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보건학석사학위논문

**Degradation mechanism of two algal odorants,
 β -cyclocitral and β -ionone under UV photolysis,
chlorination and UV-chlorination**

자외선 광분해, 염소 처리 및 자외선-염소처리를 통한
조류기인 유기물질 β -cyclocitral 과 β -ionone 의 분해
기작 규명에 관한 연구

2017 년 8 월

서울대학교 보건대학원

환경보건학과 환경보건학전공

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이 논문을 보건학석사학위 논문으로 제출함

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Abstract

Algal taste and odor compound has become one of emerging concerns affecting drinking water quality. Among several algal odorants, β -cyclocitral and β -ionone are the oxidation byproducts of β -carotene existing in algae cells. Several AOPs such as UV- H_2O_2 and ozonation had adapted for algal odorants. However, degradation kinetic and byproducts of β -cyclocitral and β -ionone under UV-chlorination is not studied much. For these reasons, two odorants were treated by UV photolysis, chlorination and UV-chlorination and the degradation kinetic and byproducts of three treatment were examined. β -ionone showed faster degradation under all reactions compared to β -cyclocitral. The double bond on carbon chain of β -ionone is a reactive site for chlorination, hydroxyl radical attack and UV induced isomerization. Among three reaction, UV-chlorination was the most effective treatment due to generation of hydroxyl radical by reaction between UV and chlorine. Alkaline pH was not favored for UV-chlorination because hypochlorite is dominant form of active chlorine at alkaline pH and it is able to consume hydroxyl radical and it is inefficient for generating hydroxyl radical. During UV-chlorination reaction, only chloroform was generated for byproducts of reaction among regulated VOCs. It is due to methyl ketone functional group of the parent compounds. UV-chlorination had enhanced the formation of chloroform compared to chlorination. However increased amount of chloroform is very little compared to guideline limit. By GC-MS scanning, several intermediates of β -ionone under UV-chlorination were observed including β -cyclocitral. These compounds were formed by UV isomerization, hydroxyl radical attack and bond scission reaction.

Keywords : UV-Chlorination, Advanced Oxidation Process, β -cyclocitral, β -ionone, degradation kinetic, degradation mechanism

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1. Introduction

1.1. Background

Algal bloom is one of the major water pollution problems caused by excessive inflow of nutrients containing nitrogen and phosphorous. Eutrophication enhances excessive growth of hazardous phytoplankton in waterbody (Glasgow et al., 2004). Accumulation of cyanobacteria can cause serious impact on water ecosystem by oxygen depletion and algal toxins (Briand et al, 2003). Furthermore, algal bloom is able to decrease efficiency of water treatment process by clogging of inflow screen and filter, disturbing of flocculation process and increased amount of disinfection byproducts and DBPs precursors etc. (Chow et al., 1999). Besides, conventional water treatment processes (WTPs) are not sufficient for removing algal derived substances such as algal toxins and taste and odor compounds (Fang et al, 2010).

One of the major problems caused by algal bloom is taste and odor causing compounds. They are generated by algal metabolic activities and able to cause odor. Several compounds causing odor generated by algal metabolic activity such as geosmin, 2-MIB, β -cyclocitral, β -ionone, 2-Isopropyl-3-methoxypyrazine, 2-Isobutyl-3-methoxypyrazine and dimethyl trisulfide etc. (Zhang et al., 2013). These compounds have low odor thresholds around ng/L level. Therefore these odorants should be monitored and treated at drinking water treatment processes (Antonopoulou et al., 2014).

There are few studies dealing with taste and odor compounds using activated carbon, coagulation and filtration (Jung et al, 2004). However, these physical removal treatments are affected by natural organic matters and granular or powder activated carbon requires additional regeneration processes (Matilainen et al., 2006). In case of geosmin and 2-MIB, it is known that several kinds of oxidants such as active chlorine, chlorine dioxide and potassium permanganate are inefficient for removal because of tertiary alcohol structure and its tolerance to oxidants (Qi et al., 2010).

For these reason, advanced oxidation processes (AOPs) has been applied to oxidize taste and odor compounds. AOPs is oxidation processes using hydroxyl radicals and other reactive species ($\cdot\text{HO}_2$, $\cdot\text{O}_2^-$, $\cdot\text{O}_3^-$) in order to degrade pollutants. Ozonation, fenton processes, photo-fenton reaction, UV- O_3 , UV- H_2O_2 , UV-Chlorination, UV- TiO_2 were common methods for removal of taste and odor compounds (Antonopoulou et al, 2014). Among these methods, fenton reaction generates iron sludge and ozonation requires quenching after reaction (Meriç et al, 2005). Most UV based AOPs needs short wavelength of UV irradiance like UV-C (200 ~ 280 nm) or vacuum ultraviolet (VUV, 10 ~ 200 nm). However, UV-Chlorination can generate hydroxyl radical under UV-A or UV-B irradiance and even sunlight. (Chan et al, 2012) For these reason, there are several studies about degradation of micropollutants using UV-chlorination. (Sun et al, 2016). However, toxic byproducts like chlorate, perchlorate and halogenated organic compound were also formed during UV-chlorination reaction. (Wang et al, 2015)

Among several algal odorants, β -cyclocitral and β -ionone are the oxidation byproducts of α , β -carotene existing in the cells of green algae and cyanobacteria like *Microcystis*, *Cyanidium caldarium*, *Synura uvella*, *P. rubescens* (Baldermann et al., 2010). These compounds are normally detected around several to tens ng/L level. However, during algal bloom events, it leaches to hundreds ng/L level. Table 1 shows the occurrences and concentration of two odorants in surface water.

Table 1. Occurrence and concentration of β -cyclocitral and β -ionone in surface water

	β -cyclocitral (ng/L)	β -ionone (ng/L)	Reference
Lake Taihu, China	9.5 ~ 284.3	0.0 ~ 185.0	Ma et al., 2013
Gonghu bay, China	0.81 ~ 538.12	0.00 ~ 50.44	Chen et al., 2010
Zurich, Swiss	-	27.5	Peter et al., 2009
Lake Chaohu, China	Maximum 714.77	11.97	Jiang et al., 2016

There are several studies dealing with treatment of these two taste and odor compounds (Table 2). These compounds were degraded well under both chlorination and ozonation and its rate constants with hydroxyl radical were reported in previous studies (Peter and Von Gunten, 2007, Zhang et al., 2012). However, only one study reported on the formation of intermediates. Granular activated carbon (GAC) can also remove 2 taste and odor compounds by physical adsorption. However, additional treatment is required for mineralization after adsorption. Thus, another AOP is needed like UV-chlorination which can utilize both UV photolysis, chlorination and hydroxyl radical.

Combination of UV photolysis and chlorination can generate hydroxyl radical and lead to additional degradation of pollutants (Watts and Linden, 2007). Hydroxyl radical has more powerful oxidation power compared to chlorine, ozone and other oxidants (Munter, 2001). Compared to other AOPs, UV-chlorination can be easily adapted to existing chlorination systems and avoid the cost of hydrogen peroxide. However, chlorinated byproducts can be formed during UV-chlorination (Lyon et al., 2012). Consequently, identifying byproducts should be considered in optimizing UV-chlorination processes.

Table 2. Publication on the treatment of β -cyclocitral, β -ionone

Treatment	Degradation kinetics	Byproduct Identification	References
Chlorination	β -cyclocitral: $0.093 \pm 0.0036 \text{ min}^{-1}$ β -ionone: $1.86 \pm 0.12 \text{ min}^{-1}$	○	Zhang et al. (2012)
Ozonation	β -cyclocitral: $3890 \text{ M}^{-1}\text{s}^{-1}$ β -ionone: $1.6 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$	X	Peter and Von Gunten (2007)
OH radical (UV/H ₂ O ₂ , γ -ray)	β -cyclocitral: $7.42 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ β -ionone: $7.79 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	X	Peter and Von Gunten (2007)
GAC	β -cyclocitral: 96.9%	N.A.	Zhang et al. (2011)

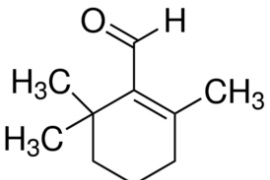
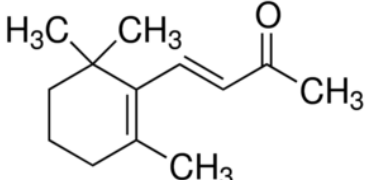
1.2. Objectives

For these reasons, the objectives of this study is to examine the degradation kinetics of β -cyclocitral and β -ionone under UV photolysis, chlorination and UV-chlorination and to identify the intermediates and byproducts formation of 2 odorants under three reactions and to suggest the degradation pathways of β -cyclocitral and β -ionone during these reactions.

2. Material and Methods

2.1. Chemicals

Table 3. Physico-chemical properties of β -cyclocitral and β -ionone

	β -Cyclocitral	β -Ionone
Chemical formula	$C_{10}H_{16}O$	$C_{13}H_{20}O$
Molecular weight	152	192
Boiling point ($^{\circ}C$)	214	239
Odor threshold (ng/L)	500	7
Density (g/mL)	0.943	0.945
Chemical structure		

Two odorants, β -cyclocitral (> 97 %) and β -ionone (> 96%) was obtained from Sigma-Aldrich (USA) and its physicochemical properties and odor threshold were presented in Table 3. These compounds were diluted only in deionized water for advanced oxidation experiment in order to avoid disinfection byproduct formation from other solvents. Sodium hypochlorite (0.2 % solution) and

Sodium thiosulfate (> 99%) were obtained from Sigma-Aldrich (USA). 1,2-dichlorobenzene-d₄ solution (2000 µg/mL in methanol, Sigma-Aldrich, USA) was used for internal standard of algal odorants and volatile compounds. Volatile organic compounds mix including chloroform, carbon tetrachloride, 1,1-dichloroethylene, tetrachloroethylene, 1,1,1-trichloroethane, trichloroethylene (100 µg/mL in methanol) and BTEX mix (2000 µg/mL in methanol) were purchased from Sigma-Aldrich (USA). Sulfuric acid (98 %, Sigma-Aldrich, USA) and Sodium hydroxide (0.1 N, Sigma-Aldrich, USA) were used for adjusting pH of solution. Sodium chloride was obtained from Wako (Japan) for the solid phase microextraction analysis. Deionized water was generated from Milli-Q deionized water generator (Millipore, USA) .

2.2. Experiment setup

UV photolysis, chlorination and UV-chlorination experiment were conducted at batch type reactor with six 80mL-quartz vials (Figure. 1). These vials have Teflon-coated septa and the sample were contained into the vials without headspace in order to prevent volatilization of sample. These vials were put on roller to mix the solution. The reactor was surrounded by aluminum foil to minimize the loss of UV irradiation. One mercury UV lamp (20 W, 254 nm, San-Kyo Electrics, Japan) were located 15 cm above the vials to avoid direct heating by UV lamp.

To identify degradation kinetic and intermediates, 500 µg/L of β-cyclocitral or β-ionone was injected to the reaction solution. Sodium hypochlorite was used to add chlorine to the solution and pH of solution was adjusted by using 0.1 N sulfuric acid and 0.1 N sodium hydroxide. The free chlorine concentration of the solution was set to 3 mg/L as Cl₂ and UV intensity on the surface was 0.6 mW/cm². After reaction, 20 µL of 0.5 M sodium thiosulfate was added to 50 mL of sample to quench residual chlorine and terminate chlorination reaction.

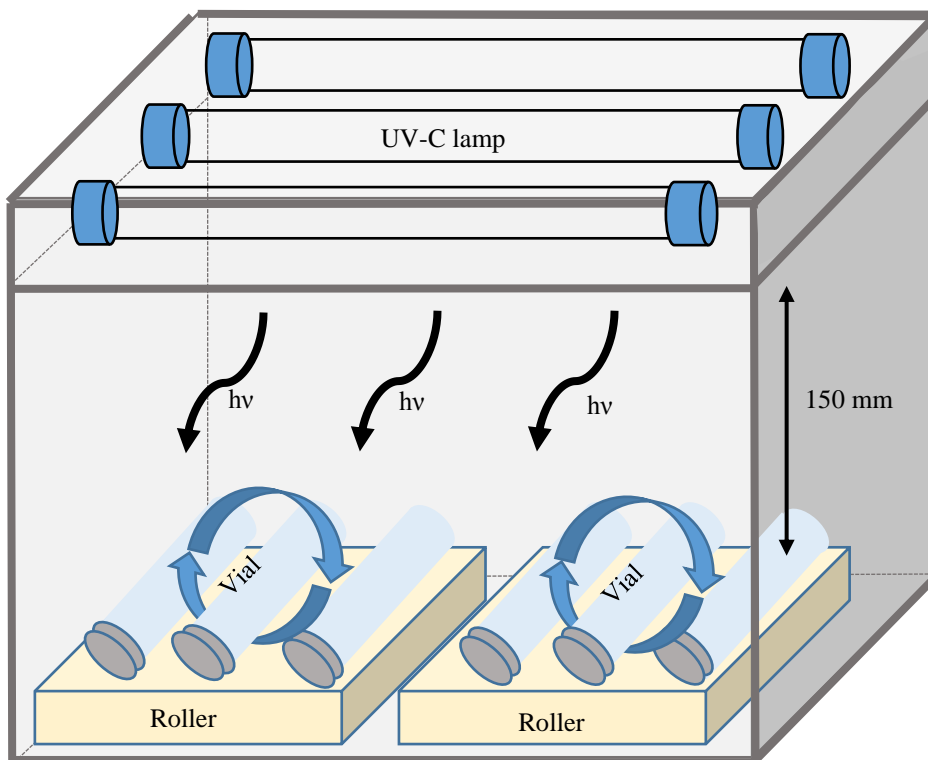


Figure 1. The schematic diagram of photolytic reactor

2.3. Analysis

The concentration of free chlorine was measured by colorimetric method using DPD reagent (N,N Diethyl-1,4 Phenylendiamine Sulfate) with HACH DR/890 colorimeter (HACH, Loveland, Colorado, USA). UV intensity was checked by using UV radiometer (VLX-3W Radiometer 9811-50, Cole-Parmer, USA)

For analyzing taste and odor compounds and volatile organic compounds, GC-MS (7890A / 5975C, Agilent, USA) was used. β -cyclocitral and β -ionone were analyzed by Headspace-SPME-GC/MS. 10 mL aliquot of sample was put into 20 mL vial with 3 g of sodium chloride and 20 μ L of 1,2-dichlorobenzene- d_4 (20 μ g/L) as internal standard. Before analysis, the sample vial was stirred at 65 $^{\circ}$ C for 1 min in order to dissolve all sodium chloride. Later, DVB/CAR/PDMS fiber (2cm, Supelco,

USA) was exposed to the headspace of the vial. The vial was agitated at 600 rpm for 10 min to adsorb taste and odor compounds onto the SPME fiber. After extraction, the fiber was thermally desorbed at the GC injection port. The GC injector was heated at 270 °C with splitless mode. DB-5MS-UI column (30 m × 0.25 mm × 0.25 μm) was used for separation. High purity helium gas (>99.999%) was used as carrier gas and the flow rate was set at 1 mL/min. The GC oven temperature was set 50 °C and held for 5 min, then increased to 65 °C at a rate of 5 °C/min and held for 2 min after that, ramped to 215 °C at a rate of 15 °C min with 4 min hold.

Volatile organic compounds were analyzed by Headspace-GC/MS. The 20 mL vial with 10 mL of sample and 20 μL of 1,2-dichlorobenzene-d₄ (20 mg/L) was agitated for 20 min at 65 °C. After agitation, 1.5 mL of headspace sample was injected to the GC inlet with headspace syringe heated for 90 °C. For headspace analysis, DB-5MS-UI column (15 m × 0.25 mm × 1.0 μm) was used. Split ratio was set to 10: 1. The oven program of GC was initially set at 35 °C with 7 min hold then ramped to 50 °C at a rate of 5 °C/min and finally increased to 150 °C at a rate of 10 °C/min. The temperature of the EI ion source and the quadrupole of the MS was set at 270 °C and 150 °C for both two methods. In order to both quantify target compounds and screening for possible intermediate candidates, synchronous SIM/Scan mode was utilized and scan range was m/z = 40 ~ 250.

To identify unknown byproducts, Purge and Trap (Stratum, Teledyne Tekmar, USA) – GC/MS (6890 / 5973, Agilent, USA) was used. 5 mL of sample was injected to Purge and Trap and purged for 11 minutes under 40 mL/min flow of helium at 20 °C. After that, the trap was desorbed at 250 °C for 2 minutes. The fragment ions of sample were scanned at m/z = 40 ~ 250 range. GC-MS conditions were same as methods for taste and odor compounds except for EI ion source temperature which was set at 240 °C.

3. Result

3.1. Degradation kinetic of β -cyclocitral and β -ionone under UV photolysis, chlorination and UV-chlorination

UV photolysis, chlorination and UV-chlorination experiment were conducted for two taste and odor compounds and degradation kinetics were presented at figure 2. Under UV photolysis, chlorination and UV-chlorination, the 80.5 %, 24.3 % and 96.6 % of β -cyclocitral was degraded in an hour. In case of β -ionone, the removal efficiency was 82.6 %, 63.1 % and 96.9 % for chlorination, UV photolysis and UV-chlorination within an hour. Overall, β -ionone degraded faster than β -cyclocitral by three reaction. In addition, the UV-chlorination showed the greatest removal among reactions. The degradation kinetics of UV photolysis, chlorination and UV-chlorination were fitted well at pseudo-first order kinetic. These degradation rate constants is shown in table 4.

Structural difference between two odorants made β -ionone more vulnerable to several oxidants. β -ionone has longer carbon chain and one more double bond compared to β -cyclocitral. Hypochlorous acid is able to react with double bond by electrophilic halogenation reaction. β -ionone degraded faster than β -cyclocitral by chlorination. In addition, hydroxyl radical and chlorine radical also attack on the double bond and carbon chain and isomerization can occur under UV irradiance at the double bond on the carbon chain of β -ionone (Borasarelli et al, 2007, Deborde and Von Gunten, 2008).

UV photolysis and chlorination also showed sufficient removal for two odorants. However, UV photolysis requires a lot of energy to decompose taste and odor compounds when using it without oxidants. Total UV irradiation energy intensity was 36,000 J/m² in an hour. On contrary to this, generation of hydroxyl radical and additional oxidation occurred during UV-chlorination. For these reasons, UV-chlorination is able to reduce energy consumption by UV and achieve improved degradation efficiency.

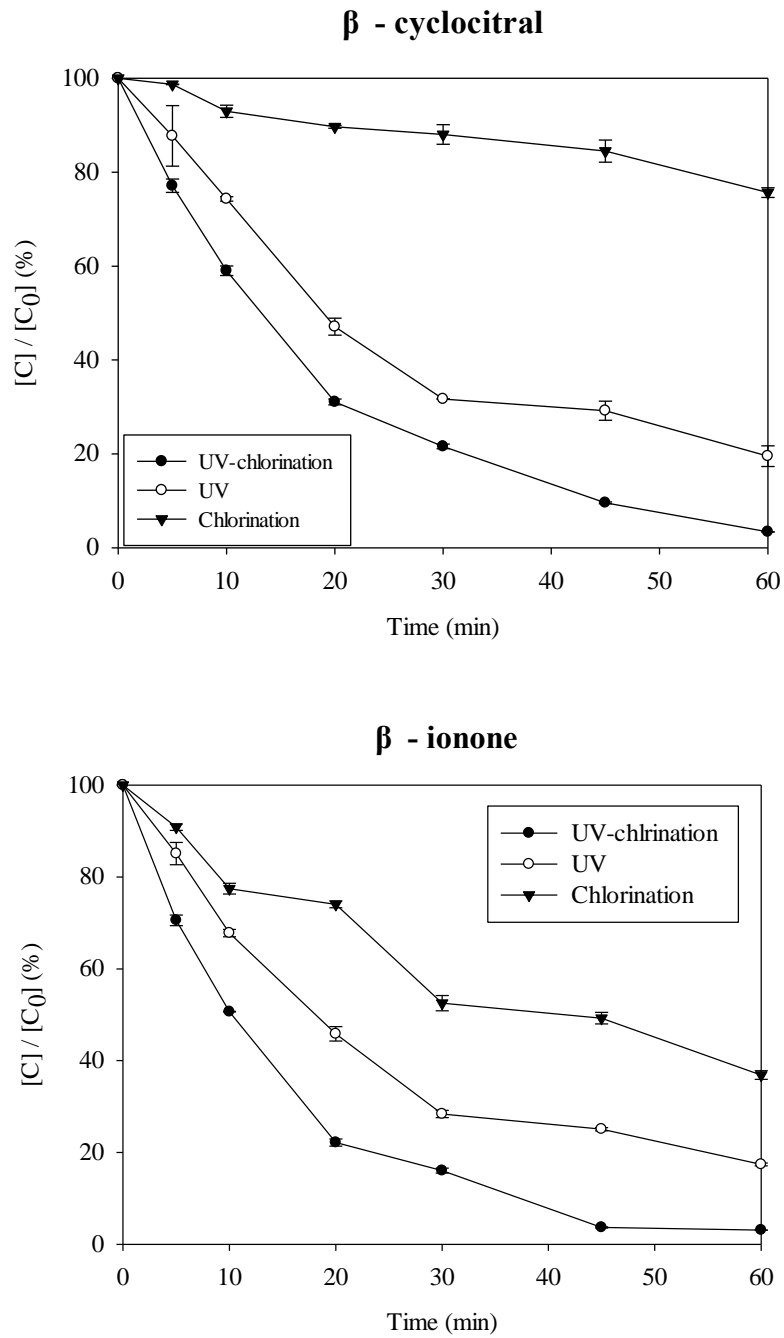
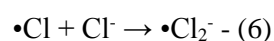
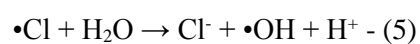
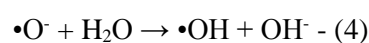
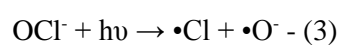
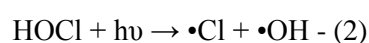
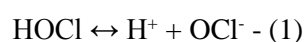


Figure 2. Degradation kinetic of β -ionone (left) and β -cyclocitral (right) under UV-chlorination, UV photolysis, chlorination ($[C_0] = 500 \mu\text{g/L}$, $[\text{Cl}_2] = 3 \text{ mg/L}$, UV intensity = 0.6 mW/cm^2 , pH = 7, 25°C , n = 2)

Table 4. Degradation rate constant of two odorants under three reaction

Odorant	Treatment	Pseudo first-order rate constant (min ⁻¹)	R ²
β-cyclocitral	UV	0.0275	0.953
	Chlorine	0.0043	0.958
	UV-Cl ₂	0.0550	0.995
β-ionone	UV	0.0296	0.956
	Chlorine	0.0162	0.966
	UV-Cl ₂	0.0617	0.970

Reactions of active chlorine species under UV irradiance are as follows (Jin et al, 2011). Dominant form of active chlorine is determined by the pH of the solution. Hypochlorous acid is prevalent when the pH is below its pKa value 7.53, and hypochlorite ion is abundant form at alkaline pH (Equation 1). The hypochlorous acid is dissociated into chlorine radical and hydroxyl radical. This hydroxyl radical plays main role in degrading pollutants (Equation 2). In case of hypochlorite ion, it is divided into the chloride radical and single oxygen atom radical (Equation 3). Later, oxygen radical reacts with water molecule to transform hydroxide ion and hydroxyl radical. (Equation 4). The chloride radical also contributes to the generation of hydroxyl radical by reaction with water (Equation 5).



3.2. pH dependency of degradation kinetic of β -cyclocitral and β -ionone under UV-chlorination

UV-chlorination experiments were conducted under different initial pH. Table 5 shows the degradation kinetic constant on different pH. For both β -cyclocitral and β -ionone, degradation reactions were promoted at acidic condition compared to alkaline pH.

Table 5. Degradation rate constant of UV-Chlorination under different pH

Odorant	pH	Pseudo-first order rate constant (min ⁻¹)	R ²
β -cyclocitral	5	0.0599	0.959
	7	0.0550	0.995
	9	0.0451	0.954
β -ionone	5	0.0922	0.953
	7	0.0617	0.970
	9	0.0449	0.928

Relative distribution of free chlorine species under different pH is main reason for enhancement of UV-chlorination at acidic pH. Hypochlorite ion is dominant form at the alkaline pH and hypochlorous acid is dominant around pH 3 to 5 (Deborde and Von Gunten, 2008). Hypochlorous acid poses not only stronger oxidation power but also higher UV absorbance compared to hypochlorite ion. The quantum yields of hydroxyl radical formation at 254 nm UV irradiance was 1.4 for hypochlorous acid and 0.278 for hypochlorite ion (Remucal and Manley, 2016). Therefore, hydroxyl radical were generated grater at acidic pH. Furthermore, equation 6 and 7 shows parasitic reactions and its reaction constants of OH radical when existing chlorine species. Hypochlorite ion has scavenging effects on hydroxyl radical 10^5 times higher than hypochlorous acid (Nowell and Hoigne, 1992). For these reasons, the degradation rate constants of two odorants appeared greater at acidic pH.



3.3. Degradation byproducts of β -cyclocitral and β -ionone under UV photolysis, chlorination and UV-chlorination

After chlorination and UV-chlorination experiments, GC-MS analysis was conducted to confirm formation of VOCs and its concentration. Among several legally regulated VOCs, only chloroform was formed during UV-chlorination of two compounds. During degradation of β -cyclocitral, chloroform concentration was kept increasing up to 75 ~ 85 $\mu\text{g/L}$ in an hour. For β -ionone, chloroform leached to maximum amount around 60 ~ 80 $\mu\text{g/L}$. On the contrary to this, the chloroform was not formed more than MDL level during chlorination.

Moreover, chloroform formation yields were calculated as ratio of actual yield to theoretical yield. This ratio was determined as 2.12% for β -cyclocitral and 1.61 % for β -ionone. In other words, β -cyclocitral had generated greater chloroform per one molecule than β -ionone. β -ionone has more reaction site for active chlorine and chlorine radical. Therefore, chlorine species contributed more to chloroform formation in UV-chlorination of β -cyclocitral.

In addition, there are difference in chloroform formation upon different initial pH. For both compounds, chloroform was formed greatest at alkaline pH. In general, it was reported that chloroform formation reaction is favored at alkaline pH since hydroxide ion acted as catalyst at chlorine addition. These experiment results also followed similar trends of previous study (Wang et al., 2015).

β -cyclocitral and β -ionone have structural similarity and methyl ketone group. This functional group is well-known precursor of chloroform. At the ketone site, keto-enol tautomerization had occurred then the hypochlorite ion reacted with the enolate by electrophilic substitution. After that, a

nucleophilic acyl substitution had taken place by hydroxide ion forming CCl_3^- anion. This anion gets proton from carboxylic acid and consequently transformed to chloroform (Johannes, 1976).

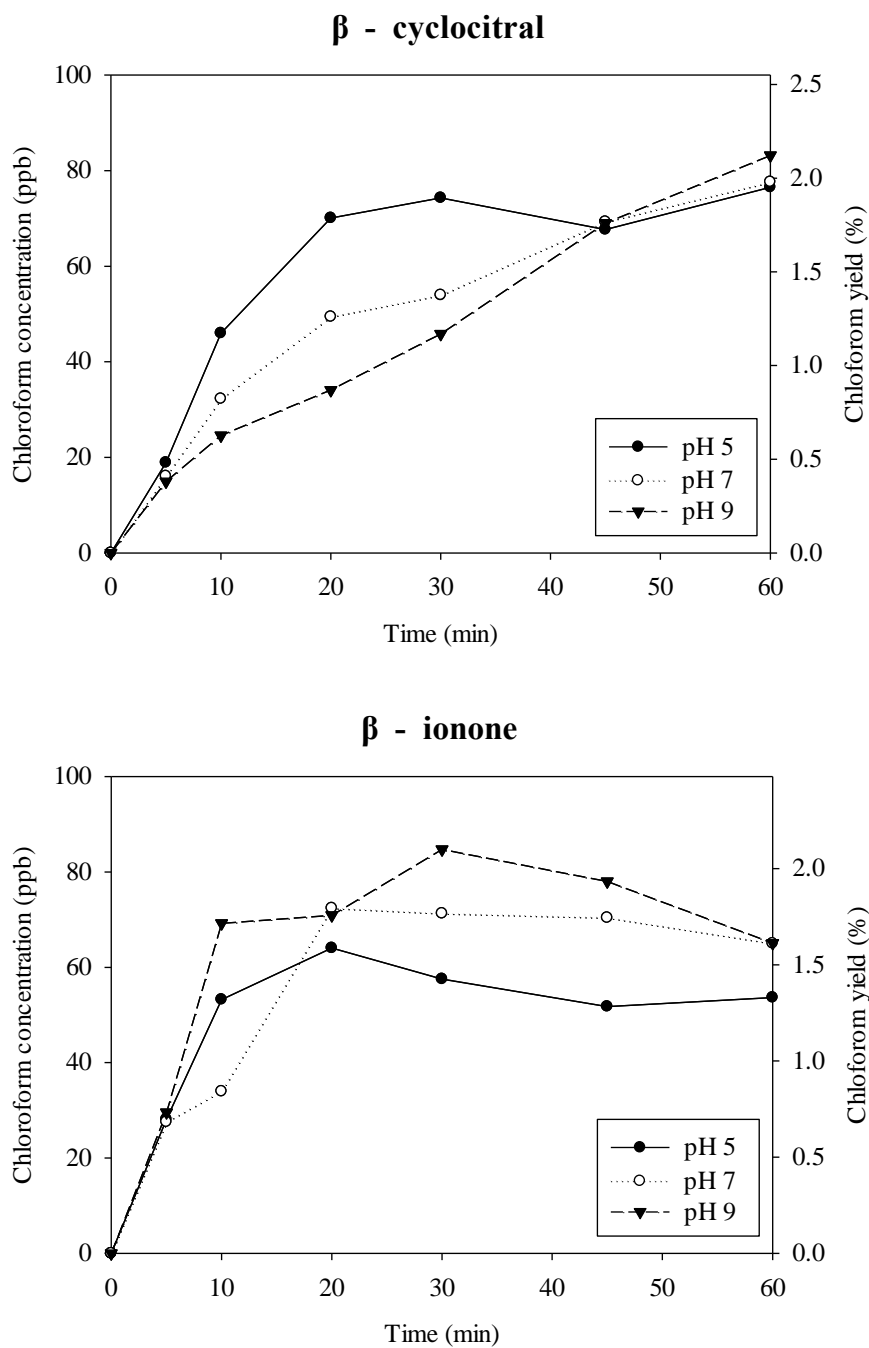


Figure 3. Chloroform formation during under UV-chlorination of β -ionone and β -cyclocitral (Chloroform was not formed under chlorination experiment)

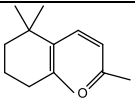
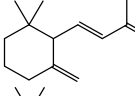
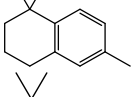
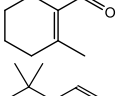
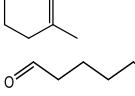
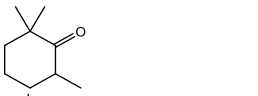
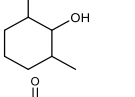
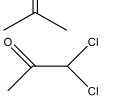
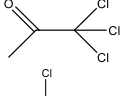
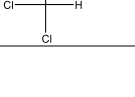


UV-chlorination prompted the additional degradation of two odorants. Overall, this reaction is able to lead increase in chloroform generation. However in this experiment condition, odorants concentration was 1000 times higher than that of surface water. Hence, the increased amount of chloroform will not be serious concern at real drinking water treatment processes.

3.4. Suggested degradation pathway of β -cyclocitral and β -ionone under UV photolysis, chlorination and UV-chlorination

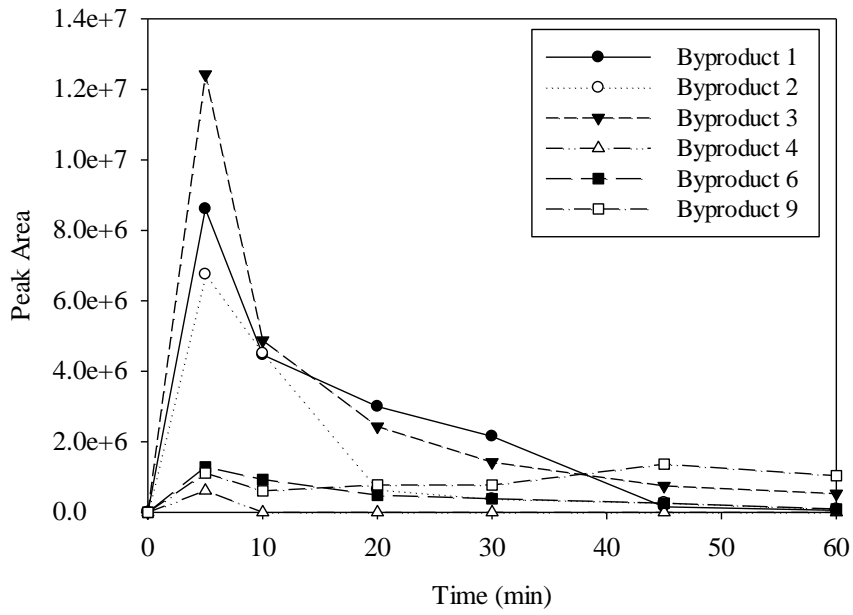
The possible degradation intermediates of odorants under UV photolysis and UV-chlorination were suggested at table 6. Notably, β -cyclocitral appeared as a byproduct of UV-chlorination. Hence, the degradation pathway of two odorants was proposed in one mechanism. Byproduct 1, 2 and 3 appeared at both UV photolysis and UV-chlorination of β -ionone. Byproduct 7 and 8 were also detected at the UV-chlorination experiment of β -cyclocitral.

Time dependent change of peak areas of each intermediates during UV-chlorination of β -ionone were presented in Figure 4. Byproduct 1 to 3 are the abundant intermediates showing high responses. However, response of these compounds peaked at 5 minutes then decreased. Other byproducts were shortly existed during the reactions. Contrary to other intermediates, byproduct 4, 7 and 8 appeared only at 5 minute. These results can be an evidence to support degradation mechanism shown in figure 7. During UV photolysis, byproducts 1, 2 and 3 was existed for one hour of reaction time (Figure 5). Furthermore, byproduct 7 and 8 also detected until 10 min at the UV-chlorination experiment of β -cyclocitral (Figure 6).

Table 6. Major byproducts during UV photolysis and UV-Chlorination of two odorants

No	Chemical structure	Name	Retention time (min)	UV photolysis of β -ionone	UV-chlorination of β -ionone	UV-chlorination of β -cyclocitral
1		cis- β -ionone	16.253	○	○	×
2		γ -ionone	16.607	○	○	×
3		α -ionone	17.857	○	○	×
4		β -cyclocitral	15.563	×	○	×
5		2-ethenyl-1,3,3-trimethyl-cyclohexene	13.918	×	○	○
6		Decanal	15.358	×	○	×
7		2,2,6-trimethyl-cyclohexanone	10.503	×	○	○
8		2,6-dimethyl-cyclohexanol	11.004	×	○	○
9		Acetone	1.911	×	○	○
10		1,1-dichloro-2-propanone	3.924	×	○	○
11		1,1,1-trichloro-2-propanone	6.123	×	○	○
12		Chloroform	2.503	×	○	○

UV-chlorination of β - ionone



UV-chlorination of β - ionone

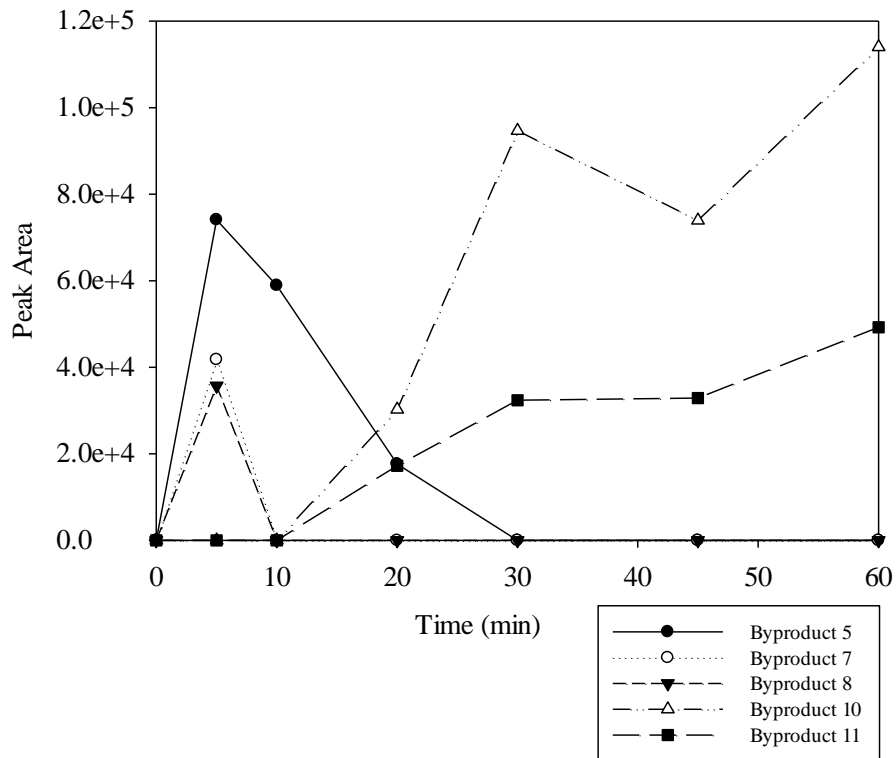


Figure 4. Time dependent byproduct formation of β -ionone under UV-chlorination

During the UV photolysis experiments of β -ionone, isomerization had occurred under UV irradiation. Byproduct 1 is isomer of *trans*- β -ionone. However in the chromatogram, these two compounds were separated as different two peaks. The double bond at the carbon chain of β -ionone is the reactive site for UV isomerization (Polyakov et al, 1999). After isomerization, oxygen at ketone group were linked to the methyl group on main ring to form another fused ring. Later, double bond at the main ring was shifted to methyl group by hydrogen shift. By this reaction, byproduct 2 (γ -ionone) was generated. (Eshuis, 1994) Byproduct 3 (α -ionene) was also formed by UV isomerization. Before isomerization, proton had attached at ketone group then formed fused ring by UV irradiance. After protonation, one more double bond had been created on fused ring to form byproduct 3 by dehydration. These compounds are main byproducts of β -ionone by UV photolysis. Although UV irradiance itself can decompose two odorants, it is not sufficient for mineralizing the target compounds because reactive sites for UV photolysis are limited. (Legrini et al, 1993)

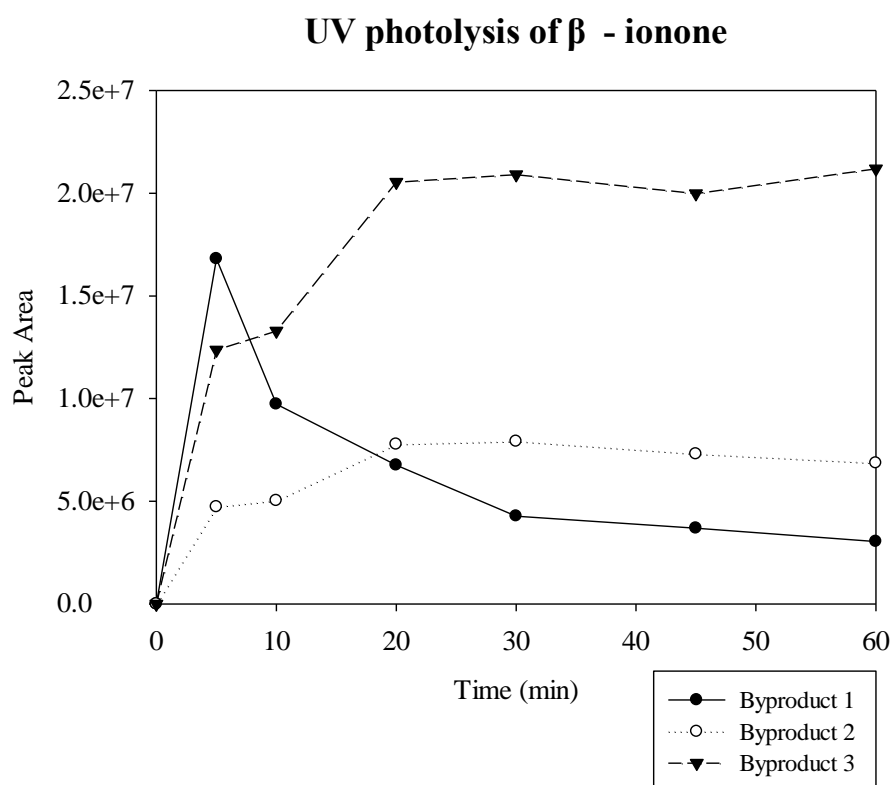


Figure 5. Time dependent byproduct formation of β -ionone under UV photolysis

In case of UV-chlorination, hydroxyl radical was able to attack on the double bond at the carbon chain of β -ionone. Subsequently, methyl ketone group at the end of carbon chain was separated and the parent compound was transformed to β -cyclocitral (byproduct 4). Other byproducts (5 ~ 8) were generated by bond scission reaction by hydroxyl radical. Occurrence of byproduct 7 and 8 was also observed at the UV-chlorination experiment of β -cyclocitral. These intermediates were degraded into smaller compounds and acted as disinfection byproduct precursors. Especially, as mentioned before, methyl ketone group is well known precursors of chloroform. In consequence, these byproducts were transformed to chloroform.

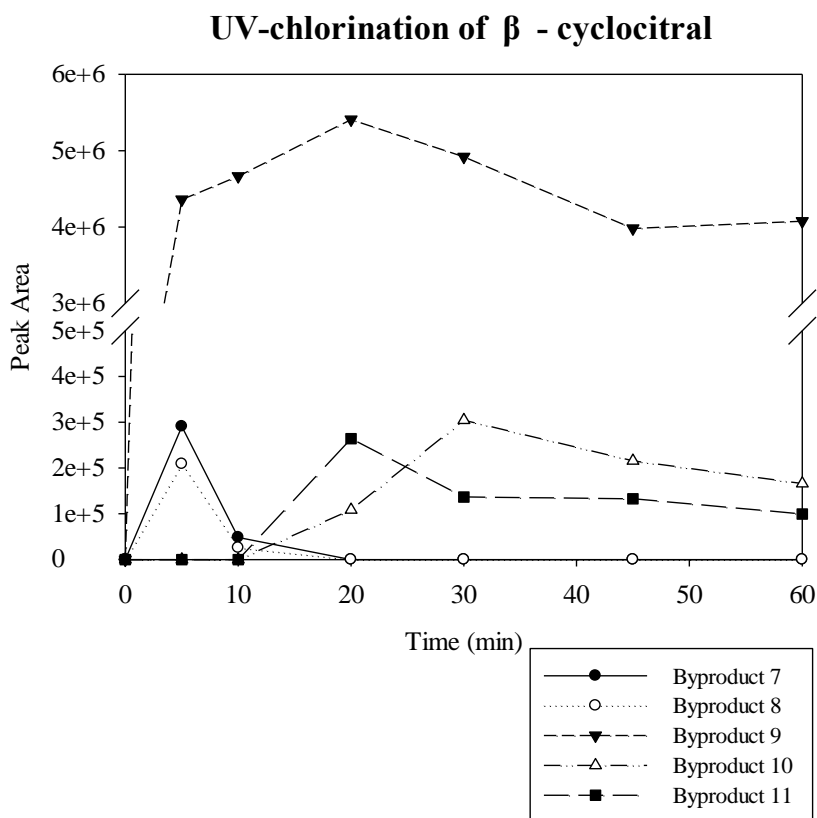


Figure 6. Time dependent byproduct formation of β -cyclocitral under UV-Chlorination

During degradation of two odorants, acetone (byproduct 9) is formed by separation of ketone group. Acetone undergoes electrophilic substitution of chlorine species and transforms to 1,1-dichloro-2-propanone (byproduct 10) and 1,1,1-trichloro-2-propanone (byproduct 11). Further, byproduct 11 is separated into carboxylic acid and chloroform.

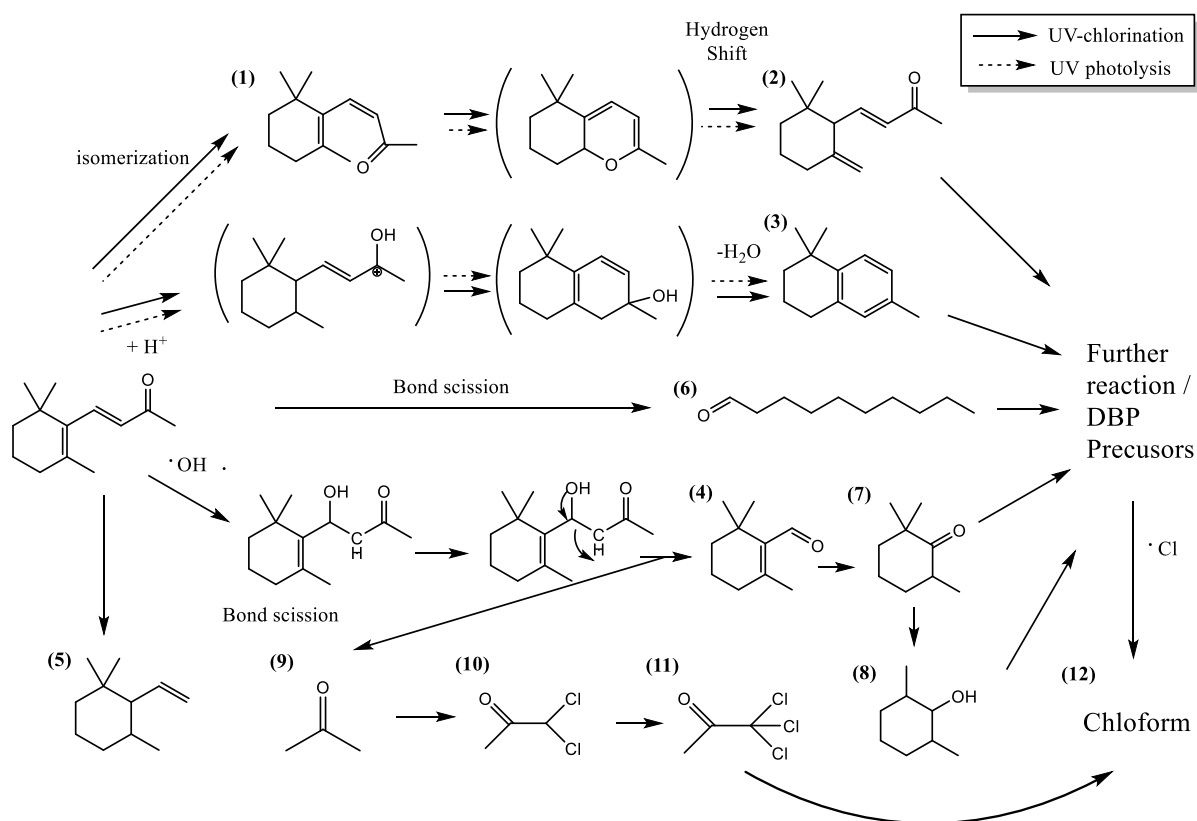


Figure 7. Proposed degradation pathway of β -ionone and β -cyclocitral (byproduct 4) by UV (dotted line) and UV-Chlorination (solid line)

4. Conclusion

In this study, UV photolysis, chlorination and UV-chlorination reaction were conducted for degradation of two algal odorants β -cyclocitral and β -ionone. Among three reactions, integration of UV and chlorine showed the greatest removal efficiency because of hydroxyl radical generation.

Between two taste and odor compounds, β -ionone was easily degraded compared to β -cyclocitral in consequence of structural difference. The degradation kinetics of UV photolysis, chlorination and UV-chlorination were fitted well pseudo first order kinetic. In addition, initial acidic condition is proper for UV-chlorination owing to active chlorine species distribution. After UV-chlorination reaction, formation of trace amounts of chloroform by UV-Chlorination was observed during UV-chlorination reaction. In addition, UV-chlorination enhanced the chloroform generation however, the increase amount of chloroform will not be serious concern. Based on the byproducts screening, possible degradation pathways of β -ionone and β -cyclocitral were suggested including UV photo-isomerization, hydroxyl radical attack and bond scission reaction. These results imply that the UV-chlorination process can be one of alternative options in water treatment plants to remove algal odorants and other algal derived organic compounds.

References

- Antonopoulou, M., Evgenidou, E., Lambropoulou, D., & Konstantinou, I. (2014). A review on advanced oxidation processes for the removal of taste and odor compounds from aqueous media. *Water research*, 53, 215-234.
- Baldermann, S., Kato, M., Kurosawa, M., Kurobayashi, Y., Fujita, A., Fleischmann, P., & Watanabe, N. (2010). Functional characterization of a carotenoid cleavage dioxygenase 1 and its relation to the carotenoid accumulation and volatile emission during the floral development of *Osmanthus fragrans* Lour. *Journal of experimental botany*, 61(11), 2967-2977.
- Borsarelli, C. D., Mischne, M., Venia, A. L., & Vieyra, F. E. M., 2007. UVA Self-Photosensitized Oxygenation of β -Ionone. *Photochemistry and photobiology*, 83(6), 1313-1318.
- Briand, J. F., Jacquet, S., Bernard, C., & Humbert, J. F. (2003). Health hazards for terrestrial vertebrates from toxic cyanobacteria in surface water ecosystems. *Veterinary research*, 34(4), 361-377.
- Chan, P. Y., El-Din, M. G., & Bolton, J. R. (2012). A solar-driven UV/Chlorine advanced oxidation process. *water research*, 46(17), 5672-5682.
- Chen, J., Xie, P., Ma, Z., Niu, Y., Tao, M., Deng, X., & Wang, Q. (2010). A systematic study on spatial and seasonal patterns of eight taste and odor compounds with relation to various biotic and abiotic parameters in Gonghu Bay of Lake Taihu, China. *Science of the Total Environment*, 409(2), 314-325.
- Chow, C. W., Drikas, M., House, J., Burch, M. D., & Velzeboer, R. M. (1999). The impact of conventional water treatment processes on cells of the cyanobacterium *Microcystis aeruginosa*. *Water Research*, 33(15), 3253-3262.
- Deborde, M., & Von Gunten, U. R. S. (2008). Reactions of chlorine with inorganic and organic compounds during water treatment—kinetics and mechanisms: a critical review. *Water research*, 42(1), 13-51.

Eshuis, J. J. (1994). Ultrasound-mediated rearrangement of β -ionone to 1, 1, 6-trimethyl-1, 2, 3, 4,- tetrahydronaphthalene. *Tetrahedron letters*, 35(42), 7833-7836.

Fang, J., Yang, X., Ma, J., Shang, C., & Zhao, Q. (2010). Characterization of algal organic matter and formation of DBPs from chlor (am) ination. *Water research*, 44(20), 5897-5906.

Glasgow, H. B., Burkholder, J. M., Reed, R. E., Lewitus, A. J., & Kleinman, J. E. (2004). Real-time remote monitoring of water quality: a review of current applications, and advancements in sensor, telemetry, and computing technologies. *Journal of Experimental Marine Biology and Ecology*, 300(1), pp. 409-448.

Jiang, Y., Cheng, B., Liu, M., & Nie, Y. (2016). Spatial and temporal variations of taste and odor compounds in surface water, overlying water and sediment of the Western Lake Chaohu, China. *Bulletin of environmental contamination and toxicology*, 96(2), 186-191.

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.

Johannes. J. R. 1976. Haloform in drinking water. *American Water Works Association*, Vol. 68 (3), pp. 168-172

Jung, S., Baek, K., Yu, M., 2004. Treatment of taste and odor materials by oxidation adsorption. *Water Sci. Technol.* 49 (9), 289-295.

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

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.

Ma, Z., Niu, Y., Xie, P., Chen, J., Tao, M., & Deng, X. (2013). Off-flavor compounds from decaying cyanobacterial blooms of Lake Taihu. *Journal of Environmental Sciences*, 25(3), 495-501.

- Matilainen, A., Vieno, N., & Tuhkanen, T. (2006). Efficiency of the activated carbon filtration in the natural organic matter removal. *Environment international*, 32(3), 324-331.
- Meriç, S., Selçuk, H., & Belgiorno, V. (2005). Acute toxicity removal in textile finishing wastewater by Fenton's oxidation, ozone and coagulation–flocculation processes. *Water Research*, 39(6), 1147-1153.
- Munter, R. (2001). Advanced oxidation processes—current status and prospects. *Proc. Estonian Acad. Sci. Chem*, 50(2), 59-80.
- 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.
- Peter, A., & Von Gunten, U. (2007). Oxidation kinetics of selected taste and odor compounds during ozonation of drinking water. *Environmental science & technology*, 41(2), 626-631.
- Peter, A., Köster, O., Schildknecht, A., & von Gunten, U. (2009). Occurrence of dissolved and particle-bound taste and odor compounds in Swiss lake waters. *Water Research*, 43(8), 2191-2200.
- Polyakov, N. E., Kruppa, A. I., Bashurova, V. S., Musin, R. N., Leshina, T. V., & Kispert, L. D. (1999). Single electron transfer in the phototransformations of β -ionone in the presence of electron acceptors. *Journal of Photochemistry and Photobiology A: Chemistry*, 128(1), 65-74.
- Qi, F., Xu, B., Chen, Z., Zhang, L., Zhang, P., Sun, D., 2010. Mechanism investigation of catalyzed ozonation of 2-methylisoborneol in drinking water over aluminum (hydroxyl) oxides: role of surface hydroxyl group. *Chem. Eng. J.* 165 (2), 490-499.
- Remucal, C. K., & Manley, D. (2016). Emerging investigators series: the efficacy of chlorine photolysis as an advanced oxidation process for drinking water treatment. *Environmental Science: Water Research & Technology*, 2(4), 565-579.
- Sun, P., Lee, W. N., Zhang, R., & Huang, C. H. (2016). Degradation of DEET and Caffeine under UV/Chlorine and Simulated Sunlight/Chlorine Conditions. *Environmental Science & Technology*, 50(24), 13265-13273.

Wang, D., Bolton, J. R., Andrews, S. A., & Hofmann, R. (2015). Formation of disinfection by-products in the ultraviolet/chlorine advanced oxidation process. *Science of the Total Environment*, 518, 49-57.

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.

Zhang, K. J., Gao, N. Y., Deng, Y., Shui, M. H., & Tang, Y. L. (2011). Granular activated carbon (GAC) adsorption of two algal odorants, dimethyl trisulfide and β -cyclocitral. *Desalination*, 266(1), 231-237.

Zhang, K. J., Gao, N. Y., Deng, Y., Zhang, T., & Li, C. (2012). Aqueous chlorination of algal odorants: Reaction kinetics and formation of disinfection by-products. *Separation and Purification Technology*, 92, 93-99.

Zhang, K., Lin, T. F., Zhang, T., Li, C., & Gao, N. (2013). Characterization of typical taste and odor compounds formed by *Microcystis aeruginosa*. *Journal of Environmental Sciences*, 25(8), 1539-1548.

국문 초록

조류 기인 이취미물질은 녹조 현상에 의해 발생하는 문제 중 수도수의 질에 영향을 미치는 심각한 문제이다. 이취미 물질의 처리는 수도수에 대한 신뢰도에 영향을 미치며 자외선-과산화수소, 오존 처리 등 고도 산화 처리 방법이 조류 기인 이취미물질 제거에 활용된다. 하지만 조류 기인 이취미 물질 중 β -cyclocitral 와 β -ionone 의 분해와 부산물에 대한 연구는 많지 않으며 두 물질에 대한 자외선-염소 처리에 의한 연구 또한 적다. 이러한 이유로 두 이취미 물질에 대해 자외선 광분해, 염소 처리, 자외선-염소 처리를 수행하였다. 두 물질 중에서는 β -ionone 이 분해가 더 빠르게 진행되었는데 이는 염소, 수산화 라디칼과 반응하며 자외선에 의한 이성질체화 반응이 발생하는 이중결합이 하나 더 존재하는 구조적 차이에 기인한다. 세 가지 반응 중에서는 자외선-염소 처리의 분해 효율이 가장 높은 것으로 나타났으며 자외선과 염소의 반응에서 발생한 수산화 라디칼 때문에 의한 추가 분해가 나타난 결과이다. 반응 초기 pH 는 분해 효율에 영향을 미치는 요인으로 염기성에서는 수산화 라디칼의 반응이 비효율적이며 차아염소산 이온이 수산화 라디칼을 소모하는 반응을 일으켜 분해 효율이 저감된다. 반응 중 규제되는 휘발성 유기화합물 중 클로로포름만 부산물로 발생하며 이는 두 이취미물질에 존재하는 메틸-케톤 그룹에서 발생하는 물질이다. 반응 중간의 용액을 스캔한 결과 자외선-염소 처리에 의한 β -ionone 의 부산물로 β -cyclocitral 을 포함한 여러 중간체를 확인하였다. 또한 이러한 부산물이 자외선 이성질체화, 수산화 라디칼 공격, 결합 절단 반응으로 일어난다.

핵심어: 자외선-염소 처리, 고도 산화 처리, β -cyclocitral, β -ionone, 분해 키네틱, 분해 기작

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