보건학석사학위논문

Kinetics and degradation mechanism of Anatoxin-a during UV-C/H_2O_2 reaction

UV-C/H_2O_2 공정 중 아나톡신-a의 분해 특성과 메커니즘에 관한 연구

2017년 2월

서울대학교 보건대학원

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지도교수 조 경 덕
이 논문을 보건학석사 학위논문으로 제출함
2016 년 11 월

서울대학교 보건대학원
환경보건학과 환경보건 전공
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탁소연의 보건학석사 학위논문을 인준함
2016 년 12 월

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Abstract

Kinetics and degradation mechanism of Anatoxin-a during UV-C/H_2O_2 reaction

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Cyanobacteria can produce toxins which are responsible for the livestock and human poisoning. Anatoxin-a is one of the toxins mainly secreted by cyanobacteria *Anabaena flos-aquae*. In this study, the removals of anatoxin-a (0.3 μM) during UV-C photolysis and UV/H_2O_2 reactions were compared using a photo-reactor system consisting of a stirred 2-L glass bottle by applying the UV intensity of 3.5-4.0 mW/cm^2 and H_2O_2 dose of 0.01 mM. All samples were measured after pre-

treated by solid-phase extraction (SPE), followed by liquid chromatography-electrospray ionization tandem mass spectrometry (LC-ESI-MS/MS). The result showed that the removal of anatoxin-a was more effective during UV/H_2O_2 reaction than either UV-C photolysis or H_2O_2 alone. Anatoxin-a was completely degraded within 30 min during UV/H_2O_2 reaction, which might be due to the effective production of OH radicals. UV/H_2O_2 reaction of anatoxin-a resulted in an approximately 60% TOC decrease after 7 hr, and 30% acetate were produced as the organic short chain by-product. For nitrogen recovery, NH_4^+, NO_2^-, and NO_3^- ions were produced from UV/H_2O_2 reaction, and more than 50% of the total nitrogen was mineralized mainly to NO_3^- ion. Using LC-ESI-MS/MS, we newly identified 6 degradation by-products during UV/H_2O_2 reaction ($[M+H]^+$ values of 142, 127, 113, 132, 117, and 124). Using the identified by-products, we proposed the degradation pathway of anatoxin-a during UV/H_2O_2 reaction based on the identified by-products. Our results imply that anatoxin-a can be effectively controlled by UV/H_2O_2 reaction during water treatment processes.

Keywords: Anatoxin-a; UV-C photolysis; UV/H_2O_2 reaction; by-

products; degradation pathway

Student Number: 2015-24066

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I. Introduction

1.1. Anatoxin-a in the environment

Blooms of cyanobacteria in aquatic environments are common and worldwide problem causing a significant adverse impact on public health and ecosystems (Smith et al., 2003; Paerl et al., 2011). It can cause water quality problems, such as bad taste and odor, color change, and production of cyanotoxins.

Cyanobacteria produces toxic secondary metabolites known as cyanotoxins including hepatotoxins (microcystins, nodularins, and cylindrospermopsin), neurotoxins (anatoxin-a and saxitoxin), and dermatotoxins (lyngbyatoxin-a) (Carmichael, 1992; Carmichael, 1994). Scientists focus on secondary metabolites of cyanobacteria because it is reported that cyanotoxins are harmful to human, fish and animals even at low range of concentration (Gademann and Portmann, 2008; Huisman, 2014). Through the ingestion of recreational water, untreated drinking water and contaminated fish, human can be exposed to cyanotoxins (Stewart et al., 2006; Svircev et al., 2009).

Anatoxin-a is the one of the neurotoxins secreted by *Anabaena flos-aqueae, Aphanizomenon, Microcystis* (Wood et al., 2007). Anatoxin-a is an alkaloid neurotoxin which has proven to be not only tumor promoter but tumor initiator as well. Anatoxin-a is neurotoxin with block the nicotinic acetylcholine receptors in human without being degraded by acetylcholinesterase or any other enzyme. It can also cause the overstimulation of muscle, paralysis and death from suffocation within minutes to hours in animals (Mahmood and Carmichael, 1987; Carmichael, 1994).

US EPA has listed three cyanotoxins including anatoxin-a in the third Candidate Contaminant List (CCL) because of cyanotoxin's adverse effects (US EPA, 2009). New Zealand and Canada have established provisional maximum acceptable value (MAV) for anatoxin-a at 6 μg/L and 3.7 μg/L, respectively (Verma and Sillanpaa, 2015). In Korea, there is no guideline for anatoxin-a.

Table 1 shows the concentrations of anatoxin-a in abroad and Korea. It is reported that anatoxin-a was detected up to 444 μg/L in lake water of Ireland (James et al., 1997) and 0.71-10.18 μg/g in plants of the United States (Al-Sammak et al., 2014). It shows the various trend of detection of anatoxin-a in abroad. Concentrations of anatoxin-a in

surface water and algae materials in Korea have been reported to be 0.01-0.08 μg/L and 0.61-8.68 μg/g (dry wt), respectively (Joung et al., 2002).

Table 1. Anatoxin-a concentrations detected worldwide (water concentrations in μg/L, aquatic plants and algae materials (in μg/g))

Country	Media	Concentration			Year	Reference
		Mean	Min	Max		
USA	Water	22.60	5.20	35.70	2009	(Al-Sammak et al., 2014)
USA	Aquatic plants	3.23	0.711	10.18	2009	(Al-Sammak et al., 2014)
Germany	Water	0.95	0.01	13.10	1998	(Bumke-Vogt et al., 1999)
Poland	Water	62.08	3.76	120.40	2003	(Pirszel and Adamczyk, 2004)
Spain	Water	0.19	0.05	0.31	2007	(Carrasco et al., 2007)
Ireland	Water	43.14	2.60	112.44	1996	(James et al., 1997)
Korea	Water	0.04	0.01	0.08	2002	(Joung et al., 2002)
Korea	Algae materials	4.64	0.61	8.68	2002	(Joung et al., 2002)

1.2. Anatoxin-a degradation by AOPs

In previous studies, they used various physicochemical treatment technologies (coagulation, flocculation and sedimentation) to treat the water contaminated with cyanotoxins. However, they had no effect on removing extracellular cyanotoxins which are released in raw water (Hitzfeld et al., 2000). Therefore, it is necessary to develop an effective treatment methods for the detoxification of water contaminated with cyanotoxins and maintaining good quality of drinking water (Pietsch et al., 2002). Advanced oxidation processes (AOPs) are considered as alternatives for the removal of such toxic chemicals.

AOPs are proved to be the effective for the removal of anatoxin-a from the water. Degradation of anatoxin-a have been studied with the use of ozone, hydrogen peroxide, chlorine, chloramine, potassium permanganate and UV photolysis. Anatoxin-a is not effectively removed by oxidant such as chlorine and chloramine. In previous studies, 3 mg/L of chlorine was able to degrade only 8% of anatoxin-a and the reactivity of anatoxin-a with chloramine was very low ($k<1\ M^{-1}\ S^{-1}$) (Rodriguez et al., 2007). However, ozone, potassium permanganate

and UV photolysis are effective to degrade anatoxin-a by producing radicals during water treatment processes (Westrick et al., 2010). At pH 8, the reactivity of anatoxin-a with ozone was very high ($k<6.4 \times 10^4$ $M^{-1} S^{-1}$) (Onstad et al., 2007). UV/H_2O_2 reaction is one of these AOPs. In previous studies, >70% of anatoxin-a was removed by use of H_2O_2 with UV photolysis (Table 2).

UV/H_2O_2 reaction involves the production of hydroxyl radicals. Organic compounds can be mineralized into CO_2 and H_2O by direct photolysis and OH radical which was produced by the hemolytic cleavage of hydrogen peroxide with having a wavelength shorter than 280 nm (Hofl et al., 1997; Andreozzi et al., 1999; Lee et al., 2003). UV/H_2O_2 reaction has been very effective in removing a wide range of environmental contaminants, such as pharmaceutical compounds, pesticides, industrial solvents and taste-and-odor causing compounds (Beltran et al., 1996; Wu et al., 2008; Yuan et al., 2009). Compared with other AOPs, UV/H_2O_2 reaction has advantage. It can be more practical due to single-step dissociation of hydrogen peroxide to form two hydroxyl radicals (·OH) as follows:

$$H_2O_2 \xrightarrow{hv} 2 \cdot OH$$

(1.1)

It means that mineralization of organic compounds can keep going under appropriate condition without any phase transfer problems (Colonna et al., 1999).

It is important to evaluate the degradation mechanism of anatoxin-a during UV/H_2O_2 reaction and investigate its by-products. Previous studies have focused on removing anatoxin-a itself. Although anatoxin-a is fully degraded in water, the major concern with drinking water treatment is the formation of unknown by-products which can result in secondary pollution of drinking water.

Formation characteristics of by-products and its pathway during UV/H_2O_2 and TiO_2 photo-catalysis of cyanotoxins such as cylindrospermopsin and microcystin-LR are investigated (Zong et al., 2013; Zhang et al., 2015). However, the previous researches only examined the UV photolysis and UV/H_2O_2 reactions for the degradation of anatoxin-a (Afzal et al., 2010; Verma and Sillanpaa, 2015). They only reported effective anatoxin-a elimination rate by UV/H_2O_2 reaction under optimized condition. Up to now, there are no studies which examine the anatoxin-a degradation by-products and

pathway during UV photolysis and UV/H_2O_2 reactions. Therefore, we need to identify the degradation mechanism of anatoxin-a during UV/H_2O_2 reaction.

Table 2. Removal efficiencies of anatoxin-a by Advanced Oxidation Processes

Research (AOPs)	Operation conditions	Removal (%)
Rositano et al., 2001 (Ozone)	[Anatoxin-a_0]= 20 μg/L; [Time]= 5 min; [O_3]= 1.5 mg/L	> 99
Rodriguez et al., 2007 (Chlorine)	[Anatoxin-a_0]= 165 μg/L; [Time]= 24 hr; [Chlorine]= 3 mg/L	8
Afzal et al., 2010 (Vacuum- UV (172 nm))	[Anatoxin-a_0]= 0.6 mg/L; [Time]= 5 min; [UV dose]= 1285 mJ/cm^2)	88
Afzal et al., 2010 (VUV/H_2O_2 Vacuum-UV (172 nm))	[Anatoxin-a_0]= 0.6 mg/L; [Time]= 5 min; [UV dose]= 200 mJ/cm^2); [H_2O_2]= 30 mg/L	>70
Verma and Sillanpaa, 2015 (UV-C/H_2O_2 (260 nm-290 nm))	[Anatoxin-a_0]= 165 μg/L; [Time]= 5 min; [UV dose]= 4032 mJ/cm^2); [H_2O_2]= 51 mg/L	97

1.3. Objectives

Therefore, in this study, we examined the anatoxin-a degradation efficiency compared with UV photolysis and UV/H_2O_2 reactions at different doses of H_2O_2. To investigate the degradation mechanism of anatoxin-a during UV/H_2O_2 reaction, we analyzed the various parameters such as TOC, NH_4^+, NO_2^-, and NO_3^- ions and organic by-products which are formed during UV/H_2O_2 reaction. By using liquid chromatography tandem mass spectrometry (LC-MS/MS) and ACD Fragmenter software, we constructed the possible by-products formation pathway of anatoxin-a during UV/H_2O_2 reaction.

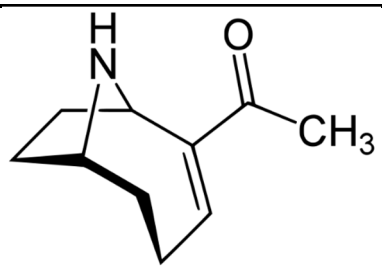
II. Materials and Methods

2.1. Chemicals

Anatoxin-a ($C_{10}H_{15}NO$) was purchased from Enzo Life Sciences (Farmingdale, USA). Table 3 shows the physicochemical properties of anatoxin-a. The standard of 1 mg anatoxin-a was dissolved in 1 mL deionized water was obtained from a Milli-Q water generator (Millipore, USA). Before the experiments, this solution was further diluted into 10 mg/L with deionized water as working solution. Anatoxin-a solution was frozen to inhibit the degradation in darkness at -20^{o}C.

Hydrogen peroxide (30%, v/v), formic acid (88%, v/v) and enzyme catalase (10,000-40,000 units/mg protein) were supplied by Sigma-Aldrich (USA). Acetonitrile and water (J.T. Baker, USA) was used as mobile phases when we measured anatoxin-a using LC-MS/MS.

Table 3. Physico-chemical properties of anatoxin-a

Molecular structure	Properties	
	Molecular formula:	$C_{10}H_{15}NO$
	Molecular weight :	165.232
	pKa :	9.4
	Solubility :	7.2×10^{4} mg/L

2.2. Experimental procedures

To examine the kinetics of removal of anatoxin-a, UV-photolysis and UV/H_2O_2 reactions were conducted using a continuous UV photo-reactor. The schematic diagram of the photolytic reactor system is shown in Figure 1(a). The reactor consists of a 2-L glass bottle, stirrer and UV-C lamp (6 W, 254 nm, San-Kyo Electrics, Japan). UV intensity was measured with a radiometer (VLX-3W Radiometer 9811-50, Cole-Parmer, USA). A single UV lamp had a light intensity of 3.5-4 mW/cm^2 at 254 nm (UV-C). The solution was magnetically stirred for the complete irradiation of the solution with UV. All experiments were

conducted in darkness for minimizing the loss of UV radiation during experiments at room temperature (24±1℃). Initial anatoxin-a concentration was 0.3 μM (50 μg/L). 0.005 mM and 0.01 mM H_2O_2 were added to the reaction mixture respectively. The concentration of anatoxin-a was investigated at 0, 10, 30, 60, 90, 120 and 180 min.

For the identification by-products of anatoxin-a, UV/H_2O_2 reactions were conducted in a batch type photo-reactor. The schematic diagram of the photolytic reactor system is shown in Figure 1(b). UV chamber consists of four UV-C lamps (20 W, 254 nm, San-Kyo Electrics Co., Kyoto, Japan) with a distance of 20 mm between them. The intensity value of UV light was 3.5-4 mW/cm^2. Initial anatoxin-a concentration was 60.6 μM (10 mg/L). 2 mM H_2O_2 was added to the reaction mixture. The concentration of anatoxin-a was investigated at 0, 10, 30, 60, 90, 120 and 180 min. After sampling, the remaining H_2O_2 was immediately quenched with enzyme catalase (Liu et al., 2003).

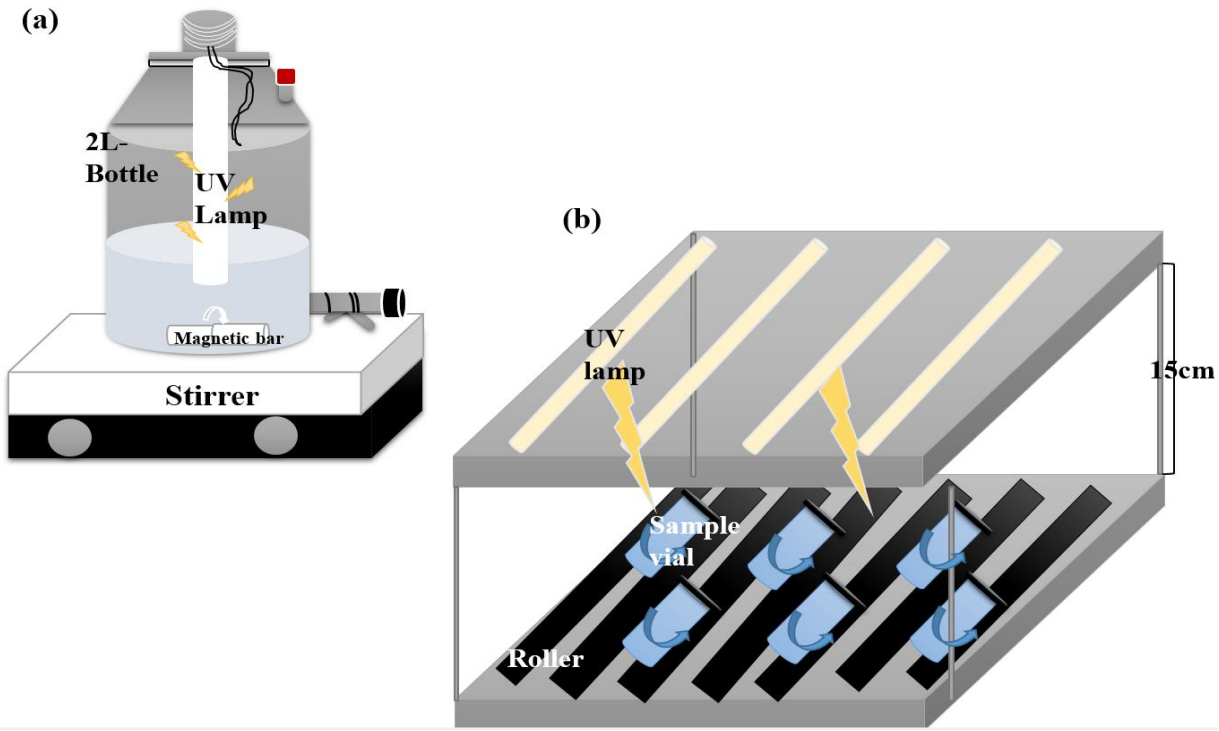


Figure 1. The schematic diagram of the photolytic reactor batch type systems (a) experimental conditions; (n=3, $[C_0]$ = 0.3 μM (50 μg/L), UV intensity = 3.5 mW/cm^2, $[H_2O_2]$ = 0.005 mM and 0.01 mM, 20℃) (b) experimental conditions; (n=3, $[C_0]$ = 60.6 μM (10 mg/L), UV intensity = 3.5 mW/cm^2, $[H_2O_2]$ = 2 mM, 20℃)

2.3. Solid phase extraction (SPE) procedure

Prior to analysis, solid phase extraction (SPE) was conducted for all samples using a hydrophile-lipophile balance (HLB) cartridge (Oasis HLB, Waters, Milford, MA, USA). Cartridges were conditioned by adding 3 mL 10% acetonitrile – 90% water – 0.1% FA (formic acid) and 3 mL 95% acetonitrile – 5% water – 0.1% FA, washed with 1.5 mL 95% acetonitrile – 5% water – 0.1% FA and eluted with 5 mL 10% acetonitrile – 90% water – 0.1% FA. Eluted samples were dried in using a centrifugal concentrator (CVE-3100, EYELA, Tokyo, Japan) reconstituted with 1 mL distilled water with 0.1% FA (Faassen et al., 2012).

2.4. Analytical methods

The concentration of anatoxin-a was determined by using UPLC (Ultra-performance liquid chromatograph) (Nexera, Shimadzu, Kyoto, Japan) equipped with API-4000 mass spectrometer (AB SCIEX, USA). Compounds were separated on an Imtakt C_{18} column (100 mm x 2.0

mm, 3 μm). An isocratic mode with 0.2 mL/min was used. Mobile phase A (0.1% FA in distilled water) and mobile phase B (0.1% FA in acetonitrile) were used (95:5, v/v) (Oehrle et al., 2010). Injection volume was 20 μL. The optimized ion pair of the anatoxin-a and MS collision condition are shown in Table 4.

Table 4. LC-MS/MS condition for the analysis of anatoxin-a

Compound	Precursor ion (m/z)	Product ion (m/z)	Declustering potential (mV)	Collision energy	Collision cell exit potential (mV)
Anatoxin-a	166	149, 121, 68	61	21	16

Limit of detection (LOD) and limit of quantification (LOQ) of anatoxin-a were shown in the range of 0.15 μg/L and 0.49 μg/L, respectively. The quality assurance/quality control (QA/QC) data were summarized in Table 5.

Table 5. The quality assurance and quality control (QA/QC) data

Compound	Retention time (min)	Detection limit (n = 7)		Recovery (%)		
		LOD (μg /L)	LOQ (μg /L)	Mean ± SD	Max.	Min.
Anatoxin-a	3.14	0.15	0.49	91.20 ± 5.01	96.21	86.19

*Recoveries were calculated with the spiked DL-2-Aminobutyric acid as internal standard (10 μg /L)

*The relative standard deviation (RSD, %) expresses the percentage of standard deviation divided by mean

The total organic carbon (TOC) of the solution was measured with a TOC analyzer (TOC-5000, Shimadzu, Japan). To analyze the concentration of acetate and N including ions (NO_2^-, NO_3^- and NH_4^+), ion chromatography (ICS-1100, Dionex, USA) was used. For separating the anions, IonPac AS14 column (250 mm (length) 4 mm (I.D.)) and IonPac AG14 guard column (50 mm (length) 4 mm (I.D.)) were used. An eluent containing a mixture of 8.0 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ was used with a flow rate 0.8 mL/min for detecting acetate. NO_2^- and NO_3^- ions were measured with a mixture of 3.5 mM

Na_2CO_3 and 1.0 mM $NaHCO_3$ at 1.2 mL/min. To detect the NH_4^+ ion, the solution including 20 mM Methane Sulfonic Acid was used as an eluent at 1.0 mL/min. IonPac CS12A column (250 mm (length) 4 mm (I.D.)) and IonPac CG12A guard column (50 mm (length) 4 mm (I.D.)) were used for analyzing cations (Kontozova-Deutsch et al., 2008; Kontozova-Deutsch et al., 2011).

2.5. Identification of by-products

By-products from anatoxin-a degradation were identified with a triple quadruple mass spectrometer (API 4000, AB Sciex, Foster City, USA) using a syringe containing 1 mL of sample. The direct injection was continuously at 0.01 mL/min by using a Harvard syringe pump (Model 975, Harvard Apparatus, Dover, MA, USA). Full scanning of the sample was performed to identify precursor ions and fragmented ions of the identified precursor ions was conducted to examine the product ions by using collision with high purity nitrogen gas. To predict the possible chemical structures and proposed pathway of by-products formation, ACD/MS Fragmenter (ACD Labs, Advanced Chemistry

Development, Inc., Toronto, Canada) was used.

III. Results and Discussion

3.1. Degradation kinetics of anatoxin-a during UV photolysis and UV/H_2O_2 reactions

We compared the kinetics of anatoxin-a photolytic degradation by using UV-A (315 nm-400 nm) photolysis and UV-C (200 nm-280 nm) photolysis with and without addition of H_2O_2. 0.3 μM (50 μg/L) of anatoxin-a was applied for 180 min at each experiments. Figure 2 shows the removal of anatoxin-a by UV photolysis and UV-H_2O_2 reactions. Anatoxin-a was not degraded until 180 min by UV-A photolysis and UV-A/H_2O_2 reactions. During UV-C photolysis, almost 80% of anatoxin-a was removed within 180 min, and it was completely removed within 30 min.

The photosensitivity of anatoxin-a was low at having wavelength range of UV-C (200 nm-280 nm) (Verma and Sillanpaa, 2015; James et al., 1998). To check the photosensitivity of anatoxin-a, its absorbance was scanned from 230 nm to 400 nm using UV spectrometer (Figure 3).

Anatoxin-a was more sensitive at 230 nm-240 nm based on the increment of initial anatoxin-a concentration (10 mg/L).

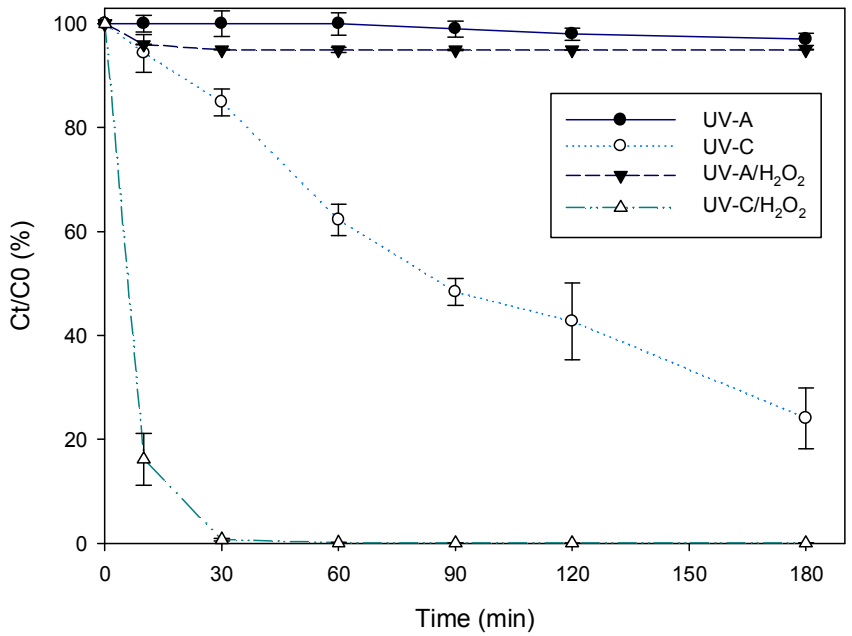


Figure 2. Removal of anatoxin-a during the UV photolysis and UV/H_2O_2 reactions with the different wavelength (experimental conditions; n=3, [C_0] = 0.3 μM (50 μg/L), UV intensity = 3.5 mW/cm^2, [H_2O_2] = 0.01 mM, pH=6.7, 20℃)

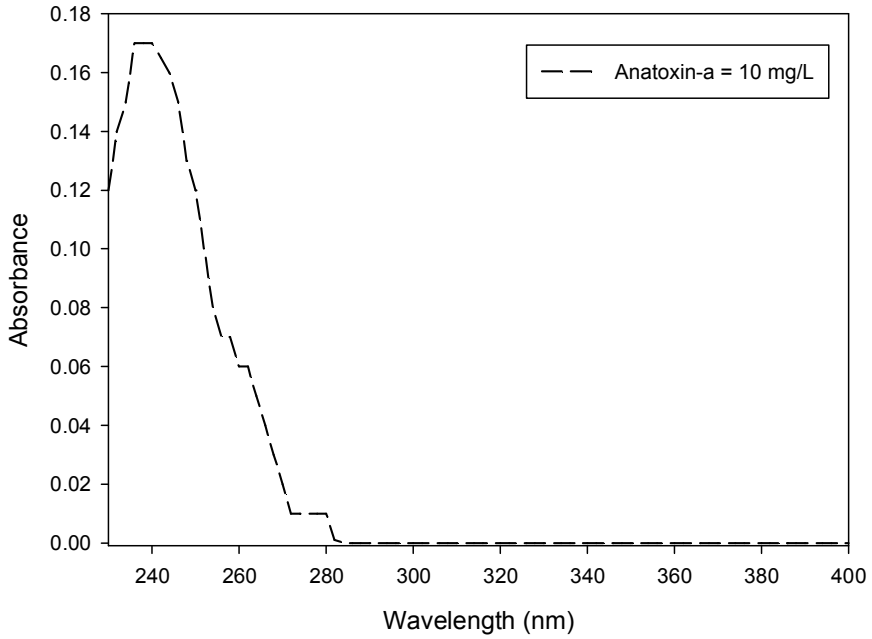


Figure 3. Light absorbance of anatoxin-a based on the UV wavelength (230 nm-400 nm).

Therefore, at UV-A wavelength (315 nm-400 nm), anatoxin-a was not degraded. When H_2O_2 is exposed to UV light, hydroxyl (·OH) radicals are generated by the mechanism of breakage of the peroxidic bond (1.2). With hydroxyl radicals, organic compounds such as anatoxin-a impose the formation of by-products (1.3) (Baxendale and Wilson, 1957; Crittenden et al., 1999; Lopez et al., 2003).

$$H_2O_2 \overset{hv}{\rightarrow} 2 \cdot OH \tag{1.2}$$

$$\cdot \mathrm{OH} + \mathrm{Organic\ compound\ (anatoxin-a)} \rightarrow \mathrm{By-products} \tag{1.3}$$

At UV-C wavelength which is short-wave ultraviolet radiations (20 0 nm-280 nm), more H_2O_2 can be converted to hydroxyl radicals compared with UV-A wavelength which is long-wave ultraviolet radiations (315 nm -400 nm) (Glaze et al., 1987). UV-A/H_2O_2 reaction had no effects to degrade anatoxin-a since it had not enough hydroxyl radicals that can degrade anatoxin-a effectively.

3.2. Removal efficiencies of anatoxin-a dependent on pH during UV-C/H_2O_2 reaction

Degradation rate of anatoxin-a is dependent on pH because the pKa of anatoxin-a is 9.4. Anatoxin-a is a neutral amine at pH higher than 8. Below pH 7, anatoxin-a is present as protonated amine, anatoxin-NH_2^+ (Onstad et al., 2007). Figure 4 shows the removal of anatoxin-a at different pHs during UV-C/H_2O_2 reaction. We compared the degradation kinetiscs of anatoxin-a at pH 3, 6.7 and 10. The degradation of anatoxin-a was more effective at neutral pH. This depicts that the solution pH significantly effects the degradation of anatoxin-a. Anatoxin-a was removed within 30 min during UV-C/H_2O_2 reaction at pH 6.7 (~99%). OH radical can be effectively produced at neutral pH compared to acidic pH and alkaline pH. Especially, at alkaline pH, OH radical can be scavenged by bicarbonate (1.4) and carbonate ions (1.5) (Buxton et al., 1986).

$$HCO_3^- + \cdot OH \rightarrow CO_3^{2-} + H_2O \quad (1.4)$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}, \qquad pK_a = 10.37$$

$$CO_3^{2-} + \cdot OH \rightarrow CO_3^{-} + OH^{-}$$

(1.5)

In addition, the intermolecular hydrogen bonding between the water molecule and the hydrogen atom of amine group of anatoxin-a can be explained as the reason of decreased rate of degradation of anatoxin-a in basic medium. The intermolecular and intramolecular hydrogen bonding might play an important role in the degradation of anatoxin-a. In previous study, at pH 6.4, the rate of degradation of anatoxin-a is the fastest (Verma and Sillanpaa, 2015). Therefore, all experiments were processed at pH 6.4 for good efficiency of removal rate.

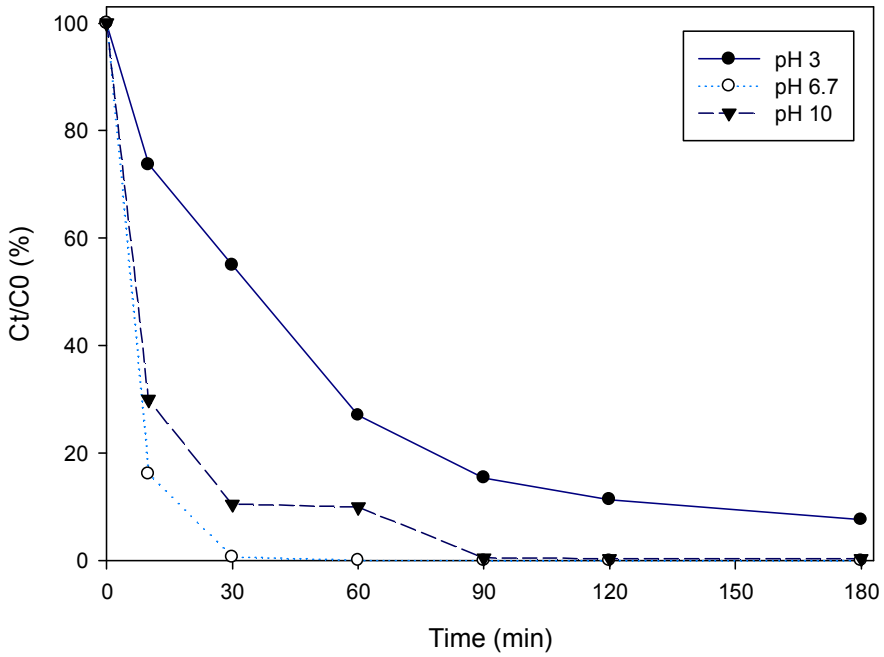


Figure 4. Removal of anatoxin-a during UV-C/H_2O_2 reaction at different pHs (experimental conditions; n=3, [C_0] = 0.3 μM (50 μg/L), UV intensity = 3.5 mW/cm^2, [H_2O_2] = 0.005 mM and 0.01 mM, 20℃)

3.3. Degradation kinetics of anatoxin-a during H_2O_2 only, UV-C photolysis and UV-C/H_2O_2 reactions

We compared the three reactions which are UV-C photolysis, two different doses of H_2O_2 only, UV-C photolysis and UV-C/H_2O_2 reactions at different doses of H_2O_2. Figure 5 shows that more effective degradation of anatoxin-a was observed in UV-C/H_2O_2 reaction than UV-C photolysis and only addition of H_2O_2. During H_2O_2 only reaction (5 μM H_2O_2,), anatoxin-a was not removed until 180 min. Only 20% anatoxin-a was removed at 10 μM dose of H_2O_2 without UV photolysis during 180 min. The removal efficiencies at 5 μM H_2O_2 and 10 μM H_2O_2 with UV photolysis reached ~90%, 99%, respectively, within 30 min.

In contrast, without the source of photolysis, hydroxyl radicals which are capable of degrading organic substances including anatoxin-a cannot occurred. Only H_2O_2 input was not effective and UV photolysis combined with H_2O_2 was effective to degrade anatoxin-a. It is reported that removal of micropollutants by UV photolysis needs more power and cost (Autin et al., 2013). To improve the degradation efficiency of

anatoxin-s in AOP, UV-C/H_2O_2 reaction can be applied despite of small amounts of H_2O_2.

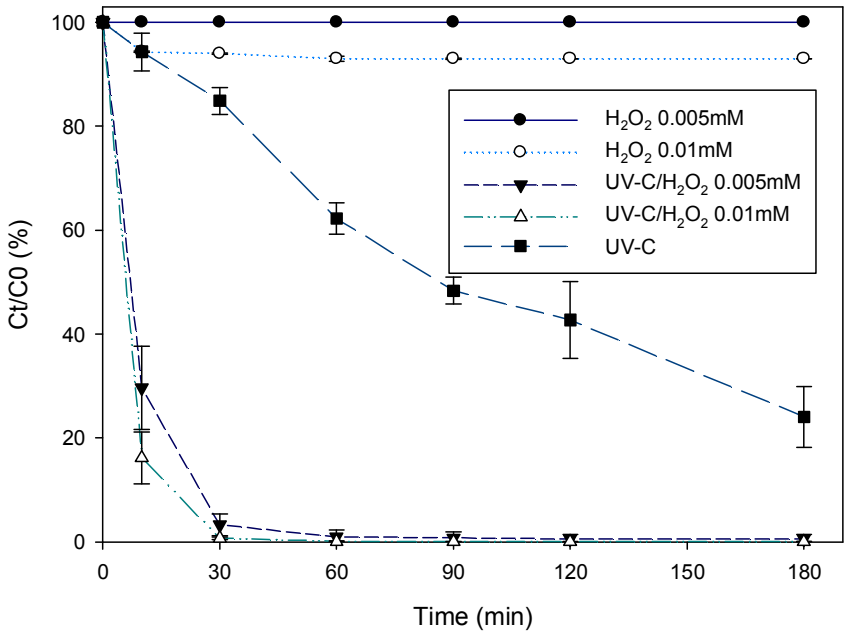


Figure 5. Removal of anatoxin-a during H_2O_2 only and UV-C/H_2O_2 reaction with the different H_2O_2 dose (experimental conditions; n=3, [C_0] = 0.3 μM (50 μg/L), UV intensity = 3.5 mW/cm^2, [H_2O_2] = 0.005 mM and 0.01 mM, pH=6.7, 20℃)

3.4. Mineralization and Identification of by-products of anatoxin-a during UV-C/H_2O_2 reaction

To observe the mineralization of anatoxin-a during UV-C/H_2O_2 reaction, we analyzed TOC of each treated samples by the time. The results are shown in Figure 6. Almost 60% anatoxin-a was mineralized within 120 min by the UV-C/H_2O_2 reaction and remained continuously. The low conversion of TOC indicates the presence of organic by-products during the degradation of anatoxin-a by UV-C/H_2O_2 reaction.

To confirm carbon type organic by-products, first, we measured the acetate by using ion chromatography. Figure 6 showed that almost 30% of carbon was changed into acetate during the degradation of anatoxin-a by UV-C/H_2O_2 reaction. This result implies that some parts of carbon of anatoxin-a was converted to acetate during UV-C/H_2O_2 reaction. The produced acetate ion can be further mineralized to CO_2 after transforming to formate, formaldehyde (Muggli et al., 1998). We could not detect the concentration of formate and formaldehyde because they were converted to CO_2 and H_2O rapidly by the lasting UV

photolysis and effect of OH radical.

As TOC was not changed until 420 min, other organic by-products can be generated simultaneously with degrading the acetate ion during UV-C/H_2O_2 reaction. To eliminate the possibility of occurring second pollution in aqueous system caused by the existence of organic by-products, we need to focus on the mechanism of degrading anatoxin-a and formation of by-products during UV-C/H_2O_2 reaction.

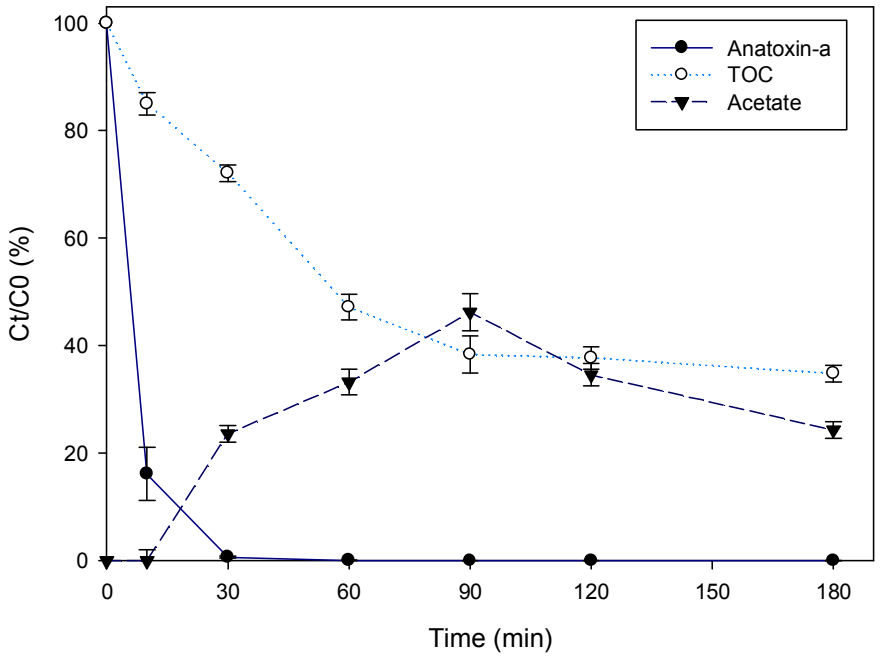


Figure 6. Time profiles of the anatoxin-a, TOC and acetate during UV-C/H_2O_2 reaction (experimental conditions; n=3, [C_0] = 60.6 μM (10 mg/L), UV intensity = 3.5 mW/cm^2, [H_2O_2] = 2 mM , pH=6.7, 20℃)

3.5. Formation of by-products including nitrogen by degradation of anatoxin-a during UV-C/H_2O_2 reaction

Since anatoxin-a ($C_{10}H_{15}NO$) contains one nitrogen in its molecular structure, the formation of nitrogen by-products is to be expected from UV photolysis with adding H_2O_2. After degradation of anatoxin-a by UV-C/H_2O_2 reaction, we analyzed the concentrations of NO_2^-, NO_3^- and NH_4^+ ions by using ion chromatography. Table 6 and Figure 7 summarized the change of NO_2^-, NO_3^- and NH_4^+ ions concentrations during the degradation of anatoxin-a by UV-C/H_2O_2 reaction.

The concentrations of anatoxin-a and nitrogen by-products are represented by the formation percentage (C_t/C_0 (%)). C (mol/L) is calculated from the original concentration of nitrogen ion which is included in anatoxin-a. This production amount was calculated as follows (1.6).

$$\frac{C_t}{C_0}\,(\%) = \frac{C_t\ (Nitrogen\ molarity\ of\ degradation\ byproducts,\ \ mol/L)}{C_0\ (Nitrogen\ molarity\ of\ initial\ concentration\ of\ anatoxin{-}a,\ \ mol/L)} \times 100$$

(1.6)

The total concentration of anatoxin-a was removed in 30 min. First, the concentration of NH_4^+ ion increased initially in 30 min. After that, the highest concentration of NH_4^+ ion reached almost 50% at 60 min and then continuously decreased. NO_3^- ion formation started at 60 min (19%). The concentration of NO_3^- ion was increasing simultaneously with decreasing the amount of NH_4^+ ion. It shows that NH_4^+ ion is converted to NO_3^- and NO_2^- ions. NO_2^- ion is not formed until 420min NO_2^- ion is produced but changed immediately to NO_3^- ion (Zoh and Stenstrom., 2002). NO_3^- ion is the most predominant because NO_2^- and NH_4^+ ions becomes rapidly changing to NO_3^- ion by oxidizing with hydroxyl radicals (Low et al., 1991).

Total nitrogen ion form mass balance increases until 120 min and reaches almost 108%, remaining at 420 min. Until 120 min, its nitrogen mass balance is below 100% because the nitrogen also remains in the form of nitrogen-containing organic intermediates and nitrogen during UV-C/H_2O_2 reaction and finally they can be broken as the form of NO_2^-, NO_3^- and NH_4^+ ions. It shows that total nitrogen which is contained in anatoxin-a is finally converted to nitrogen by-products form.

Table 6. Time profiles of N-including ions (NO_2^-, NO_3^- and NH_4^+) during UV-C/H_2O_2 (experimental conditions; n=3, [C_0] = 60.6 μM (10 mg/L), UV intensity = 3.5 mW/cm^2, [H_2O_2] = 2 mM , pH=6.7, 20℃)

C_t/C_0 (%) (mean±SD)	NO_2^-	NO_3^-	NH_4^+	Total (%)
0 min	0	0	0	0
30 min	0	0	8.3±0.14	8.3
60 min	0	19.3±1.2	50.2±0.5	69.5
120 min	0	63.6±0.3	46.0±0.4	109.6
180 min	0	52.0±0.5	34.8±0.5	86.8
420 min	6.6±0.6	73.8±1.2	27.9±1.2	108.3

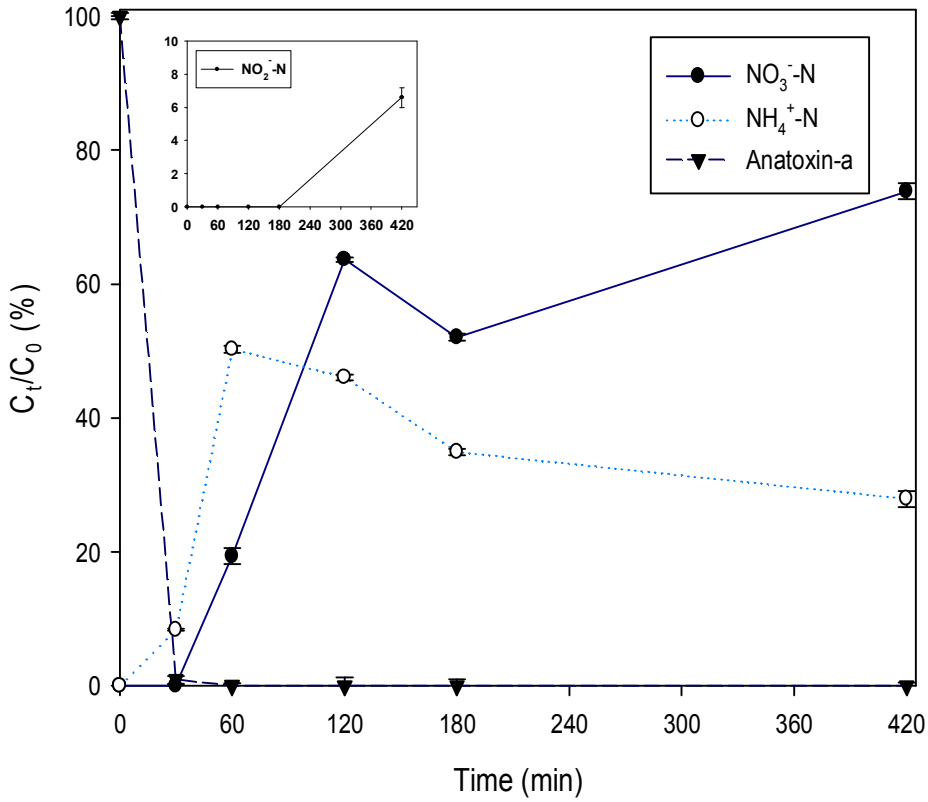


Figure 7. Time profiles of the N-by-products during UV-C/H_2O_2 (experimental conditions; n=3, [C_0] = 60.6 μM (10 mg/L), UV intensity = 3.5 mW/cm^2, [H_2O_2] = 2 mM , pH=6.7, 20℃)

3.6. By-products identification and formation pathways during UV-C/H_2O_2 reaction

To identify other carbon type degradation by-products, we used the electrospray ionization (ESI) full scan mode of mass spectrometer. The highest intensities of precursor ions were selected as the list of degradation by-products. The detailed information of selected precursor ions and product ions are summarized in Table 7. During UV-C/H_2O_2 reaction, six by-products were identified from the degradation of anatoxin-a, with $[M+H]^+$ values of 142, 127, 113, 132, 117 and 124. The peak areas of all by-products in each treated samples were measured by using LC-MS/MS and the time profiles of the degradation by-products during UV-C/H_2O_2 reaction are shown in Figure 8. All by-products are removed in 7 hours by further reaction.

Table 7. Fragmentation results of anatoxin-a degradation by-products during the UV-C/H_2O_2 reaction

Compounds	Predicted molar weight	Precursor ion (m/z)	Product ion (m/z)
Anatoxin-a	165	166	149, 121, 68
By-product 1	141	142	123, 99, 81
By-product 2	126	127	81, 71, 72
By-product 3	112	113	83, 69, 67
By-product 4	131	132	103, 85, 81
By-product 5	116	117	99, 61, 89
By-product 6	123	124	113, 95, 61

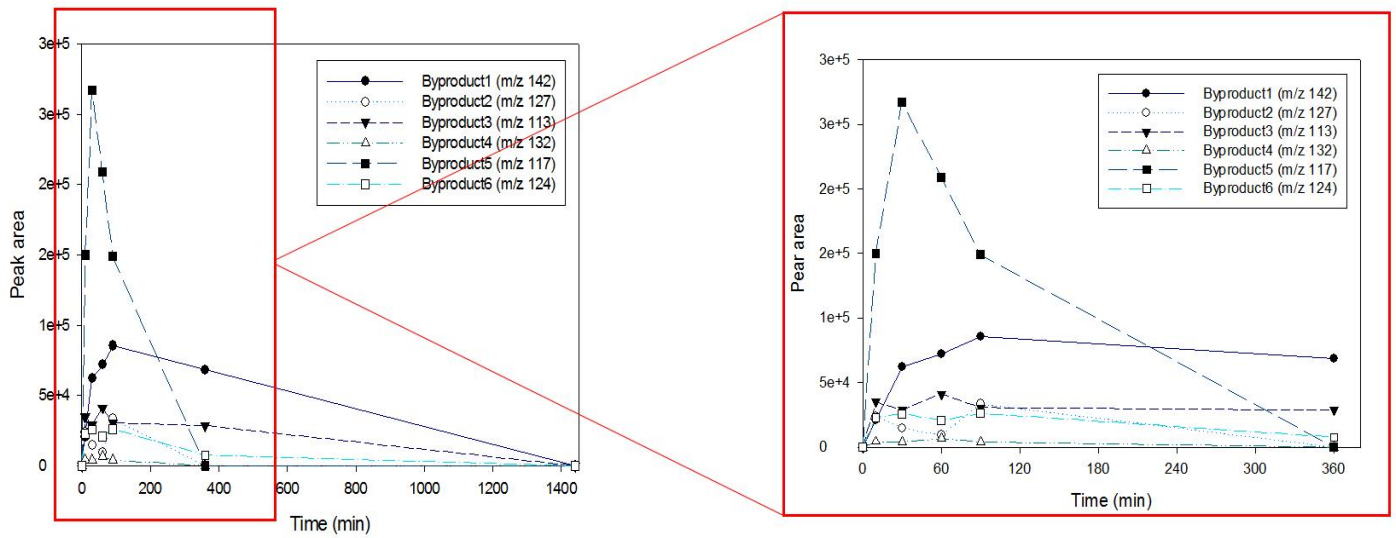


Figure 8. Peak area changes of anatoxin-a by-products during the UV-C/H_2O_2 reaction (experimental conditions; n=3, $[C_0]$ = 0.3 μM (50 μg/L), UV intensity = 3.5 mW/cm^2, $[H_2O_2]$ = 0.01mM, pH=6.7, 20℃)

Figure 9 shows the proposed anatoxin-a degradation by-products pathways for UV-C/H_2O_2 reaction. By-product 1 ($[M+H]^+$ value of 142) was produced from ring opening of anatoxin-a structure. OH radicals attack on the aromatic ring and on the aliphatic carbon chain (Vogna et al., 2002; Vogna et al., 2004).

Anatoxin-a structure is having a ring with a branch chain (C_2H_3O-). This branch was cut by OH radical with photolysis and led to the production of by-product 6 ($[M+H]^+$ value of 124). The branch attached to ring is the site which can be easily attacked by OH radical. By detecting the acetate ion by using ion chromatography, we confirmed the separation of acetate from anatoxin-a structure.

By-product 2 $[M+H]^+$ value of 127 and by-product 3 $[M+H]^+$ value of 113 are formed by the removal of amine group (NH_2^-) from by-product1 $[M+H]^+$ value of 142. During this reaction, nitrogen was separated and formed N-by-products which were identified during UV-C/H_2O_2 reaction. By using ion chromatography, we detected N including ions (NO_2^-, NO_3^- and NH_4^+ ions) and proved that amine group is separated from some organic by-products during UV-C/H_2O_2 reaction. By-product 4 $[M+H]^+$ value of 132 and by-product 5 $[M+H]^+$ value of 117 were produced by the addition of OH at by-product 1

$[M+H]^+$ value of 142. In previous studies, reaction with OH radical can suggest cleavage of branch side such as phosphate and acetate (Zhang et al., 2015). The hydroxylation can yield various by-product forms such as By-product 4 and By-product 5. By-product 5 $[M+H]^+$ value of 117 also had the removal of amine group during UV-C/H_2O_2 reaction. All by-products were finally mineralized as the form of CO_2, H_2O and N-by-products (NO_2^-, NO_3^- and NH_4^+ ions).

These organic by-products were remained in treated water after AOP in water treatment plant and can cause other second pollution by combining with various organic compounds derived from disinfection by-products and halogen ions such as chlorine and bromine. Formation of Br-by-products and Cl-by-products have the potential risks to be harmful to human (Ji et al., 2016). In further studies, we need to know detoxification of anatoxin-a during UV/H_2O_2 reaction for upgrading and conserving the drinking water quality.

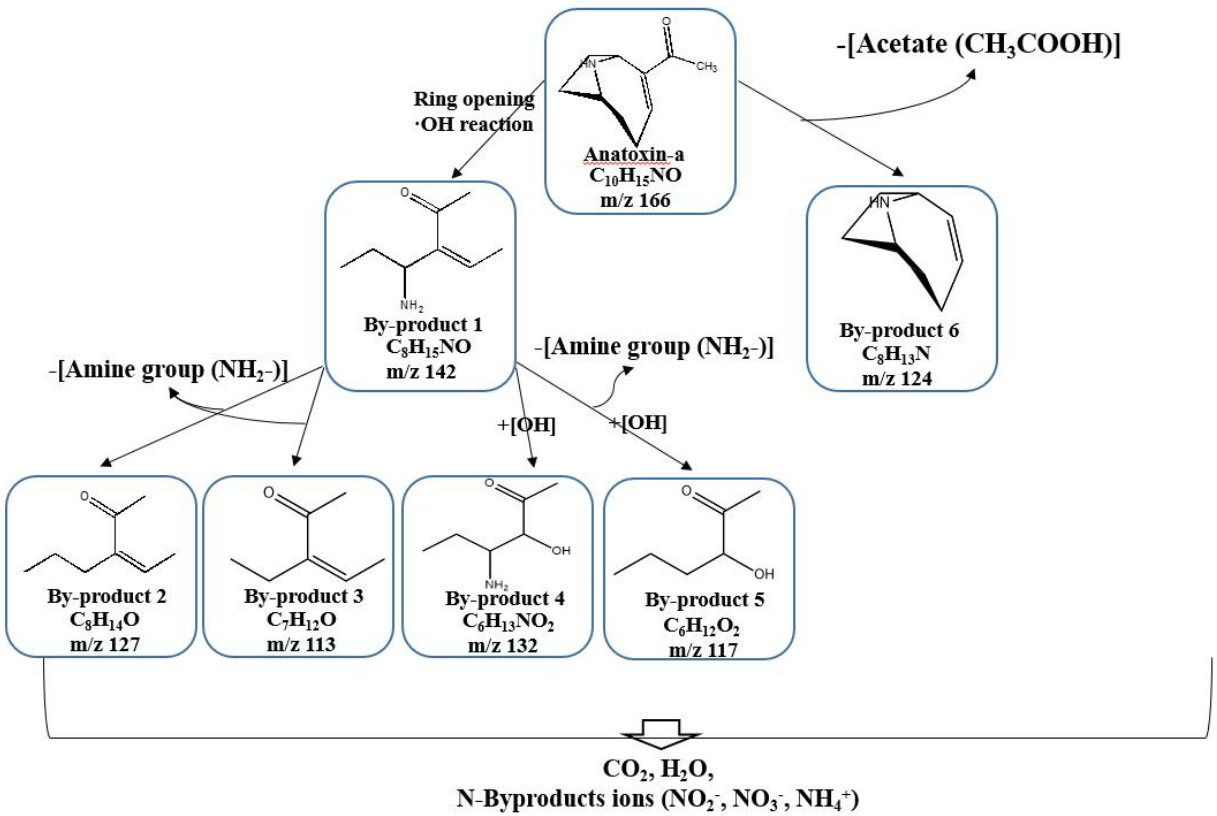


Figure 9. Proposed anatoxin-a degradation pathways for UV-C/H_2O_2 reaction

V. Conclusion

In this study, we examined the degradation efficiencies of anatoxin-a during UV photolysis and UV/H_2O_2 reactions. The most effective process for removing anatoxin-a is UV-C/H_2O_2 reaction compared to UV-A photolysis, UV-C photolysis and UV-A/H_2O_2 reactions. The removal of anatoxin-a increased as the H_2O_2 dose increased. Significant mineralization of anatoxin-a into N-by-products (NH_4^+, NO_2^- and NO_3^- ions) and acetate was achieved during UV-C/H_2O_2 reaction. Total six by-products ([M+H] values of 142, 127, 113, 132, 117 and 124) were newly identified during UV-C/H_2O_2 reaction and these by-products were degraded with further reaction. This study provides that UV-C/H_2O_2 reaction can be an option to treat anatoxin-a in WTPs.

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국문초록

$UV-C/H_2O_2$ 공정 중 아나톡신-a의 분해 특성과 메커니즘 연구

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지도교수 조 경 덕

남조류는 가축과 사람에게 유해한 영향을 미치는 독소 물질을 생성한다. 사람은 조류 독소 물질이 제거되지 않은 물질을 마시거나 독소가 축적된 물고기를 섭취함으로써 독소 물질에 노출된다. 조류 독소 물질은 미량의 농도로도 사람의 건강에 영향을 미칠 수 있다.

아나톡신-a는 남조류의 한 종인 *Anabaena flos-aquae* 에서 주로 분비되는 조류 독소 물질 중 하나이다. 아나톡신-a는 사람이나 동물에게 청색증, 마비, 근육의 과다자극 증상등을 유발하며 해로운 영향을 미친다. 특히, 아나톡신-a가 사람의 호흡근에 영향을 미칠 경우 질식에 의해 죽음에 이를 수도 있다.

이전연구에 의하면, UV/H_2O_2에 의한 아나톡신-a의 제거는 매우 효과적이다. 하지만, 공정 중에 생성되는 부산물에 대한 연구는 미흡한 실정이므로 UV/H_2O_2 공정 중 아나톡신-a의 분해 특성 및 부산물 생성 메커니즘을 규명하고자 하였다. 이를 위하여 본 연구에서는 (1) UV, H_2O_2, UV/H_2O_2 에 의한 아나톡신-a의 제거 효율을 비교하여 분해 특성을 파악 하는 것과, (2) UV/H_2O_2 공정 중의 시간대별 처리수를 샘플링하여 MS, MS/MS 크로마토그램을 통해 생성되는 부산물의 분자구조를 예측하는 것, (3) TOC, 아세테이트 이온, 질소원소를 포함한 이온 (NO_2^-, NO_3^-, NH_4^+)을 확인하고자 하였다.

광분해 반응기를 제작하여 자외선 광강도 3.5-4.0 mW/cm^2, H_2O_2 주입량 0.005 mM, 0.01 mM 조건 하에서 실험을 진행하였다. 모든 샘플은 고체상 추출 방법으로 전처리 한 후에, LC-MS/MS로 분석하였다.

아나톡신-a는 UV 광분해 또는 H_2O_2만 주입한 공정과 비교하였을때, UV/H_2O_2 공정에 의하여 제일 효과적으로 제거되었다. UV-A/H_2O_2와 UV-C/H_2O_2 공정에 의한 아나톡신-a의 제거 효율을 비교하였을 때, 짧은 파장인 UV-C/H_2O_2 공정이 높은 제거율을 보였다. 아나톡신-a는 UV-C/H_2O_2 공정시에, OH 라디칼 생성 효과로 인하여 30분안에 모두 제거 되었다. UV-C/H_2O_2 공정에 의하여 아나톡신-a의 분해 과정 중에, TOC는 시간에 따라 일정하게 감소하다가 일정하게 유지되었다. 이는 아나톡신-a가 CO_2와 H_2O의 형태로 전부 미네랄라이제이션 되지 않고, 부산물의 형태로 남아 있는 것을 알 수 있었다. 이온크로마토그래피를 이용하여 아세테이트이온과 질소가 포함된 이온들의 분석 결과, UV-C/H_2O_2 공정에 의한 아나톡신-a의 분해 반응 과정 중에 아세테이트와 질소가 포함된 이온들이 부산물로 생성되는 것을 확인하였다. LC-MS/MS를 이용하여 UV-C/H_2O_2 공정에 의하여 6개의 새로운 부산물들(m/z: 142, 127, 113, 132, 117, 124)을 확인하였다.

국내에서는 연구가 미흡한 조류 독소인 아나톡신-a에 대하여 고도산화처리에 의한 제거 특성을 제시함으로써, 정수장에서 조류 독소 처리시에 수질 관리에 기여할 수 있을 것이다. 또한, 고도산화처리에 의해 생성되는 부산물에 대한 염려가 증가되고 있는 상황에

서 아나톡신-a의 분해 메커니즘 규명을 통하여 처리수에 대한 고찰이 진행 될 수 있을 것이다.

주요어: 아나톡신-a; UV-C 광분해; UV/H_2O_2 공정; 부산물; 분해 경로

학번: 2015-24066