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보건학석사학위논문

**Degradation Mechanisms and Byproducts
Formation of Geosmin and 2-MIB during
UV photolysis and combined UV/Chlorine
Reaction**

자외선/염소반응 및 광분해를 통한 지오스민과 2-MIB의
제거기작 및 부산물생성 규명에 관한 연구

2016년 2월

서울대학교보건대학원

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김태경

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지도교수 조 경 덕

이 논문을 보건학석사학위 논문으로 제출함

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Abstract

The treatment and control of Geosmin (GSM) and 2-methylisoborneol (2-MIB) have become a priority task in the drinking water industry because these odorants have been associated with the quality and safety of drinking water. While the removals of common taste and odor (T&O) compounds by ozonation, ultrasonication and UV/AOP have been widely reported, only a little were reported on the formation of by-products during the treatment. GSM and 2-MIB have no health effect. However, these compounds have the possibility to be the precursors of THM as well as other hazardous by-products due to their strong oxidation potential. Therefore, the investigation of their by-products formed during treatment is needed. In this study, chlorination, UV photolysis and combined UV/chlorine reactions were conducted to investigate the degradation mechanisms and byproducts formation of geosmin (GSM) and 2-methylisoborneol (2-MIB) in aqueous system. Chlorination was ineffective for the removal of GSM and 2-MIB, while UV irradiation and UV/chlorine reactions efficiently removed both compounds. Kinetics during UV photolysis and UV/chlorination followed the pseudo first-order reaction. Chloroform was found as a chlorinated byproduct during UV/chlorine reaction of both GSM and 2-MIB with the yield up to 87% while other chlorinated byproducts were not detected. The pH affected on both removal rate and chloroform production. The removal rate was highest at pH 5-7 and formation of chloroform was lowest at this condition. The byproducts of GSM and 2-MIB were identified by GC/MS and LC-MS/MS. The identified open ring and dehydration compounds were 1,4-dimethyl-adamantane, 1,3-dimethyl-adamantane, 2-methylenebornane, 2-methyl-2-bornene, respectively. These byproducts were removed with further reaction. Furthermore, possible degradation pathways for the UV/Chlorine of both compounds were suggested.

Keywords: Geosmin, 2-Methylisoborneol, UV/Chlorine, Degradation kinetics, By-products

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1. Introduction

1.1. Background

The increasing frequency and intensity of harmful cyanobacterial proliferation in water sources is a growing global issue (Zayamaldi et al., 2015). Algal blooms can affect the quality of drinking water sources through the release of algae-derived organic matter such as geosmin and 2-methylisoborneol (2-MIB). Geosmin and 2-MIB are representative algae-derived taste and odor (T&O) compounds that mainly result from the metabolism and biodegradation of certain types of cyanobacteria and actinomycetes (Juttner et al., 2007; Son et al., 2015). Geosmin and 2-MIB have no adverse health effect. However, these compounds have a possibility to be the precursors of THMs and other hazardous byproducts due to their strong oxidation power (Sagehashi et al., 2005). In addition, these compounds have strong musty/earthy flavors and extremely low odor threshold (4 to 8.5 ng L⁻¹) (Pirbazari et al., 1992). The guideline limits for their level in drinking water is under 20 ng L⁻¹ and 10 ng L⁻¹ in South Korea and Japan respectively (MOE, 2015; MHLW, 2015). Typical level of GSM and 2-MIB in surface water are summarized in Table. 1.

Conventional water treatment processes (sedimentation, chlorination, coagulation, flocculation) cannot remove geosmin and 2-MIB efficiently (Watson et al., 2008; Yuan et al., 2013). Air stripping systems are not economical for GSM and 2-MIB due to their low Henry's constants (Song et al., 2007). Chlorine, chlorine dioxide and potassium permanganate is also ineffective for removing both T&O compounds (Glaze et al., 1990). Those oxidants are relatively weaker than other oxidants and not enough to break down the tertiary alcohol structure which has a resistance to oxidation (Munter et al., 2001). Therefore, more effective water treatment processes have been used to remove both compounds from water, and include the use of activated carbon and alum coagulation/sand filtration (Jung et al., 2004; Zamyadi et al., 2015). However, reduced adsorption efficiency by activated carbon is often observed when natural organic matter (NOM) is present in water. Additional treatment is also needed for spent activated carbon to regenerate (Chestnutt et al., 2007). Also, coagulation/sand

filtration cannot completely remove these T&O compounds.

Table. 1. Typical concentration of geosmin (GSM) and 2-MIB in different country

Water system	Details	Concentration	Reference
Reservoir	Eutrophic; Lake Kasumigaura, Japan	700 ng GSM Liter ⁻¹ 900 ng 2-MIB Liter ⁻¹	Yagi et al., 1985
	Eutrophic; Daechung Reservoir, South Korea	963 ng GSM Liter ⁻¹	Kim et al., 2015
	Paldang Reservoir, South Korea	< 130 ng GSM Liter ⁻¹ < 180 ng 2-MIB Liter ⁻¹	Ministry of Environment (MOE) 2015
River	Han River, South Korea	18 ng GSM Liter ⁻¹ 10 ng 2-MIB Liter ⁻¹	Our investigation data (2014.03 ~ 2014.09)
	St. Lawrence River, Canada/USA	5-40 ng GSM Liter ⁻¹ 2-40 ng 2-MIB Liter ⁻¹	Watsons et al., 2004
	Ruhr River, Germany	35 ng GSM Liter ⁻¹	Juttner et al., 1995

1.2. Removals in water treatment

Recently, advanced oxidation processes (AOPs) have been used to more efficiently remove T&O compounds. Table. 2 summarizes recent studies that have used AOP methods. While the removal of geosmin and 2-MIB has been studied, only a few studies have reported the formation of byproducts. While the removals of geosmin and 2-MIB have been studied, only a few studies reported on the identification of byproducts formation. Among the AOP processes, the combined UV/chlorine process is more cost-effective than the UV/H₂O₂ process because the additional chemical costs associated with H₂O₂ and quenching residual peroxide can be saved, and the residual chlorine from the UV/chlorine reaction can be used as a secondary disinfectant (Nam et al., 2015; Watts et al., 2012). Wang (Wang et al., 2015) reported that the removal of geosmin and 2-MIB by a UV/chlorine process was superior to

that by a UV/H₂O₂ process. However, the UV/chlorine reaction potentially allows the formation of disinfection by-products (DBP) due to the use of chlorine. Therefore, byproduct formation during the UV/chlorination of geosmin and 2-MIB must be examined before the process is used, but no studies have identified the byproducts formed during the UV/chlorination of geosmin and 2-MIB.

Table.2. Publications on the treatment of taste and odor compounds with chlorination and other AOPs.

Publication (author, year)	Treatment process	Removal	Byproducts research
Song et al. (2007)	Ultrasonic irradiation	100% in 40 min	○
Huang et al. (2010)	O ₃ /H ₂ O ₂	90 % in 20 min <u>(2-MIB only)</u>	○
Bamuza-pemu et al. (2012)	UV/TiO ₂	99.6% in 60 min <u>(GSM only)</u>	○
Zhang et al. (2012)	Chlorination	100% in 90 min <u>(Both GSM and 2-MIB were not included)</u>	○ (Including DBP)
Yuan et al. (2013)	Ozonation	100% in 60 min	○
Wang et al. (2015)	UV/Chlorine UV/H ₂ O ₂	80% ↑ removal of GSM 50% ↑ removal of 2MIB	-

1.3. Objectives

Therefore, the objectives of this study were: (1) to compare the removal of geosmin and 2-MIB by chlorination, UV irradiation, and UV/chlorine reaction; (2) to determine the kinetics of each removal process; (3) to examine the time-dependence of chlorinated byproduct formation at different pHs; and (4) to identify degradation byproducts produced during each reaction, and propose possible

degradation pathways of both algal odorants.

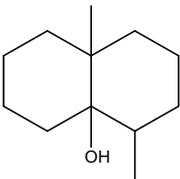
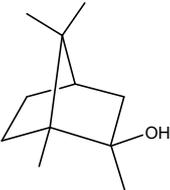
2. Materials and Methods

2.1. Chemicals

Geosmin (>99%) and 2-methylisoborneol solution (>98%) that diluted in methanol was purchased from Sigma-Aldrich (USA) for standard calibration. To eliminate the effect of methanol on the chloroform production during experiments, geosmin (>97%, Sigma-Aldrich, USA) and 2-methylisoborneol (>98%, Sigma-Aldrich, USA) without methanol were used and diluted in deionized water. The physicochemical properties of geosmin and 2-MIB were summarized in the supplementary materials (Table S1) [5]. 1,2-dichlorobenzene- d_4 (>99%, Sigma-Aldrich, USA) and fluorobenzene (>99%, Sigma-Aldrich, USA) were used as the internal standards for algal odorants and chlorinated byproducts, respectively. $Na_2S_2O_3$ and NaOCl were obtained from Sigma-Aldrich and each compound was used as chlorine quencher and chlorine disinfectant, respectively.

To adjust the initial pH of the solution, 0.5 N NaOH or HCl (Sigma-Aldrich, USA) were used. For the solid phase micro extraction (SPME), NaCl was purchased from Wako (Japan) was used. Halogenated volatiles mix standard including chloroform, carbon tetrachloride, 1, 2-dichloroethane, 1, 1-dichloroethylene, 1,2-dichloroethylene, dichloromethane, 1,2-dichloropropane, 1,3-dichloropropene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, Trichloroethylene (TCE), and Perchloroethylene (PCE) (>99%) for chlorinated byproducts identification was obtained from Sigma-Aldrich (USA). All solutions were prepared with deionized water produced from Milli-Q water generator (Millipore, USA).

Table.3. Physico-chemical property of GSM and 2MIB (Pirbazari et al., 1992)

Parameter	Geosmin	2-Methylisoborneol
Structure		
Molecular formula	C ₁₂ H ₂₂ O	C ₁₁ H ₂₀ O
Molecular weight	182.3	168.3
Boiling Point (°C)	165.1	196.7
K _{ow}	3.7	3.13
Aqueous solubility (mg/L)	150.2	194.5

2.2. Experimental procedures

Chlorination experiments were conducted using a batch type reactor without UV irradiation as shown in Fig. 1. The concentration of chlorine with NaOCl dose (mL) was determined using the *N,N*-diethyl-*p*-phenylenediamine (DPD) powder pillow colorimetric method (EPA approved HACH 8021 method) with a HACH DR/890 colorimeter (HACH, Loveland, Colorado, USA).

UV photolysis and UV/chlorine experiments were conducted using the same batch type reactor (Fig. 1). UV chamber consists of three mercury UV lamps (20 W, 254 nm, San-Kyo Electrics, Japan). The reactor consists of a roller for circulating the reaction solution. The batch type reactor system is covered with aluminum foil to prevent the loss of radiation and UV exposure. UV intensity was measured with a radiometer (VLX-3W Radiometer 9811-50, Cole-Parmer, USA). To adjust the initial pH of solution, 0.5 N NaOH and HCl (Sigma-Aldrich, USA) were used. Sampling was achieved using the headspace free 80mL quartz vials with Teflon-faced septa to minimize the loss of target compounds and its byproducts.

To minimize the loss of target compounds, samples were filled with out headspace and sealed with Teflon-faced septa. To avoid the heat of mercury lamp, vials and lamps have enough gap with each other.

For kinetics and the byproduct identification experiments, 5 μg of geosmin and 2-MIB stock were spiked in 1 L solution, and NaOCl solution (0.5%) was also added into the solution when the residual chlorination was needed. At each designated sampling, one quartz vial (80 mL) was sacrificed for the analysis. Then, 0.8 mL of (1 M) was injected to the collected sample to quench residual chlorine. The method for the DBP formation experiments were the same as above.

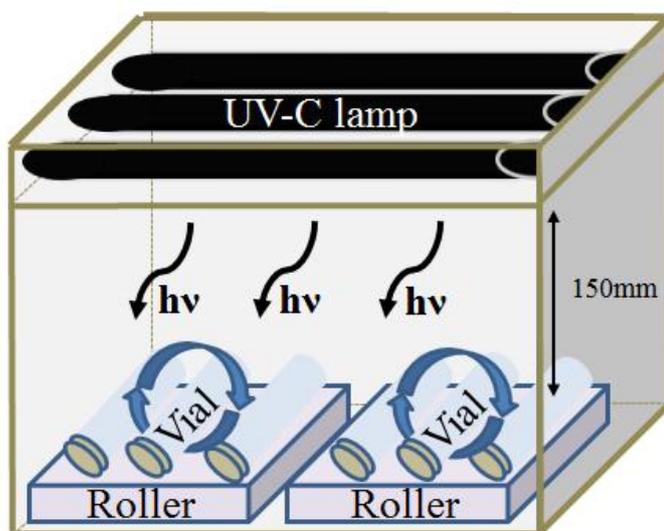


Figure. 1. The schematic diagram of photolytic reactor

2.3. Analytical methods

SPME-GC/MS was used for the analysis of geosmin and 2-MIB. 3 g of NaCl was weighted in 20 mL screw type SPME vial. 10 mL standard or sample was placed into the vial and 10 μL of internal

standard (1, 2-dichlorobenzene- d_4 , $20 \mu\text{g L}^{-1}$) injected. Before the headspace extraction, NaCl was melted into the sample at 65°C under stirring at 400 rpm for 1 min to minimize the analytical precision. Then, the extraction was carried out at 65°C under stirring at 600 rpm on an auto sampler (PAL-xt, PAL System, USA). After the 10 min of extraction, a 2 cm DVB/CAR/PDMS fiber (Supelco, USA) placed in the injector of GC (7890A, Agilent, USA) which connected to MS (5975C, Agilent, USA). The injector temperature was set at 270°C . SPME fiber was thermally desorbed at split mode (10:1) for 5 min at 270°C and then cleaned at 270°C for 5 min. For separation, DB-5MS-UI column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$) was used, and the helium carrier gas was flowed at 1.3 mL min^{-1} . Oven temperature was programmed from an initial temperature of 50°C held for 5 min, increased the temperature to 65°C at a rate of 5°C min^{-1} with 2 min hold, then increased up to 215°C at a rate of 15°C with a 4 min hold. The electron impact (EI) ion source of the MS and the quadrupole temperature was set at 250°C and 150°C , respectively (MOE, 2015).

For the identification of byproducts, purge and trap (P&T)- GC/MS (Stratum, Teledyne Tekmar, USA; 6890/5973, Agilent, USA) and API4000 mass spectrometer (AB SCIEX, USA) were used. 5 mL of the reaction samples were scanned (m/z 50 to 250) by GC/MS. The analytical conditions of GC/MS for byproduct of geosmin and 2MIB analysis are the same as HS-SPME-GC/MS conditions. To obtain the mass spectrum using API4000 mass spectrometer, 5 mL of samples were injected using Harvard syringe pump (975, Harvard Apparatus, USA). Then to check the product ions from precursor ion, fragmentation of the precursor ion was carried out with nitrogen gas. The fragmentation data were obtained by scan mode (m/z 10 to 210).

To analyze chloroform and other chlorinated compounds in aqueous sample, the same P&T-GC/MS with DB-VRX ($20 \text{ m} \times 0.18 \text{ mm} \times 1.0 \mu\text{m}$) column was used. 50 mL of standard or sample was placed into the 50 mL vial and $10 \mu\text{L}$ of internal standard (Fluorobenzene, $10 \mu\text{g L}^{-1}$) was injected. In the split mode (10:1) temperature of injection port was set at 250°C for purge and trap. Oven temperature was programmed from an initial temperature of 40°C held for 3 min and then increased

temperature up to 200°C at a rate of 8°Cmin⁻¹. The ion source of the MS and the quadrupole temperature was set at 230°C and 150°C. These methods were modified from official methods of drinking water quality in Korea (MOE, 2015).

3. Results and discussion

3.1 Degradation kinetics and mechanisms

The kinetics of algal odorants during chlorination, UV irradiation and UV/chlorine reaction were examined. The rate constants were calculated using a first order kinetic model. The rate constant of each experiment is shown in Table. 3. UV photolysis and UV/chlorine experiments followed pseudo-first order reaction. UV photolysis and UV/chlorine experiments followed a pseudo-first order reaction. In each reaction, 5 µg L⁻¹ of geosmin and 2-MIB were applied for 2 h. Figure 2 compares the removal of geosmin and 2-MIB during the three reactions.

Chlorination was ineffective for the removal of GSM and 2-MIB (Fig.2 (a), (b)). Srinivasan (2011) also reported that common oxidants such as Cl₂, ClO₂, and KMnO₄ are ineffective at removing geosmin and 2-MIB. This is mainly due to the molecular structures of both compounds. Geosmin and 2-MIB contain a tertiary alcohol, which is resistant to oxidation. The tertiary alcohol structure is resistant to oxidation because the carbon atom that carries the OH group does not have an attached hydrogen atom, but is instead bonded to other carbon atoms (Timberlake, 2014).

Table.4. Pseudo first-order reaction rate and correlation coefficients for the UV-C and UV/Cl₂ of GSM and 2MIB at pH7

UV-C	k (min ⁻¹)	R ²	UV/Cl ₂	k (min ⁻¹)	R ²
GSM	0.0420±0.0027	0.9935	GSM	0.0795±0.0015	0.9867
2MIB	0.0091±0.0069	0.9931	2MIB	0.0493±0.0041	0.9604

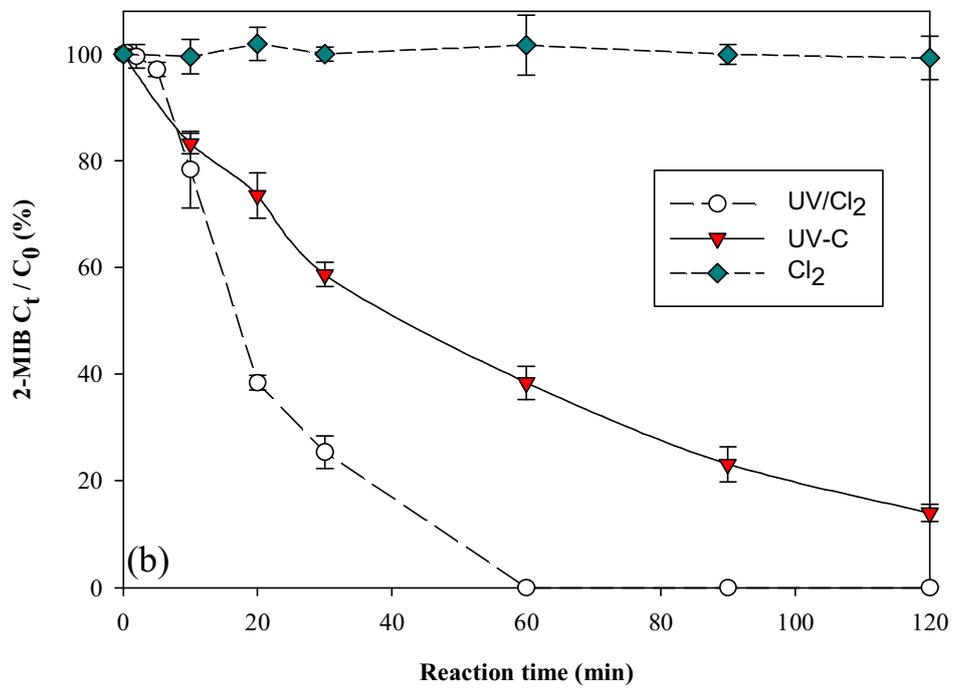
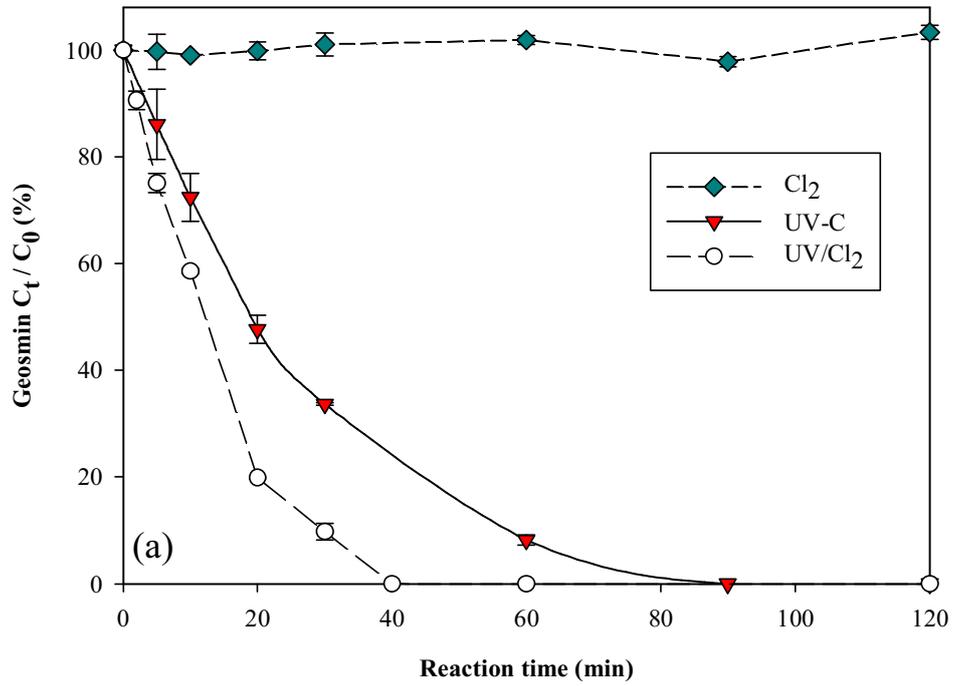


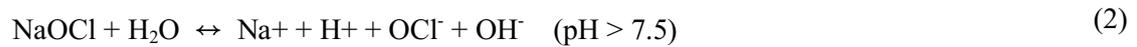
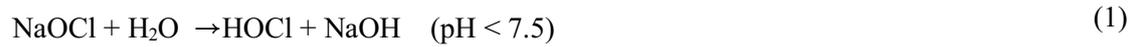
Figure. 2. Degradation of (a) GSM and (b) 2MIB using Cl_2 , UV-C and UV/ Cl_2 process. ($n = 2$, $[T\&O_0] = 5 \mu\text{g/L}$, $[Cl_2] = 0.5 \text{ mg/L}$, $UV-C_{\text{intensity}} = 3.2 \text{ mW/cm}^2$, $\text{pH} = 7$, $25 \text{ }^\circ\text{C}$)

The photosensitivity for GSM and 2-MIB were reported to be low at 254nm (Rosenfeldt et al., 2005). An absorbance scan of geosmin and 2-MIB measured in the UV range is shown in Fig.3. The absorbance coefficient of geosmin and 2-MIB measured at 254 nm was less than 0.002. Previous studies also demonstrated the ineffectiveness of UV-C irradiation for geosmin and 2-MIB. Linden (2002) reported that low-pressure or medium-pressure UV irradiation (UV fluence: 10,000J m⁻²) not effective at removing algal odorants.. Kutschera (2009) also reported that UV-C irradiation (UV fluence: 10,000J m⁻²) yielded low degradation rates for both odorants.

UV photolysis degraded both compounds almost completely when the energy was sufficient. Modifii (2002)] reported that more than 92% of geosmin and 2-MIBwas removed by UV-C irradiation (applied UV fluence: 101,000 J m⁻²). In this study, UV-C photolysis (applied UV fluence: 115,200 J m⁻²) removed more than 80% of these compounds within an hour, and followed pseudo first-order kinetics. Geosmin was removed faster than 2-MIB due to the greater steric hindrance of 2-MIB (Antonopoulou et al., 2014). UV photolysis can degrade both odorants, but requires considerable energy. Therefore, UV-C photolysis without additives should be reconsideredfor removinggeosmin and 2-MIB.

The UV/chlorine reaction completely removed geosmin within 40 min (Fig. 2 (a)) and removed 2-MIB within 1 h (Fig. 2 (b)). Both compounds also followed pseudo first-order kinetics. Although the destruction pathway in the UV-based AOPs was complex and involved numerous steps, the overall kinetics of the degradation could usually be described phenomenologically by simple pseudo first-order kinetics. Geosmin was also oxidized faster than 2-MIB both during UV/chlorination and in the UV photolysis experiment. This can be explained by the smaller steric hindrance, and slower reaction of 2-MIB with OH radicals. The reaction rate constants of the geosmin and 2-MIB compounds with OH radicals are reported to be $1.40 \times 10^{10} \text{ mol}^{-1} \text{ s}^{-1}$ and $8.20 \times 10^9 \text{ mol}^{-1} \text{ s}^{-1}$, respectively (Glaze et al., 1990). Previous studies (Nowell et al., (1992); Feng et al., (2007); Jin et al., (2011))] have suggested several reactions involving the production of $\cdot\text{Cl}$ and $\cdot\text{OH}$ radicals during the UV/chlorine process in

aqueous systems as follows:



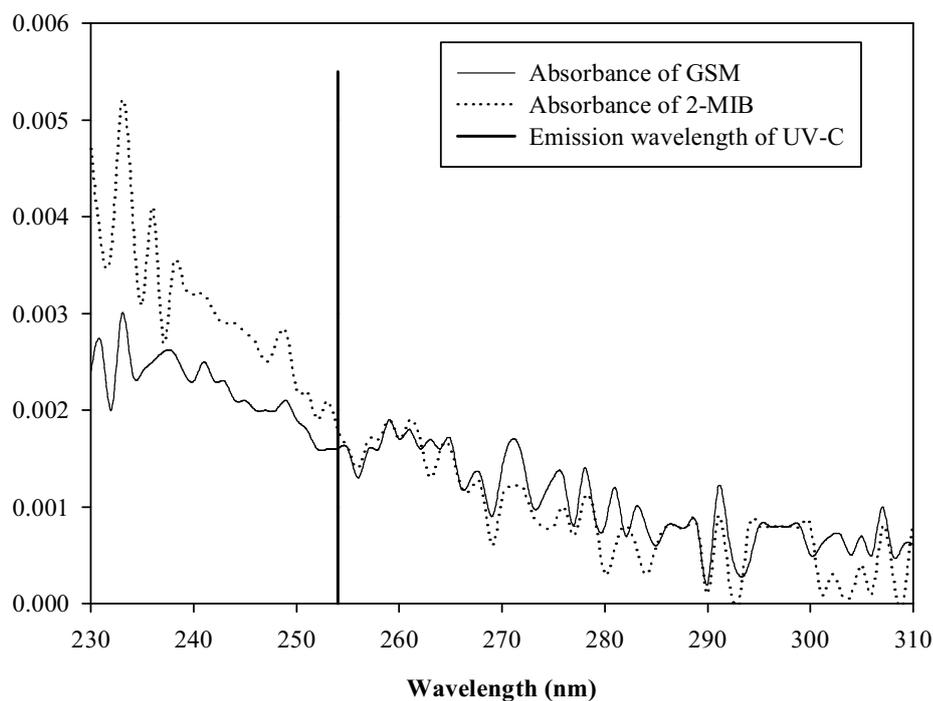


Figure.3. Absorbance spectrum of geosmin, 2-MIB (1 mg L⁻¹ dissolved in D.I. water) and UV-C emission wavelength

Chlorine radicals react with water and generating more hydroxyl radical (Eqs. (7)), or combine with excess of chloride ion to form $\text{Cl}_2^{\cdot-}$ radical anion (Eqs. (8)) (Deng et al., 2014). Hydroxyl and chlorine radicals yielded in the combined UV/chlorine process are strongly electrophilic species and may react with organic compounds by electron transfer and H-abstraction (Algre et al., 2000). Several studies suggest that chlorine radicals react with alcohols primarily via an H-abstraction mechanism. However, hydrogen abstraction from the hydroxyl group by chlorine radical was not observed (Wicktor et al., 2003). Accordingly, chlorine radical might effect on the decay of GSM and 2-MIB indirectly. Hydroxyl radicals play a major role during degradation of both compounds by UV/chlorine reaction. Antonopoulou (2014) also indicated that available literature indicated the major role of hydroxyl radicals on the mechanisms leading to the destruction of target compounds during AOPs.

To apply this process to water treatment plant, energy time load investigated. To degrade both odorants more efficiently, initial concentration of free chlorine and applied UV fluence adjusted. Results are shown in Fig. 4. The level of each T&O compounds also adjusted to actual detected level in surface water (100 ng L^{-1}). Both compounds were completely removed within 15 sec with low energy consumption (225 J m^{-2}). However, further research is needed for optimization of this process.

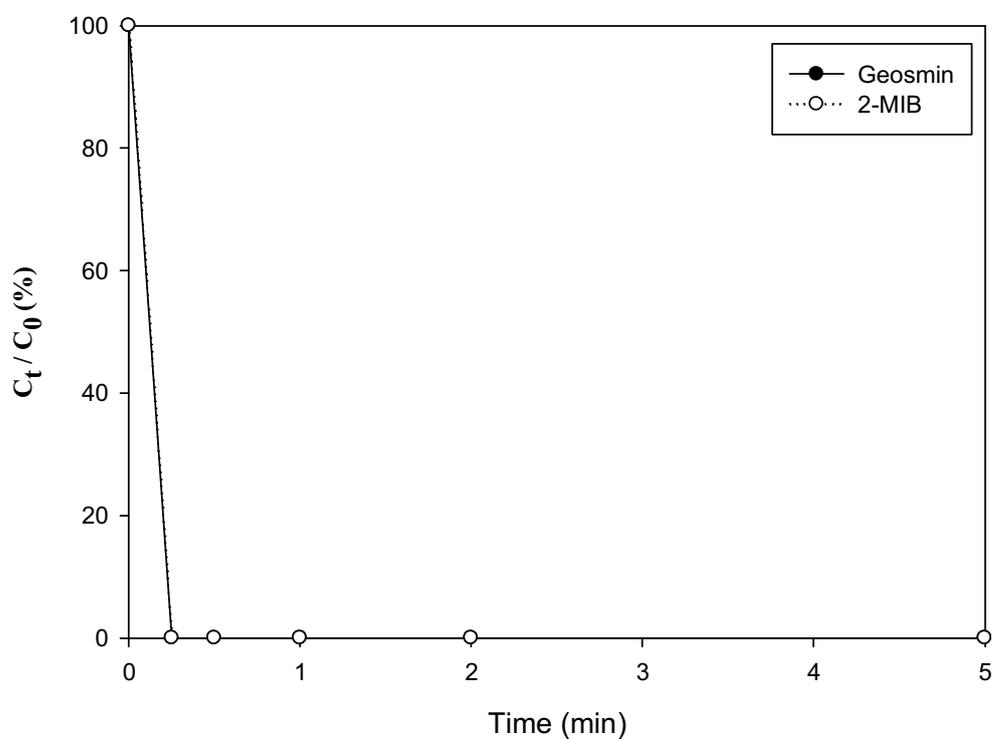


Figure. 4. Simultaneous degradation of GSM and 2MIB using combined UV/ Cl_2 reaction. ($n = 2$, $[\text{T\&O}_0] = 100 \text{ ng/L}$, $[\text{Cl}_2] = 2 \text{ mg/L}$, $\text{UV-}C_{\text{intensity}} = 1.5 \text{ mW/cm}^2$, $\text{pH} = 7$, $25 \text{ }^\circ\text{C}$)

3.2 pH dependence

The effect of pH on the removals of geosmin and 2-MIB during combined UV/chlorine reaction were examined. Figure 2 shows the rate constants for the removal of both compounds under various pH conditions. The result showed that pH ranges between 5 and 7 showed the fastest degradation of both odorants. The observed lower rate constants at alkaline pH condition can be explained by radical scavenging reactions by HOCl and OCl⁻. Previous research reported the rate constants of OH radical scavenging by HOCl and OCl⁻ species as 8.5×10^4 (Eqs. (4)) and $8.0 \times 10^9 / \text{M}\cdot\text{s}$ (Eqs. (5)), respectively (Nowell and Hoigne, 1992; Watts and Linden, 2007). This indicates that the scavenging of OH radicals is more dominant in the presence of hypochlorite ion (OCl⁻). Nowell and Hoigne (1992) also reported the production ratio of OH radical generated by OCl⁻ is only about 0.1 while HOCl yielded 0.9 OH radical with 254 nm UV light

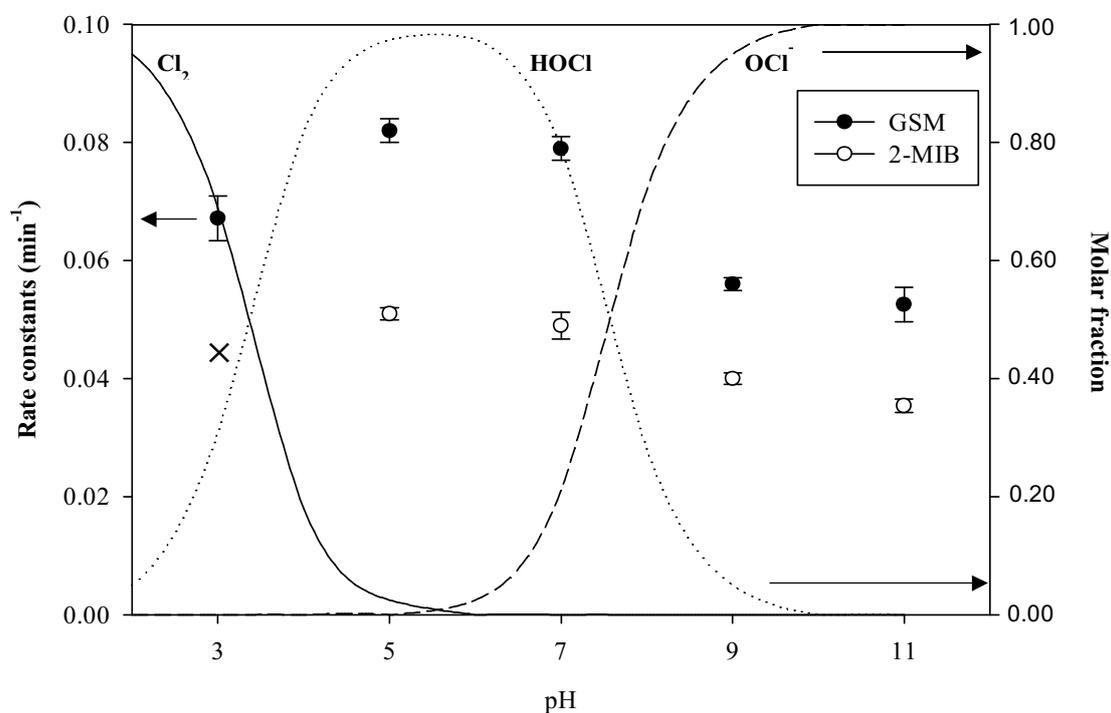


Figure 5. The pH and the evolution of chlorine in its various forms as a function of pH ($n = 2$, $[\text{T}\&\text{O}_0] = 5 \mu\text{g/L}$, $[\text{Cl}_2] = 0.5 \text{ mg/L}$, $\text{UV-C}_{\text{intensity}} = 3.2 \text{ mW/cm}^2$, $\text{pH} = 3\text{--}11$, $25 \text{ }^\circ\text{C}$)

During the UV/chlorine reaction 2-MIB could not be removed because it was unstable at pH 3. Kutschera (2009) also reported this compound not to be stable under this condition. The observed lower rate constants of geosmin at pH 3 can be explained by the production of chlorine in its various forms as a function of pH. This result is probably due to the decrease of HOCl proportion. Cl_2 species are dominant under pH 3. As shown in Eq. (4) as the proportion of HOCl decreases, yield of OH radicals can also decrease. Our result implies that pH conditions should be maintained at 5-7 during UV/chlorination for effective removal of geosmin and 2-MIB.

3.3 Formation of chlorinated byproducts during the UV/chlorine process

Generation of chlorinated byproducts during UV/chlorine reaction was investigated. The chloroform formation during UV/chlorination of geosmin and 2-MIB was observed while other chlorinated byproducts were not detected such as carbon tetrachloride, 1, 2-dichloroethane, 1, 1-dichloroethylene, 1,2-dichloroethylene, dichloromethane, 1,2-dichloropropane, 1,3-dichloropropene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, TCE and PCE. Figure 3(a) and 3(b) indicate the chloroform is produced during UV/chlorine reaction of both geosmin and 2-MIB respectively. The formation of chloroform increased until 60-90 min, but the levels were declined with further reaction.

Chloroform formation was strongly affected by pH. When the pH was alkaline or acidic, we rarely observed chloroform formation during the UV/chlorine reaction (Fig. 4). This may be due to the low degradation rate under both extreme acidic and alkaline pH conditions. Alkaline conditions favored the formation of chloroform; at pH 9, there was a significant difference in chloroform formation between neutral and acidic conditions. Comparable results have been reported previously: Wang (2015) reported a high THM formation at high pH during UV/chlorine reaction. Qin (2014) also reported increasing of solution pH enhanced the formation of DBPs precursors. The positive effect of alkaline pH on chloroform formation can be explained as follows.

First, the photolysis of free chlorine species can directly produce inorganic DBPs with potential health effects, such as chlorite, chlorate (Kang et al., 2006), and chloral hydrate (Linden, 2012). However, unlike chloroform, other inorganic DBPs (e.g., chloral hydrate) and organic DBPs (e.g., haloacetonitrile) can be readily decomposed due to base-catalyzed hydrolysis (Yang et al., 2007). Second, the hydrolysis of other DBPs at alkaline pH can result in their transformation into chloroform (Zhang et al., 2002).

During UV/chlorine reaction, chloroform formation of geosmin and 2-MIB were compared. Although the removal rate of geosmin was higher than 2-MIB, the significant enhancement of chloroform generation were observed during the 2-MIB treatment. Geosmin and 2-MIB showed higher rate of chloroform production, up to 75% and 87% respectively. Since the maximum level of both odorants reported in surface water which flow into WTP is not high ($< 180 \text{ ng L}^{-1}$) in Korea (MOE, 2015). Despite of the high chloroform conversion rate of these compounds, the substantive level of contribution will be quite low for this reason. Except for pH 3 and 11, the chloroform formation was the lowest at pH 5-7. Considering the removal efficiency and formation of byproducts, the pH should be maintain at pH 5-7.

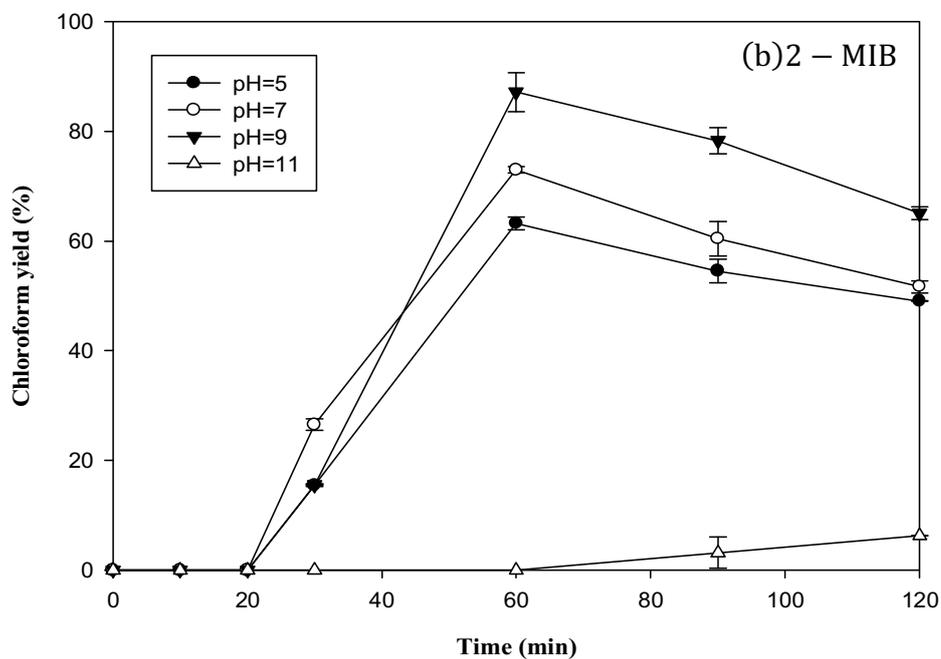
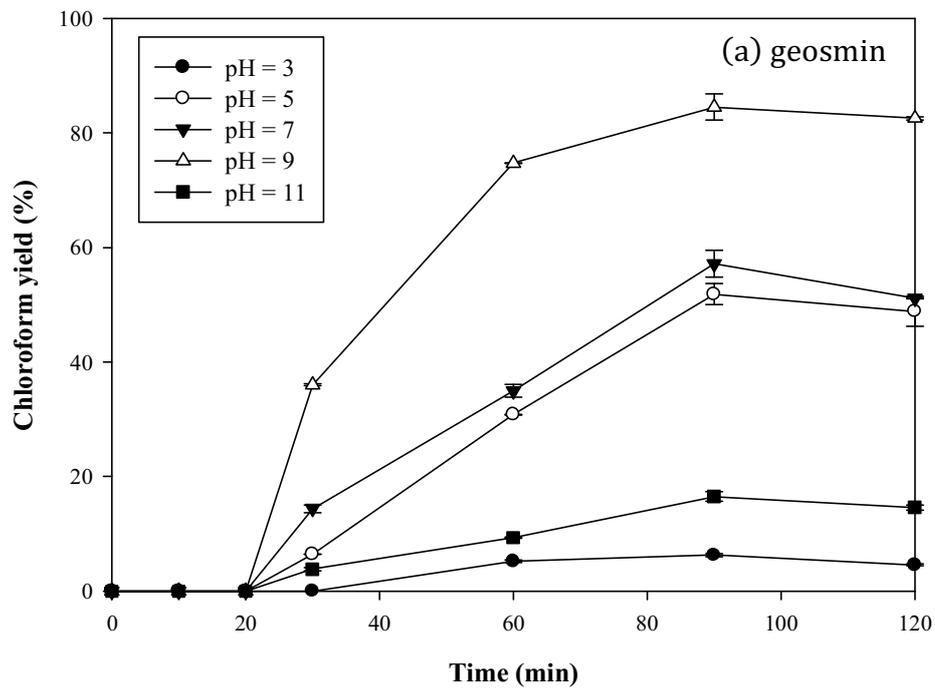


Figure.6. Time-dependent formation of chloroform during degradation of (a) GSM and (b) 2-MIB by UV/Cl₂ process at different pH conditions ([C₀] = 5 μg/L, [Cl₂] = 0.5 mg/L, UV-C_{intensity} = 3.2 mW/cm², pH = 7, 25°C)

3.4 Proposed degradation pathways of GSM and 2-MIB by UV irradiation and UV/Chlorine processes

The identification of byproduct during UV/chlorination reaction was conducted for better understanding of processes and the effect of byproducts to human health and environment. A few studies have been conducted for the identification of byproducts of geosmin and 2-MIB using AOP processes such as ultrasonic irradiation, photocatalytic degradation and ozonation. Song and O'shea (2007) investigated degradation of geosmin and 2-MIB during ultrasonic irradiation. Open ring and dehydrated compounds were main byproducts. Bamuza-pemu and Chirwa (2011) reported the byproducts and degradation pathway of geosmin during photocatalytic reaction. In this process, geosmin undergoes subsequent bond scission and rapid ring opening at several sites to produce acyclic saturated and unsaturated compounds including some alkanones and esters. Yuan (2013) also reported open ring and dehydrated compounds were main by-products of geosmin and 2-MIB by ozonation. In this study, 10 degradation byproducts from UV/chlorination reaction of algal odorants were found by P&T-GC/MS and LC-MS/MS analysis. The identified byproducts of geosmin and 2-MIB were listed in Table 5 and Table 6, respectively. Among these, byproduct 1,2,3 (Fig. 8) and byproduct 1,2 (Fig.10) have also been found in other AOP processes. Interestingly, 2,4-dimethyl-1-heptene, 4-methyl-2-heptanone, 2-methyl-3-pentanol, and chloroform were byproducts that were found for the first time.

GC-MS analysis indicate the two directly dehydrated products from geosmin. Byproduct (1) (1,3-dimethyladamantane) and byproduct (2) (1,4-dimethyladamantane). Byproducts 1, and 2 were identified during UV/chlorine reaction of geosmin. Dehydration and rearrangement of byproduct (1) and byproduct (2) result in byproduct (3) (cis-1-ethyldecahydro-7a-methyl-1H-indene). Previous study also reported that byproduct (1), (2) and (3) also identified after the ozonation of geosmin (Yuan et al., 2013). The elimination of H₂O molecule played a key role during UV/chlorine reaction. Tertiary alcohol is susceptible to dissociation of C-C bond. The dissociation energy of C-C bond (83 kcal/mol)

is more likely lower than C-O (86 kcal/mol), C-H (99 kcal/mol) and O-H (111 kcal/mol) bonds based on relative homolytic-bond scission energies(Song and O'shea, 2007).

Table. 5. Identified by-products of GSM during UV and combined UV/chlorine reaction.

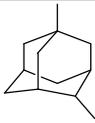
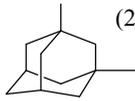
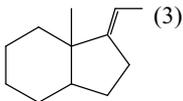
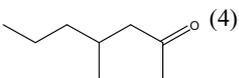
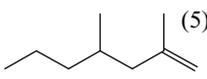
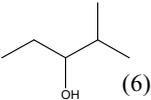
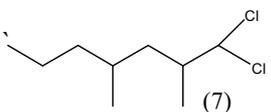
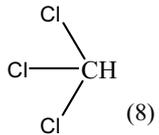
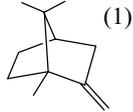
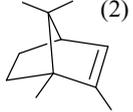
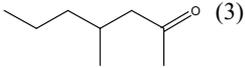
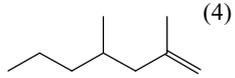
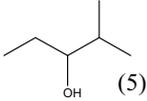
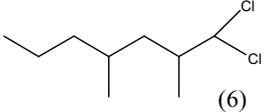
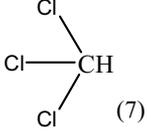
Retention time	Compounds	Structure
14.36 (PT-GC/MS)	1,4-Dimethyl-Adamantane	 (1)
14.738 (PT-GC/MS)	1,3-Dimethyl-Adamantane	 (2)
14.616 (PT-GC/MS)	Cis-1-Ethylideneoctahydro-7a-Methyl-1H-Indene	 (3)
7.255 (PT-GC/MS)	2,4-Dimethyl-1-Heptene	 (4)
4.287 (PT-GC/MS)	4-Methyl-2-Heptanone	 (5)
1.800 (PT-GC/MS)	2-Methyl-3-Pentanol	 (6)
m/z 196 (149,129,81) (LC-MS/MS)	By-product (a)	 (7)
4.800 (P&T-GC/MS)	Chloroform	 (8)

Table. 6. Identified by-products of 2-MIB during UV and combined UV/chlorine reaction.

Retention time	Compounds	Structure
8.928 (PT-GC/MS)	2-Methylenebornane	 (1)
10.306 (PT-GC/MS)	2-Methyl-2-Bornene	 (2)
7.255 (PT-GC/MS)	4-Methyl-2-Heptanone	 (3)
4.287 (PT-GC/MS)	2,4-Dimethyl-1-Heptene	 (4)
1.800 (PT-GC/MS)	2-Methyl-3-Pentanol	 (5)
m/z 196 (149,129,81) (LC-MS/MS)	By-product (a)	 (6)
4.800 (P&T-GC/MS)	Chloroform	 (7)

Ring opening reactions and homolytic bond scissions due to free radical attacks on geosmin led to the production of byproducts 4 (2-methyl-3-pentanol), 5 (2,4-dimethyl-1-heptene), and 6 (4-methyl-2-heptanone) (Fig. 8). Byproducts 5 and 6 contained the C-C double bond, which is highly reactive with HOCl. Previous studies have also reported a higher reactivity of chlorine with the algal odorants (β -ionone, β -cyclocitral), which contain carbon double bonds (Zhang et al., 2012). Especially, byproduct (6) contains a methyl ketone group that is well-known to readily produce THMs (Joll et al., 2010). Electrophilic addition of hypochlorous acid to the C-C double bond of the byproducts can lead to the production of chlorinated byproducts.

From LC-MS/MS analysis, byproduct (7) (m/z 196) was identified. Byproduct (7) is a product of electrophilic addition of HOCl from byproduct (5) and (6) (Fig. 8). Following the attack of free radicals, chlorine substitution and subsequent nucleophilic attack of H₂O on the electrophilic carbocation create more DBP precursors and chloroform. Figure 4 indicates the proposed degradation pathway of GSM during UV/chlorine reaction.

The two directly dehydrated products from 2-MIB were found. Byproduct (1) (2-methylenebornane) and byproduct (2) (2-methyl-2-bornene). Both dehydrated compounds were identified during UV/chlorine reaction and UV photolysis of 2-MIB. Previous study reported that byproduct (1), (2) identified after ultrasonic irradiation and ozonation of 2-MIB (Song et al., 2007; Yuan et al., 2013). Electrophilic substitution and ring opening reaction by bond scission will lead to byproducts (3), (4), (5) and (6). Further bond scission and chlorine addition reaction produce chloroform. Figure 8 indicates the proposed degradation pathway of 2-MIB during UV/chlorine reaction.

Time dependent byproducts formation during combined UV/chlorine reaction of geosmin and 2-MIB were shown in Fig. 6 and Fig. 8, respectively. Molecular weights of byproducts (1,3-dimethyladamantane, 1,4-dimethyladamantane, 2-methylenebornane, and 2-methyl-2-bornene) were lower than parent compounds (GSM, 2-MIB). These byproducts were rapidly decomposed while

other byproducts increased over time. Other byproducts were removed at the end of the reaction, except for 2-methyl-2-pentanol. In this study, 1,3- dimethyladamantane, 1,4- dimethyladamantane, 2-methylenebornane, and 2-methyl-2-bornene were found which responsible for undesired odor (Martin et al., 1988; Ventura et al., 1997). However, these compounds were completely removed with further reaction. All other byproducts were almost completely removed at the end of the reaction, except for 2-methyl-2-pentanol. Finally, we propose degradation pathways based on these findings (Fig. 7, Fig. 9). The OH and Cl radicals led to the ring opening and bond scission of geosmin and 2-MIB by bond dissociation and dehydration during UV/Chlorination. Electron transfer and hypochlorous acid addition to the C-C double bond may lead to the production of chlorinated byproducts. Despite the high chloroform conversion rate of geosmin and 2-MIB, the actual level of chloroform produced was quite low compared to the typical water quality standard in Korea (80 µg/L).

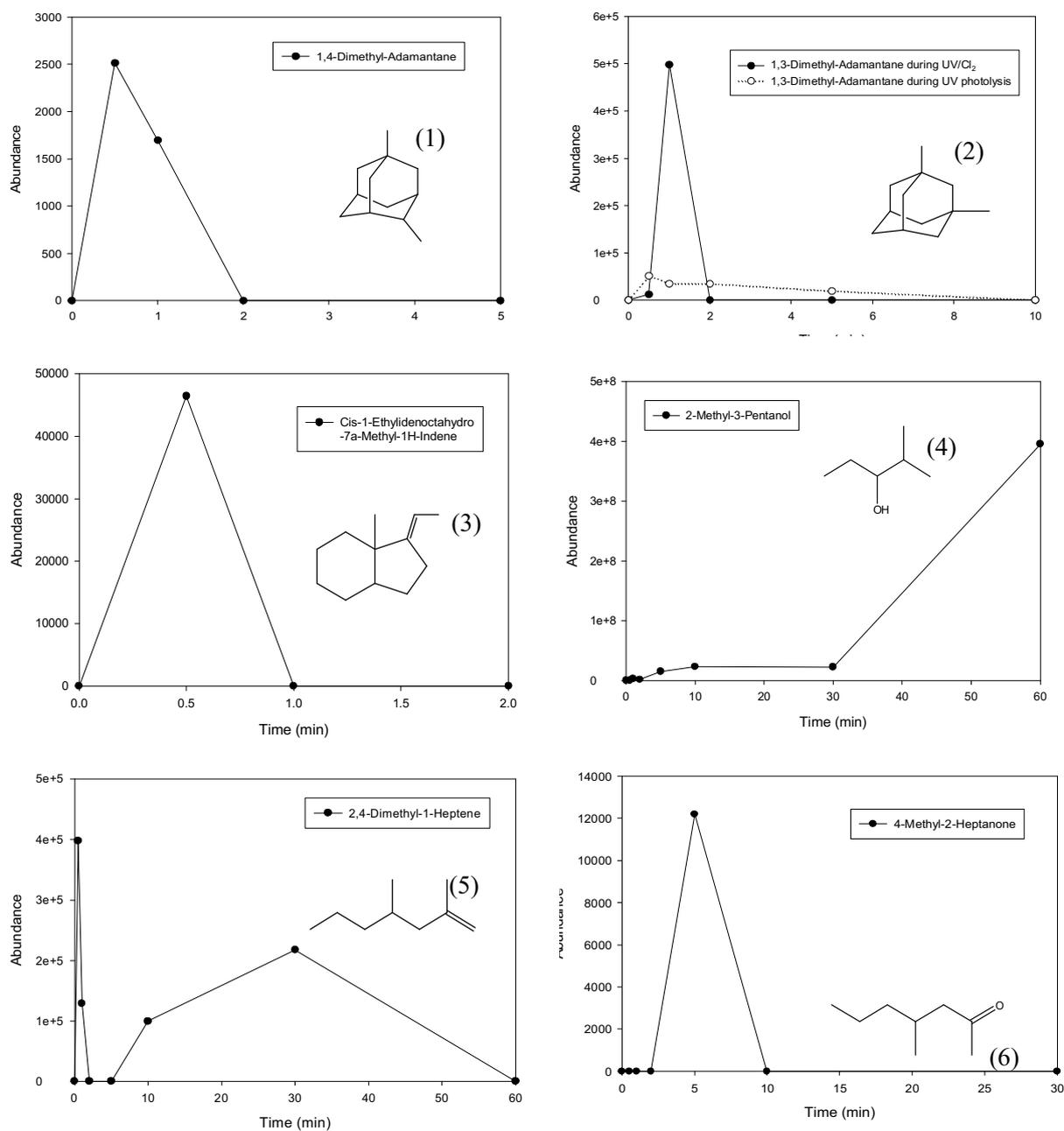


Figure.7. Time-dependent by-products formation during UV/chlorination of geosmin ($[GSM_0] = 5 \mu\text{g/L}$, $[Cl_2] = 0.5 \text{ mg/L}$, $UV-C_{intensity} = 3.2 \text{ mW/cm}^2$, $\text{pH} = 7$, 25°C , $0 \text{ min} \sim 60 \text{ min}$)

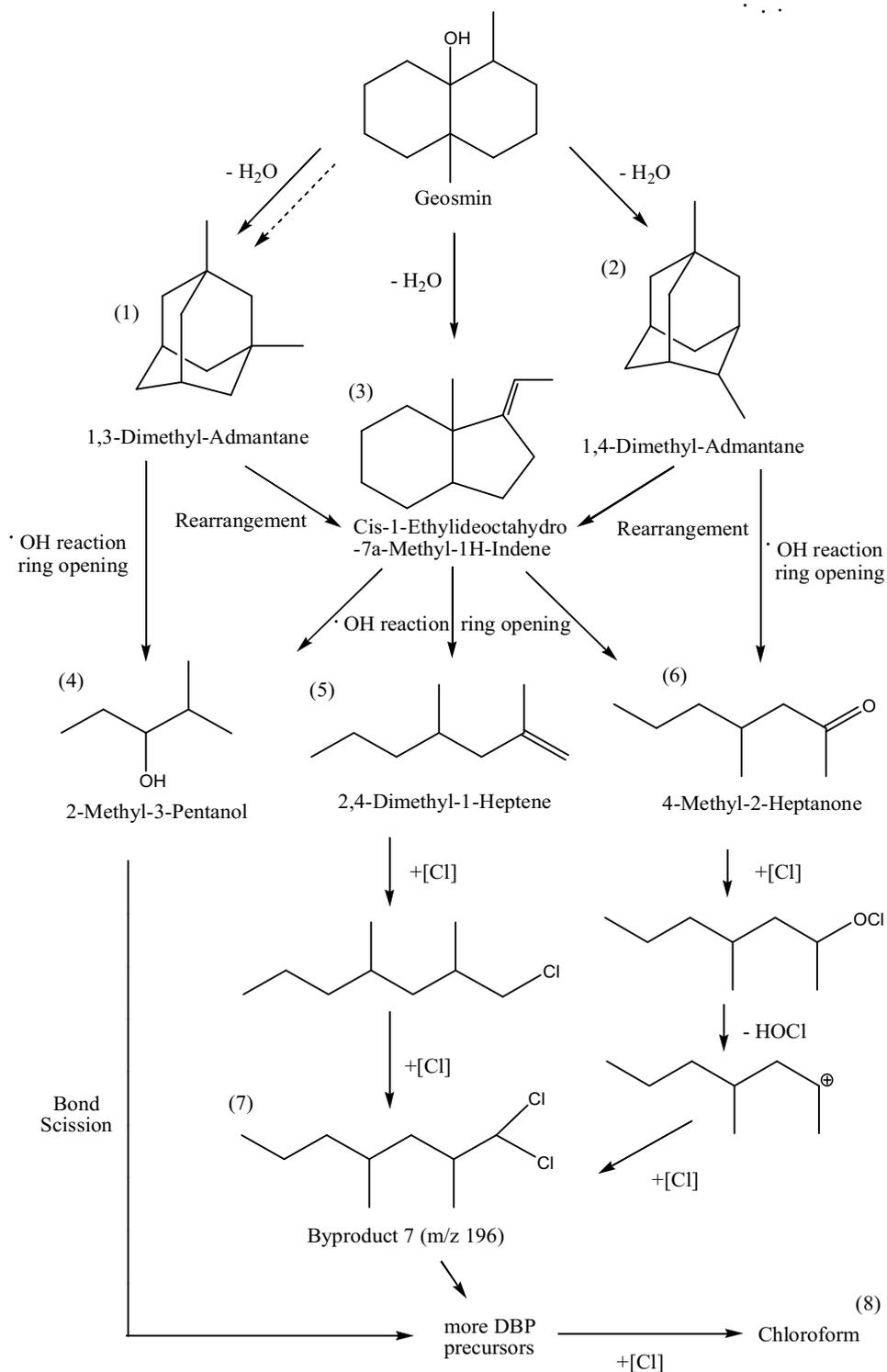


Figure.8. Proposed degradation pathway of GSM by UV (dotted line) and UV/Cl₂ (solid line) based on GC/MS and LC/MS/MS analysis. ([GSM₀] = 5 μg/L, [Cl₂] = 0.5 mg/L, UV-C_{intensity} = 3.2 mW/cm², 0~60min of reaction time, pH=7, 25°C, 0-60min, Byproducts 4,5,6,7, and 8 were commonly found in both geosmin and 2-MIB during UV/chlorine reaction)

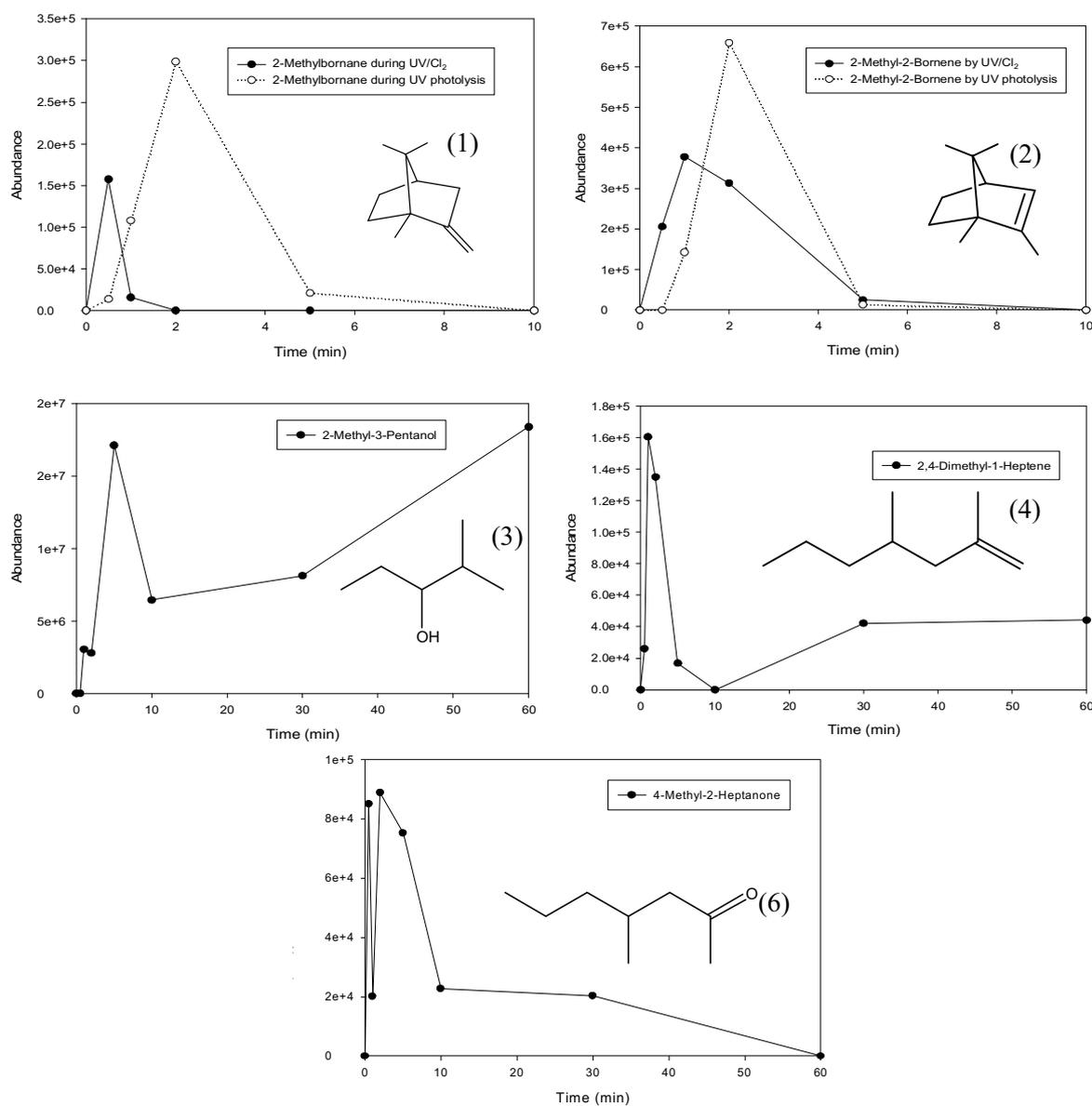


Figure.9. Time-dependent by-products formation during UV/chlorination of 2-MIB ([2-MIB₀] = 5 μg/L, [Cl₂] = 0.5 mg/L, UV-C_{intensity}=3.2mW/cm², pH=7, 25°C, 0min-60min)

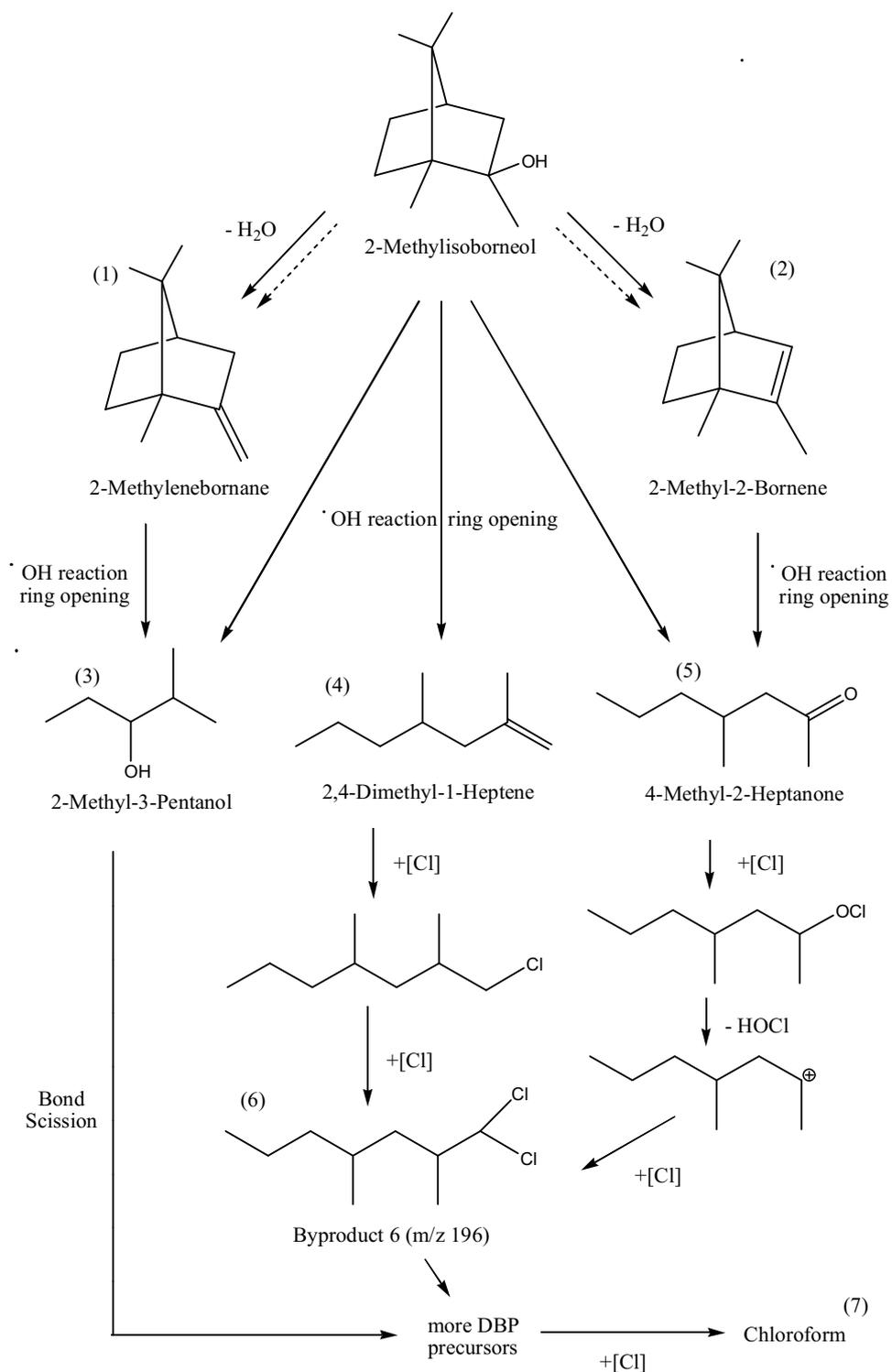


Figure.10. Proposed degradation pathway of 2-MIB by UV (dotted line) and UV/Cl₂ (solid line) based on GC/MS and LC/MS/MS analysis. ([2-MIB]₀) = 5 µg/L, [Cl₂] = 0.5 mg/L, UV-C_{intensity}=3.2 mW/cm², 0~60min of reaction time, pH=7, 25°C, 0-60 min, Byproducts 3,4,5,6, and 7 were commonly found in both geosmin and 2-MIB during UV/chlorine reaction)

4. Conclusions

In this study, we investigated the degradation kinetics and mechanisms of geosmin and 2-MIB during chlorination, UV photolysis, and UV/chlorination. Chlorination was ineffective for geosmin and 2-MIB degradation. Free chlorine had an indirect effect on the removal of these algal odorants and directly affected the formation of byproducts. UV and UV/Chlorination reactions could almost completely degrade geosmin and 2MIB. UV photolysis and UV/chlorination followed a pseudo first-order reaction. Geosmin and 2MIB were more effectively removed at neutral pH during the UV/chlorine reaction, due to the production of OH radicals by HOCl at pH 5 to 7, and the OH radical scavenging effect of OCl^- at higher pH values. Alkaline conditions favored the formation of chloroform, which we observed as a chlorination byproduct in both geosmin and 2MIB degradation. Considering the formation of byproducts and their removal efficiency, the pH should be maintained at 5 to 7.

The results of our study will be useful when applying the combined UV/chlorine process in water treatment to remove taste- and odor-causing compounds. To the best of our knowledge, our study is the first to investigate degradation mechanisms and byproduct formation during UV photolysis and the combined UV/chlorine reaction of geosmin and 2-MIB.

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국문초록

지오스민과 2-MIB는 수질에 대한 안정성과 소비자 신뢰도와 직접적인 연관성이 있기 때문에 이들 물질의 관리 및 처리는 먹는물 산업의 주요 화두로 떠오르고 있다. 이러한 이유로 지오스민과 2-MIB의 처리에 관한 연구는 광범위하게 이루어졌지만, 처리 부산물에 관한 연구는 부족한 실정이다. 이들 이·취미 유발물질들은 독성이 없는 것으로 알려져 있으나, 이 화합물들의 높은 산화잠재력으로 인해 소독부산물 및 기타 유해 부산물들을 생성할 수 있는 가능성이 존재한다. 그러므로 본 연구에서는 두 물질의 처리 부산물에 대한 연구를 중점적으로 진행하였다. 자외선/유리염소 반응을 통한 지오스민과 2-MIB의 수중 분해 메커니즘 및 부산물 생성을 평가하기 위해 염소처리, 자외선 조사, 자외선/염소 동시 반응을 진행하였다. 두 물질은 내염소성을 지니고 있었음을 밝혔으며, 자외선 및 자외선/염소 처리에 의해 발생하는 라디칼에 의한 제거가 가능하다는 것을 확인하였다. 자외선 조사 및 자외선/염소 처리에 의한 두 물질의 제거 반응은 유사 1차 반응을 따랐으며, 처리 부산물들은 GC-MS와 LC-MS/MS를 이용하여 확인하였다. 탈수 반응 및 화합물의 고리 열림 반응에 의하여 발생하는 부산물들이 주로 발견 되었으며, 자외선 조사 및 자외선/자유염소반응에 의해 발생하는 부산물 생성 과정을 제시하였다. 또한, 염소계 소독부산물 중 하나인 클로로포름의 시간 별, pH 별 평가도 이루어졌다. 클로로포름을 제외한 다른 염소계 부산물은 확인되어 지지 않았으나, 두 이·취미 유발물질들은 높은 클로로포름 배출량을 보였다(최대 87%). 하지만, 실제 수계에서 두 물질의 검출수준은 매우 미비하여(200 ng/L 이하) 본 공정 적용 시 이·취미 유발물질들에 의한 유해 부산물 생성은 그 수준이 낮을 것으로 사료된다.

핵심어: 지오스민, 2-MIB, 자외선/자유염소 반응, 제거 키네틱, 부산물