**Figure 9.** Time profiles of acridine by-products during UV photolysis reaction ([Acridine]$_0$ = 100 ng/L, UV-C $_{intensity}$ = 4.0 mW/cm^2, pH = 7).
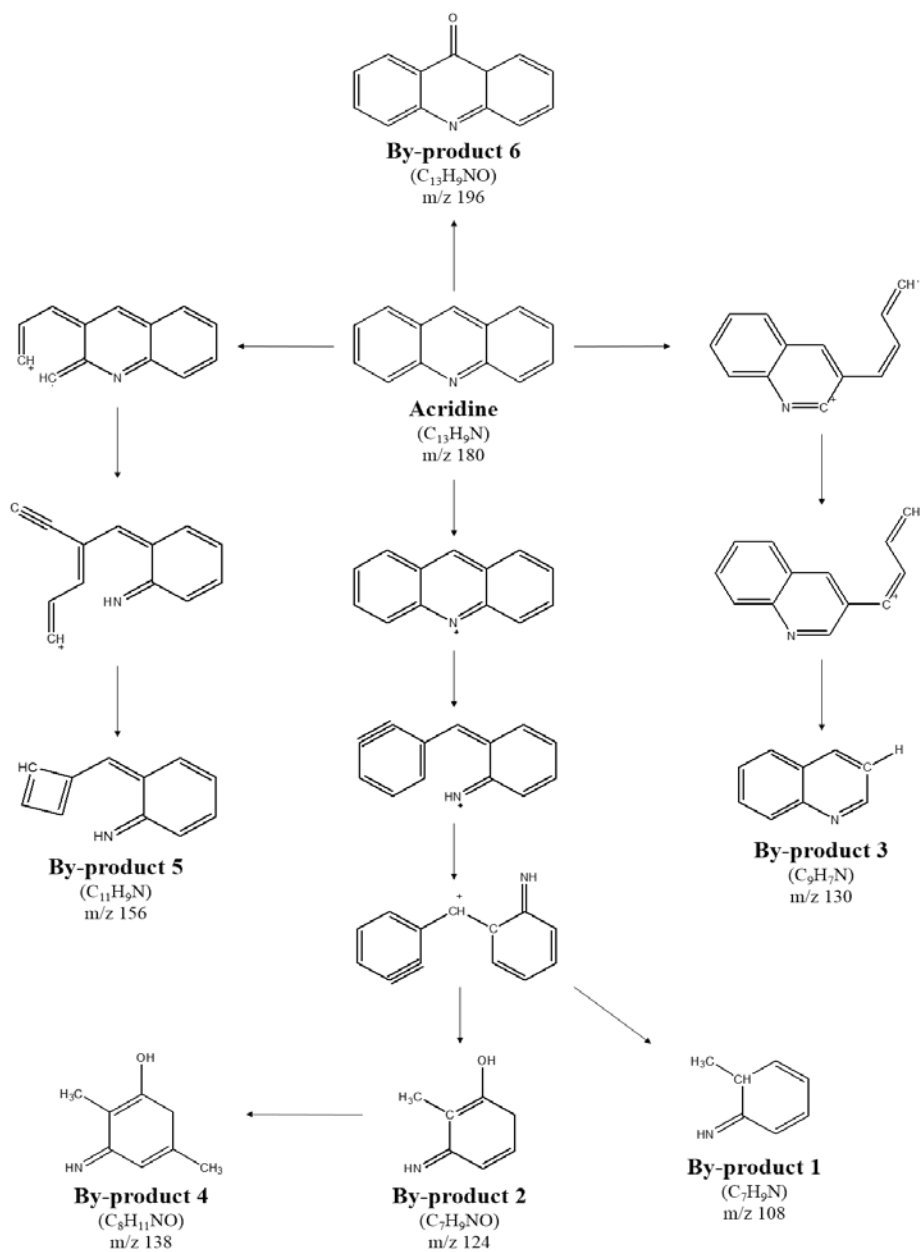
Figure 10. Proposed degradation pathways of acridine by-products during UV photolysis reaction ([Acridine]$_0$ = 100 ng/L, UV-C $_{intensity}$ = 4.0 mW/cm^2, pH = 7).

3.2. By-products in chlorination reaction

During chlorination reaction, three acridine by-products were identified from the degradation of acridine, with m/z 114, 239 and 255. Acridine by-products, which had high ionization intensities, is selected in ESI full scan mode. Information of acridine by-products is shown in Table 7.

Time profiles of acridine by-products during chlorination reaction is shown in Figure 11. By-product 7 (m/z 114) and 9 (m/z 255) increased at the beginning of the reaction, but it represented a decreasing tendency after 120 min. Though this results, we confirmed that by-product 9 was removed well in chlorination reaction. By-product 9 was generated by combining OH radical at by-product 8 (m/z 239). By-product 9 decreased after 120 min due to slight reduction of by-product 8 during 60 to 120 min. Also, by-product 8 continue to increase after 120 min, indicating that by-product 8 was not removed in chlorination reaction. Peak area of acridine by-products in the reaction was lower than acridine by-products generated during UV photolysis reaction. It was judged that generation of acridine by-products was less in chlorination reaction or simultaneous analytical method was not suitable.

Figure 12 shows the proposed degradation pathways of acridine by-products by using ACD/MS fragmenter software during chlorination reaction. Acridine By-products during chlorination reaction was generated from main

mechanism. The main mechanism during chlorination reaction is shown in Equation from (5) to (7).

Table 7. Information of acridine by-products generated during chlorination reaction.

Compound	Chemical Formula	Predicted molecular weight	Precursor ion (m/z)	Product ions (m/z)
Acridine	$C_{13}H_9N$	179	180	152, 151
By-product 7	C_5H_4ClN	113	114	73, 74
By-product 8	$C_{12}H_9Cl_2N$	238	239	221, 57
By-product 9	$C_{12}H_9Cl_2NO$	254	255	223, 137

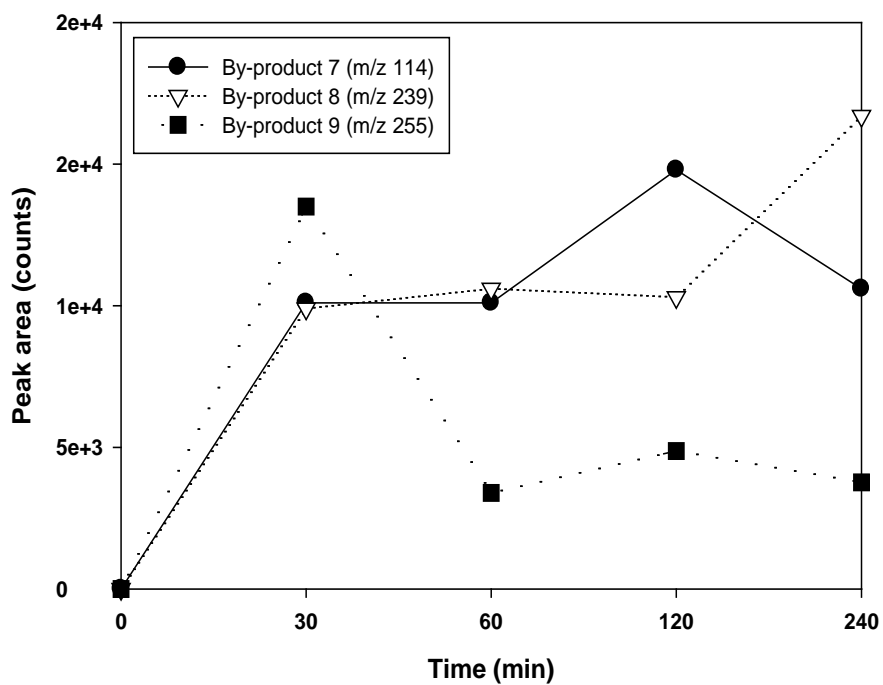**Figure 11.** Time profiles of acridine by-products during chlorination reaction ([Acridine]$_0$ = 100 ng/L, [Cl$_2$]$_0$ = 5 mg/L, pH = 7).

Figure 12. Proposed degradation pathways of acridine by-products during chlorination reaction ([Acridine]$_0$ = 100 ng/L, [Cl$_2$]$_0$ = 5 mg/L, pH = 7).

3.3. By-products in UV/chlorination reaction

During UV/chlorination reaction, three by-products were identified from the degradation of acridine. Precursor ion of three by-products was m/z 220, 273 and 314 (Table 8).

Figure 13 shows the time profiles of acridine by-products during UV/chlorination reaction. Acridine by-products 11 (m/z 273) and 12 (m/z 314) represented continue increase tendency during 240 min. By-products 10 (m/z 220) increased at the beginning of the reaction and peak area value was nearly maintained from 30 to 240 min.

Figure 14 shows the proposed degradation pathways of acridine by-products during UV/chlorination reaction. Three acridine by-products during UV/chlorination reaction was proposed by using ACD/MS fragmenter software. We confirmed precursor ions of by-product and composed acridine by-products with the results of ACD/MS fragmenter software. Acridine By-products during UV/chlorination reaction was generated from mechanism (Eq. (5) ~ (12)). By-products was generated that OH and Cl radicals attack acridine ring bond during UV/chlorination reaction (Nam et al., 2015). However, acridine by-products was not removed during UV/chlorination reaction. Therefore, additional study is necessary that time profiling of generated by-products is performed to large time reaction.

Table 8. Information of acridine by-products generated during UV/chlorination reaction.

Compound	Chemical Formula	Predicted molecular weight	Precursor ion (m/z)	Product ions (m/z)
Acridine	$C_{13}H_9N$	179	180	152, 151
By-product 10	$C_{11}H_6ClNO_2$	219	220	186, 150
By-product 11	$C_{15}H_{10}ClNO_2$	272	273	185, 127
By-product 12	$C_{17}H_{12}ClNO_3$	313	314	295, 223

Figure 13. Time profiles of acridine by-products during UV/chlorination reaction ([Acridine]$_0$ = 100 ng/L, [Cl$_2$]$_0$ = 5 mg/L, UV-C $_{intensity}$ = 4.0 mW/cm^2, pH = 7).
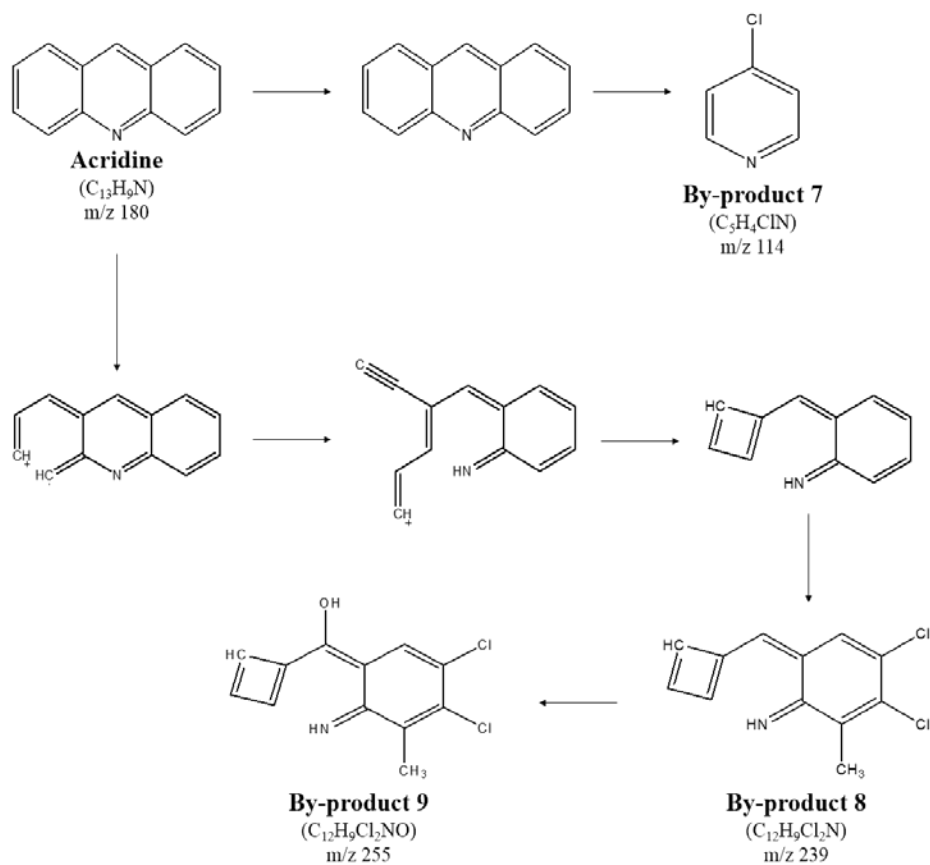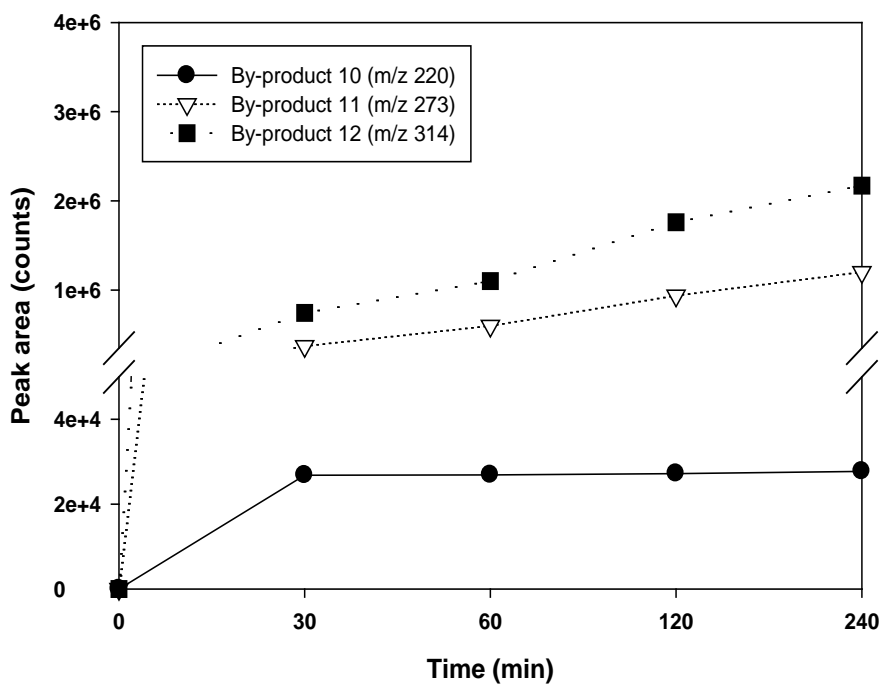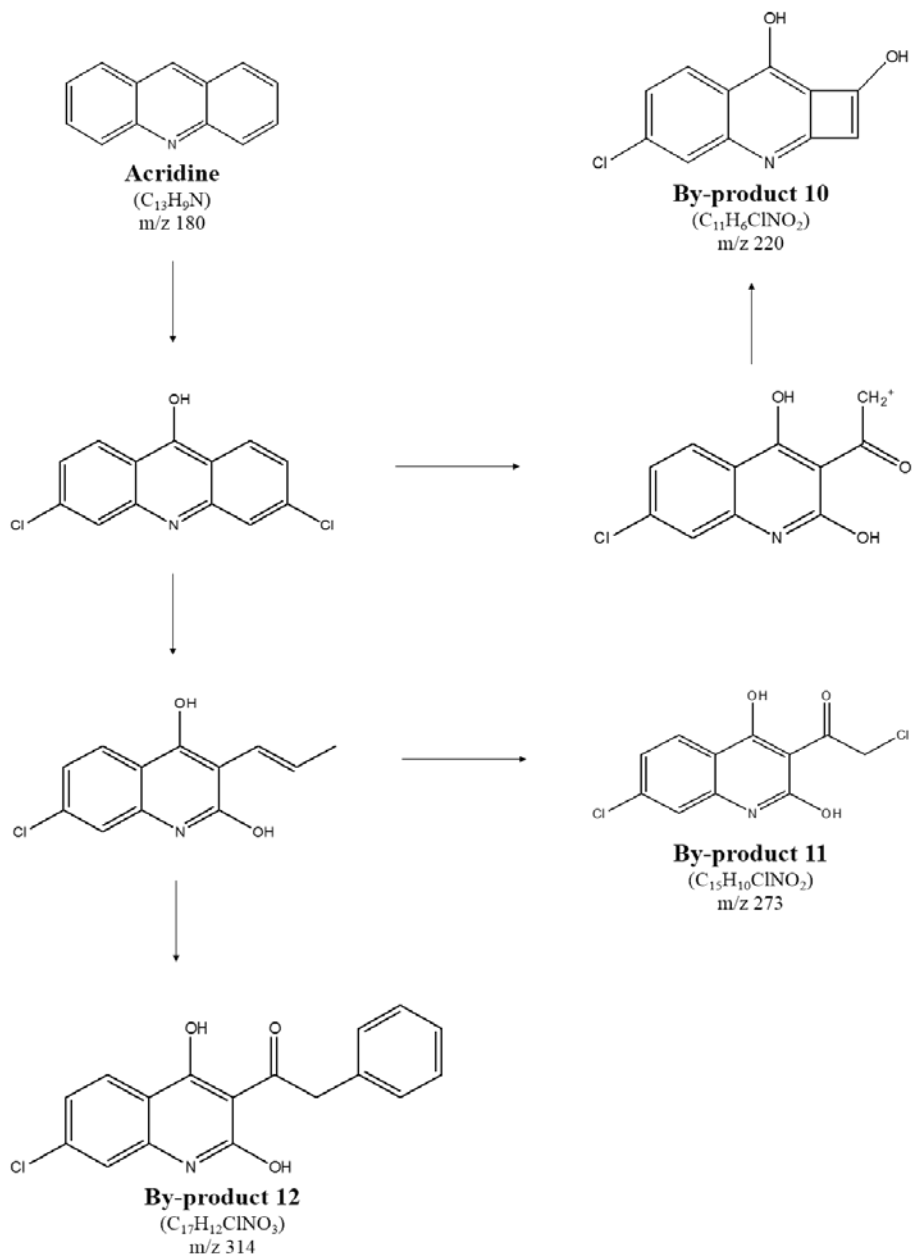
Figure 14. Proposed degradation pathways of acridine by-products during UV/chlorination reaction ([Acridine]$_0$ = 100 ng/L, [Cl$_2$]$_0$ = 5 mg/L, UV-C $_{intensity}$ = 4.0 mW/cm^2, pH = 7).

Ⅳ. Conclusions

In this study, we investigated degradation characteristics of acridine during UV photolysis, chlorination, UV/chlorination reaction. The UV-C light more effectively removed acridine than UV-A and UV-B lights in water. Under the UV/chlorination reaction combined UV photolysis and chlorination, acridine was more effectively removed than by UV photolysis and chlorination only reaction. 100 ng/L acridine was removed to 80% within 60 min and completely removed after 240 min. The removal efficiency of acridine was higher in the lower pH condition. The chlorine dose was a significant factor in the degradation of acridine in UV/chlorination reaction. DOM in real water condition was removed by using filtration process before water treatment system, because DOM can inhibit degradation of pollutants.

In addition, by-products of acridine was confirmed by using mass spectrometer in three reactions (UV photolysis, chlorination, UV/chlorination). Also, the proposed degradation pathways and time profiles of acridine by-products were identified by using LC-MS/MS and ACD/MS Fragmenter software. Six acridine by-products was identified during UV photolysis reaction (with m/z 108, 124, 130, 138, 156 and 196). And, three acridine by-products was identified during chlorination (with m/z 114, 239 and 255) and UV/chlorination reaction (with m/z 220, 273 and 314), respectively. Time

profiles of acridine by-products were confirmed and degradation pathway of acridine by-products was also proposed during UV photolysis, chlorination, UV/chlorination reaction.

The results of our study can provide important information when the UV/chlorination reaction was conducted to remove acridine or pharmaceuticals, PPCPs and EDCs in WWTP and DWTP. Also, the methods of analyzing acridine and by-products during UV/chlorination reaction can contribute to next study in water environment. However, the studies about degradation and identify of potential toxic by-products have to be conducted in water treatment processes. Ultimately, this study is helpful to improvement in the public health though maintaining clean water.

References

Acero, J. L., Benitez, F. J., Real, F. J., & Roldan, G. (2010). Kinetics of aqueous chlorination of some pharmaceuticals and their elimination from water matrices. *Water Research, 44*(14), 4158-4170.

Behera, S. K., Kim, H. W., Oh, J.-E., & Park, H.-S. (2011). Occurrence and removal of antibiotics, hormones and several other pharmaceuticals in wastewater treatment plants of the largest industrial city of Korea. *Science of the Total Environment, 409*(20), 4351-4360.

Benotti, M. J., Trenholm, R. A., Vanderford, B. J., Holady, J. C., Stanford, B. D., & Snyder, S. A. (2008). Pharmaceuticals and endocrine disrupting compounds in US drinking water. *Environmental Science & Technology, 43*(3), 597-603.

Chiffre, A., Degiorgi, F., Buleté, A., Spinner, L., & Badot, P.-M. (2016). Occurrence of pharmaceuticals in WWTP effluents and their impact in a karstic rural catchment of Eastern France. *Environmental Science and Pollution Research, 23*(24), 25427-25441.

Chiron, S., Minero, C., & Vione, D. (2006). Photodegradation processes of the antiepileptic drug carbamazepine, relevant to estuarine waters. *Environmental Science & Technology, 40*(19), 5977-5983.

Choi, K., Kim, Y., Park, J., Park, C. K., Kim, M., Kim, H. S., & Kim, P.

(2008). Seasonal variations of several pharmaceutical residues in surface water and sewage treatment plants of Han River, Korea. *Science of the Total Environment, 405*(1), 120-128.

Cooney, J. D., Beauchamp, J., & Gehrs, C. W. (1983). Effects of temperature and nutritional state on the acute toxicity of acridine to the calanoid copepod, Diaptomus clavipes Schacht. *Environmental Toxicology and Chemistry, 2*(4), 431-439.

Cushman, R. M., & McKamey, M. I. (1981). AChironomus tentans bioassay for testing synthetic fuel products and effluents, with data on acridine and quinoline. *Bulletin of Environmental Contamination and Toxicology, 26*(1), 601-605.

De la Cruz, N., Giménez, J., Esplugas, S., Grandjean, D., De Alencastro, L., & Pulgarin, C. (2012). Degradation of 32 emergent contaminants by UV and neutral photo-fenton in domestic wastewater effluent previously treated by activated sludge. *Water Research, 46*(6), 1947-1957.

De Laurentiis, E., Chiron, S., Kouras-Hadef, S., Richard, C., Minella, M., Maurino, V., Vione, D. (2012). Photochemical fate of carbamazepine in surface freshwaters: laboratory measures and modeling. *Environmental Science & Technology, 46*(15), 8164-8173.

Dijkman, N. A., van Vlaardingen, P. L., & Admiraal, W. A. (1997). Biological variation in sensitivity to N-heterocyclic PAHs; effects of

acridine on seven species of micro-algae. *Environmental Pollution, 95*(1), 121-126.

Dimou, A. D., Sakkas, V. A., & Albanis, T. A. (2004). Trifluralin photolysis in natural waters and under the presence of isolated organic matter and nitrate ions: kinetics and photoproduct analysis. *Journal of Photochemistry and Photobiology A: Chemistry, 163*(3), 473-480.

Donner, E., Kosjek, T., Qualmann, S., Kusk, K. O., Heath, E., Revitt, D. M., Andersen, H. R. (2013). Ecotoxicity of carbamazepine and its UV photolysis transformation products. *Science of the Total Environment, 443*, 870-876.

Eisentraeger, A., Brinkmann, C., Hollert, H., Sagner, A., Tiehm, A., & Neuwoehner, J. (2008). Heterocyclic compounds: toxic effects using algae, daphnids, and the Salmonella/microsome test taking methodical quantitative aspects into account. *Environmental Toxicology and Chemistry, 27*(7), 1590-1596.

Emmanuel, E., Keck, G., Blanchard, J.-M., Vermande, P., & Perrodin, Y. (2004). Toxicological effects of disinfections using sodium hypochlorite on aquatic organisms and its contribution to AOX formation in hospital wastewater. *Environment international, 30*(7), 891-900.

Fang, J., Fu, Y., & Shang, C. (2014). The roles of reactive species in micropollutant degradation in the UV/free chlorine system.

Environmental Science & Technology, 48(3), 1859-1868.

Fatta-Kassinos, D., Vasquez, M., & Kümmerer, K. (2011). Transformation products of pharmaceuticals in surface waters and wastewater formed during photolysis and advanced oxidation processes–degradation, elucidation of byproducts and assessment of their biological potency. *Chemosphere, 85*(5), 693-709.

Feng, Y., Smith, D. W., & Bolton, J. R. (2007). Photolysis of aqueous free chlorine species (HOCl and OCl) with 254 nm ultraviolet light. *Journal of Environmental Engineering and Science, 6*(3), 277-284.

Furst, S. M., & Uetrecht, J. P. (1993). Carbamazepine metabolism to a reactive intermediate by the myeloperoxidase system of activated neutrophils. *Biochemical Pharmacology, 45*(6), 1267-1275.

Gao, P., Ding, Y., Li, H., & Xagoraraki, I. (2012). Occurrence of pharmaceuticals in a municipal wastewater treatment plant: mass balance and removal processes. *Chemosphere, 88*(1), 17-24.

Jin, J., El-Din, M. G., & Bolton, J. R. (2011). Assessment of the UV/chlorine process as an advanced oxidation process. *Water Research, 45*(4), 1890-1896.

Kaiser, J.-P., Feng, Y., & Bollag, J.-M. (1996). Microbial metabolism of pyridine, quinoline, acridine, and their derivatives under aerobic and anaerobic conditions. *Microbiological Reviews, 60*(3), 483-498.

Kasprzyk-Hordern, B., Dinsdale, R. M., & Guwy, A. J. (2008). The

occurrence of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs in surface water in South Wales, UK. *Water Research, 42*(13), 3498-3518.

Kasprzyk-Hordern, B., Dinsdale, R. M., & Guwy, A. J. (2008). The occurrence of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs in surface water in South Wales, UK. *Water Research, 42*(13), 3498-3518.

Kim, I., Yamashita, N., & Tanaka, H. (2009). Performance of UV and UV/H2 O2 processes for the removal of pharmaceuticals detected in secondary effluent of a sewage treatment plant in Japan. *Journal of Hazardous Materials, 166*(2), 1134-1140.

Kim, J.-W., Jang, H.-S., Kim, J.-G., Ishibashi, H., Hirano, M., Nasu, K., Arizono, K. (2009). Occurrence of pharmaceutical and personal care products (PPCPs) in surface water from Mankyung River, South Korea. *Journal of Health Science, 55*(2), 249-258.

Kim, T.-K., Moon, B.-R., Kim, T., Kim, M.-K., & Zoh, K.-D. (2016). Degradation mechanisms of geosmin and 2-MIB during UV photolysis and UV/chlorine reactions. *Chemosphere, 162*, 157-164.

Klavarioti, M., Mantzavinos, D., & Kassinos, D. (2009). Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. *Environment International, 35*(2), 402-417.

Knezovich, J. P., Bishop, D. J., Kulp, T. J., Grbić-Galić, D., & Dewitt, J.

(1990). Anaerobic microbial degradation of acridine and the application of remote fiber spectroscopy to monitor the transformation process. *Environmental Toxicology and Chemistry, 9*(10), 1235-1243.

Kosjek, T., Andersen, H. R., Kompare, B., Ledin, A., & Heath, E. (2009). Fate of carbamazepine during water treatment. *Environmental Science & Technology, 43*(16), 6256-6261.

Lai, W. W.-P., Lin, Y.-C., Tung, H.-H., Lo, S.-L., & Lin, A. Y.-C. (2016). Occurrence of pharmaceuticals and perfluorinated compounds and evaluation of the availability of reclaimed water in Kinmen. *Emerging Contaminants*.

Leclercq, M., Mathieu, O., Gomez, E., Casellas, C., Fenet, H., & Hillaire-Buys, D. (2009). Presence and fate of carbamazepine, oxcarbazepine, and seven of their metabolites at wastewater treatment plants. *Archives of Environmental Contamination and Toxicology, 56*(3), 408-415.

Legrini, O., Oliveros, E., & Braun, A. (1993). Photochemical processes for water treatment. *Chemical Reviews, 93*(2), 671-698.

Lekkerkerker-Teunissen, K., Benotti, M. J., Snyder, S. A., & Van Dijk, H. C. (2012). Transformation of atrazine, carbamazepine, diclofenac and sulfamethoxazole by low and medium pressure UV and UV/H 2 O 2 treatment. *Separation and Purification Technology, 96*, 33-43.

Lyon, B. A., Dotson, A. D., Linden, K. G., & Weinberg, H. S. (2012). The effect of inorganic precursors on disinfection byproduct formation during UV-chlorine/chloramine drinking water treatment. *Water Research, 46*(15), 4653-4664.

Matta, R., Tlili, S., Chiron, S., & Barbati, S. (2011). Removal of carbamazepine from urban wastewater by sulfate radical oxidation. *Environmental Chemistry Letters, 9*(3), 347-353.

Mompelat, S., Le Bot, B., & Thomas, O. (2009). Occurrence and fate of pharmaceutical products and by-products, from resource to drinking water. *Environment International, 35*(5), 803-814.

Murray, K. E., Thomas, S. M., & Bodour, A. A. (2010). Prioritizing research for trace pollutants and emerging contaminants in the freshwater environment. *Environmental Pollution, 158*(12), 3462-3471.

Nakada, N., Hanamoto, S., Jürgens, M. D., Johnson, A. C., Bowes, M. J., & Tanaka, H. (2016). Assessing the population equivalent and performance of wastewater treatment through the ratios of pharmaceuticals and personal care products present in a river basin: Application to the River Thames basin, UK. *Science of the Total Environment*.

Nam, S.-W., Jo, B.-I., Yoon, Y., & Zoh, K.-D. (2014). Occurrence and removal of selected micropollutants in a water treatment plant. *Chemosphere, 95*, 156-165.

Nam, S.-W., Yoon, Y., Choi, D.-J., & Zoh, K.-D. (2015). Degradation characteristics of metoprolol during UV/chlorination reaction and a factorial design optimization. *Journal of Hazardous Materials, 285*, 453-463.

Nowell, L. H., & Hoigné, J. (1992). Photolysis of aqueous chlorine at sunlight and ultraviolet wavelengths—II. Hydroxyl radical production. *Water Research, 26*(5), 599-605.

Paíga, P., Santos, L. H., Ramos, S., Jorge, S., Silva, J. G., & Delerue-Matos, C. (2016). Presence of pharmaceuticals in the Lis river (Portugal): Sources, fate and seasonal variation. *Science of the Total Environment, 573*, 164-177.

Parkhurst, B. R., Bradshaw, A. S., Forte, J. L., & Wright, G. P. (1981). The chronic toxicity to Daphnia magna of acridine, a representative azaarene present in synthetic fossil fuel products and wastewaters. *Environmental Pollution Series A, Ecological and Biological, 24*(1), 21-30.

Pereira, V. J., Linden, K. G., & Weinberg, H. S. (2007). Evaluation of UV irradiation for photolytic and oxidative degradation of pharmaceutical compounds in water. *Water Research, 41*(19), 4413-4423.

Pereira, V. J., Weinberg, H. S., Linden, K. G., & Singer, P. C. (2007). UV degradation kinetics and modeling of pharmaceutical compounds in laboratory grade and surface water via direct and indirect photolysis

at 254 nm. *Environmental Science & Technology, 41*(5), 1682-1688.

Qin, L., Lin, Y.-L., Xu, B., Hu, C.-Y., Tian, F.-X., Zhang, T.-Y., Gao, N.-Y. (2014). Kinetic models and pathways of ronidazole degradation by chlorination, UV irradiation and UV/chlorine processes. *Water Research, 65*, 271-281.

Quintana, J. B., Rodil, R., López-Mahía, P., Muniategui-Lorenzo, S., & Prada-Rodríguez, D. (2010). Investigating the chlorination of acidic pharmaceuticals and by-product formation aided by an experimental design methodology. *Water Research, 44*(1), 243-255.

Roberts, J., Kumar, A., Du, J., Hepplewhite, C., Ellis, D. J., Christy, A. G., & Beavis, S. G. (2016). Pharmaceuticals and personal care products (PPCPs) in Australia's largest inland sewage treatment plant, and its contribution to a major Australian river during high and low flow. *Science of the Total Environment, 541*, 1625-1637.

Shemer, H., Kunukcu, Y. K., & Linden, K. G. (2006). Degradation of the pharmaceutical metronidazole via UV, Fenton and photo-Fenton processes. *Chemosphere, 63*(2), 269-276.

Sichel, C., Garcia, C., & Andre, K. (2011). Feasibility studies: UV/chlorine advanced oxidation treatment for the removal of emerging contaminants. *Water Research, 45*(19), 6371-6380.

Singer, P. C., & Reckhow, D. A. (1999). CHEMICAL OXIDATION. *Water Quality & Treatment : a Handbook on Drinking Water*.

Snyder, S. A., Westerhoff, P., Yoon, Y., & Sedlak, D. L. (2003). Pharmaceuticals, personal care products, and endocrine disruptors in water: implications for the water industry. *Environmental Engineering Science, 20*(5), 449-469.

Soufan, M., Deborde, M., Delmont, A., & Legube, B. (2013). Aqueous chlorination of carbamazepine: kinetic study and transformation product identification. *Water Research, 47*(14), 5076-5087.

Stackelberg, P. E., Furlong, E. T., Meyer, M. T., Zaugg, S. D., Henderson, A. K., & Reissman, D. B. (2004). Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant. *Science of the Total Environment, 329*(1), 99-113.

Stackelberg, P. E., Gibs, J., Furlong, E. T., Meyer, M. T., Zaugg, S. D., & Lippincott, R. L. (2007). Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds. *Science of the Total Environment, 377*(2), 255-272.

Ternes, T. A. (1998). Occurrence of drugs in German sewage treatment plants and rivers. *Water Research, 32*(11), 3245-3260.

Ternes, T. A., Meisenheimer, M., McDowell, D., Sacher, F., Brauch, H.-J., Haist-Gulde, B., Zulei-Seibert, N. (2002). Removal of pharmaceuticals during drinking water treatment. *Environmental Science & Technology, 36*(17), 3855-3863.

Togola, A., & Budzinski, H. (2008). Multi-residue analysis of pharmaceutical compounds in aqueous samples. *Journal of Chromatography A, 1177*(1), 150-158.

Torrents, A., Anderson, B. G., Bilboulian, S., Johnson, W. E., & Hapeman, C. J. (1997). Atrazine photolysis: mechanistic investigations of direct and nitrate-mediated hydroxy radical processes and the influence of dissolved organic carbon from the Chesapeake Bay. *Environmental Science & Technology, 31*(5), 1476-1482.

Vogna, D., Marotta, R., Andreozzi, R., Napolitano, A., & d'Ischia, M. (2004). Kinetic and chemical assessment of the UV/H 2 O 2 treatment of antiepileptic drug carbamazepine. *Chemosphere, 54*(4), 497-505.

Watts, M. J., & Linden, K. G. (2007). Chlorine photolysis and subsequent OH radical production during UV treatment of chlorinated water. *Water Research, 41*(13), 2871-2878.

Wei, C., Bandowe, B. A. M., Han, Y., Cao, J., Zhan, C., & Wilcke, W. (2015). Polycyclic aromatic hydrocarbons (PAHs) and their derivatives (alkyl-PAHs, oxygenated-PAHs, nitrated-PAHs and azaarenes) in urban road dusts from Xi'an, Central China. *Chemosphere, 134*, 512-520.

Westerhoff, P., Yoon, Y., Snyder, S., & Wert, E. (2005). Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. *Environmental Science*

    & Technology, 39(17), 6649-6663.

Yoon, Y., Ryu, J., Oh, J., Choi, B.-G., & Snyder, S. A. (2010). Occurrence of endocrine disrupting compounds, pharmaceuticals, and personal care products in the Han River (Seoul, South Korea). *Science of the Total Environment, 408*(3), 636-643.

Zhang, Y., Geißen, S.-U., & Gal, C. (2008). Carbamazepine and diclofenac: removal in wastewater treatment plants and occurrence in water bodies. *Chemosphere, 73*(8), 1151-1161.

국문초록

UV/chlorination 반응에서의
아크리딘 저감 특성에 관한 연구

서울대학교 보건대학원

환경보건학과 환경보건 전공

최 대 진

최근 의약품, 개인위생용품, 내분비계 장애물질이 전 세계의 수계에서 미량의 농도로 검출되고 있다. 심지어, 일부 미량오염물질들은 하수처리장 및 사람들이 매일 섭취하는 정수처리장 유출수에서 검출되고 있다. 이러한 물질들은 미량의 농도로 존재하지만, 지속적으로 노출된다면 환경과 생태계에 부정적인 영향을 초래할 수 있다. 3개의 링으로 구성된 아크리딘은 돌연변이와 발암 가능성을 지닌 오염물질 중 하나이다. 아크리딘은 염료의 제조와 의약품의 합성의 중간 화학물질로 사용되며,

콜타르의 연소 등에서 발생한다, 뿐만 아니라, 최근 연구에서는 아크리딘이 항 간질약의 하나인 카바마제핀의 고도산화처리 (AOPs) 과정에서 부산물로 생성된다고 알려져 있다. 수 처리 과정에서 이러한 잔류 오염물질들에 의한 위험이 증가함에 따라, 과거 연구에서는 다양한 수 처리 기술들을 개발해왔다. 강력한 산화 라디칼을 생성하는 고도산화처리는 난분해성 유기물질의 제거에 적용할 수 있다. 본 연구에서는 UV 반응과 chlorination 반응을 결합한 UV/chlorination 반응을 활용하여 수체 내 아크리딘을 제거하였다. UV-C는 UV-A, UV-B 보다 아크리딘을 더 효과적으로 제거하였다. 그리고 UV/chlorination 반응은 UV, chlorination 단독반응에서 보다 효과적으로 아크리딘을 제거했다. UV/chlorination 반응 동안, 100 ng/L 의 아크리딘은 60분 내에 80% 제거 되었으며 240분 후에는 완전히 제거 되었다. 아크리딘의 처리효율은 산성 pH 조건에서 더 좋았다. 그리고 염소의 양은 제거반응에서 아크리딘을 처리하는데 중요한 지표이며, 용존유기물질 (DOM)은 처리반응에서 수체 내 오염물질의 제거를 저해할 수 있다. 아크리딘의 분해 부산물들은 질량분석기를 사용하여 확인되었다. UV 단독반응에서는 6개의 부산물을 확인하였으며, chlorination 단독반응과 UV/chlorination

반응에서는 각각 3개의 부산물을 확인할 수 있었다. UV/chlorination 반응에서 OH라디칼과 Cl라디칼에 의해 아크리딘이 분해될 때, 부산물이 발생하게 된다. UV, chlorination, UV/chlorination 반응에서 아크리딘 부산물들의 시간에 따른 변화를 확인 하였고, 아크리딘 부산물의 생성과정을 제안하였다. 본 연구의 결과는 하수처리장과 정수처리장에서 아크리딘의 제거를 위하여 UV/chlorination 반응을 적용할 때, 중요한 정보들을 제공할 수 있다. 궁극적으로, 본 연구는 깨끗한 물을 유지하게 함으로써 환경보건의 증진에 도움이 될 수 있을 것이다.

주요어: 아크리딘, 고도산화처리(AOPs), UV/chlorination, pH, 용존유기물질(DOM), OH라디칼, Cl라디칼, 부산물

학 번: 2012-23702