



저작자표시-비영리-변경금지 2.0 대한민국

이용자는 아래의 조건을 따르는 경우에 한하여 자유롭게

- 이 저작물을 복제, 배포, 전송, 전시, 공연 및 방송할 수 있습니다.

다음과 같은 조건을 따라야 합니다:



저작자표시. 귀하는 원저작자를 표시하여야 합니다.



비영리. 귀하는 이 저작물을 영리 목적으로 이용할 수 없습니다.



변경금지. 귀하는 이 저작물을 개작, 변형 또는 가공할 수 없습니다.

- 귀하는, 이 저작물의 재이용이나 배포의 경우, 이 저작물에 적용된 이용허락조건을 명확하게 나타내어야 합니다.
- 저작권자로부터 별도의 허가를 받으면 이러한 조건들은 적용되지 않습니다.

저작권법에 따른 이용자의 권리는 위의 내용에 의하여 영향을 받지 않습니다.

이것은 [이용허락규약\(Legal Code\)](#)을 이해하기 쉽게 요약한 것입니다.

[Disclaimer](#)

보건학석사 학위논문

**Photodegradation Kinetics and Mechanism of
Bisphenol-A and 4-tert-octylphenol in Aqueous
Solution**

광분해를 이용한 **Bisphenol-A**와 **4-tert-octylphenol**의

분해반응속도와 기전에 대한 연구

2012 년 8 월

서울대학교 보건대학원

환경보건학과 환경보건학 전공

강영민

Abstract

Bisphenol-A (BPA) and 4-tert-octylphenol (t-OP), known as endocrine disrupting compounds (EDCs), were hardly removed in conventional waste water treatment processes. The pollutants should be removed from environment since they can cause adverse health effects such as breast cancer, hyperspadiasm, and testicular cancer. Photolysis can effectively remove organic compounds from water. However, if we apply photolysis as EDCs removal process at WWTPs without estimation of influencing factors and intermediates, it will cause energy, cost and by-product problems.

In order to better understand and predict the behavior of BPA and t-OP photodegradation at aqueous, we investigated kinetics and degradation mechanism of photodegradation of BPA and t-OP using a photo-reactor system with UV. The objectives of this study are to examine the effects of initial concentrations, UV intensity, pH, and NO_3^- concentrations on the photodegradation of BPA and t-OP in aqueous and to identify intermediate products at photolysis of BPA and t-OP when NO_3^- is present.

The pseudo-first-order rate constants (k_1) of BPA and t-OP decreased from 8.5×10^{-3} to $3.7 \times 10^{-3} \text{ min}^{-1}$ and from 7.72×10^{-2} to $3.28 \times 10^{-2} \text{ min}^{-1}$ with increasing initial concentration of BPA from 2 mg L^{-1} to 40 mg L^{-1} and t-OP from 0.5 mg L^{-1} to 5 mg L^{-1} because of complete absorption of the incident photon

flux by higher initial concentration and the scattering effect. The pseudo-first-order rate constants of BPA and t-OP increased from 5.74×10^{-3} to $14.50 \times 10^{-3} \text{ min}^{-1}$ and from 5.06×10^{-2} to $12.07 \times 10^{-2} \text{ min}^{-1}$, respectively when UV intensity increased, which causes the more chemical to move $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$, from 3.65×10^{-5} to $9.68 \times 10^{-5} \text{ Einstein L}^{-1} \text{ min}^{-1}$. The quantum yields of BPA and t-OP were found to be 0.0364 and 0.409 mol Einstein⁻¹ in UV photolysis. The degradation efficiencies were significantly improved by increasing pH close to values which are 10.2 for BPA and 10.33 for t-OP. The degradation rate of BPA and t-OP enhanced with increasing nitrate concentration, up to 40 mg L⁻¹ for BPA and 30 mg L⁻¹ for t-OP, and then decreased after this concentration. This result indicates that OH and NO₂ radicals might play important roles in photolysis of BPA, but at higher nitrate concentration, nitrate ion might act as a radical inhibitor. Intermediates during photolysis of BPA and t-OP were identified by using LC/MS/MS in the presence of nitrate ion. Eight intermediates were identified from photolysis of BPA and five intermediates were identified from photolysis of t-OP in the presence with nitrate. The presence of nitrate induced the formation of nitro-intermediates in photodegradation of BPA. Also, the production and destruction of intermediates as well as degradation pathway were observed to examine the degradation behavior of BPA and t-OP. Our results can be helpful to understand the kinetics and removal mechanisms of BPA and t-

OP by photolysis in the treatment process and in the natural water environment containing nitrate ions.

Keywords: photolysis, nitrate, pH, intermediate, OH radical, nitro-intermediate

Student Number: 2010-23779

Contents

Abstract	i
List of Figures	vi
List of Tables	viii
I. Introduction	1
1. Background	1
2. Information on the study compounds	3
3. Photolysis	8
4. Additives effects and degradation mechanism	12
5. Objectives	12
II. Materials and Methods	13
1. Chemicals	13
2. Intensity and quantum yield	13
3. Photoreactor	15
4. Analytical method	17

III. Results and Discussion	19
1. The initial concentration influence	19
2. UV intensity effects on direct photolysis	24
3. The effect of pH	31
4. The effect of NO ₃ ⁻	36
5. Intermediates	42
IV. Conclusions	54
References	58
국문초록	68
Appendix	71

List of Figures

Figure 1. Schematic diagram of the photolysis reactor	16
Figure 2. Direct photodegradation of BPA with various initial concentrations	22
Figure 3. Direct photodegradation of t-OP with various initial concentrations	23
Figure 4. Direct photodegradation of BPA with various UV intensities	25
Figure 5. Direct photodegradation of t-OP with various UV intensities	26
Figure 6. The effect of solution pH on BPA photodegradation	33
Figure 7. The effect of solution pH on t-OP photodegradation	34
Figure 8. The UV-visible absorption spectra of nitrate	37
Figure 9. The pseudo-first-order rate constants for BPA	39
Figure 10. The pseudo-first-order rate constants for t-OP	40

Figure 11. LC/MS/MS spectrum of BPA	43
Figure 12. LC/MS/MS spectrum of t-OP	43
Figure 13. Intermediates products change during photolysis	48
Figure 14. t-OP intermediates products change during photolysis	48
Figure 15. Intermediates products change during BPA photolysis with H ₂ O ₂	50
Figure 16. The proposed photodegradation reaction pathway of BPA in NO ₃ ⁻ /UVC process	52
Figure 17. The proposed photodegradation reaction pathway of t-OP in NO ₃ ⁻ /UVC process	53

List of Tables

Table 1. Physical and chemical properties of bisphenol-A and 4-tert-octylphenol	5
Table 2. Occurrence BPA and t-OP in various water systems at ng/L concentration	6
Table 3. Fate of BPA and t-OP in various water systems at ng/L concentration	7
Table 4. Research on BPA and t-OP removal by AOPs	9
Table 5. Photolysis of BPA at various intensities	29
Table 6. Photolysis of t-OP at various intensities	29
Table 7. Structures and mass spectral data for BPA and postulated transformation products, as determined from LC/MS/MS	45
Table 8. Structures and mass spectral data for t-OP and postulated transformation products, as determined from LC/MS/MS	46

I. Introduction

1. Background

The human species is increasingly facing the significant problem of water supply degradation as the planet's water resources are continually being threatened by growing pollution of our hydrosphere from the developing civilization. The WHO reported that more than 40 % of the world population has suffered a shortage or even lack of clean water and more than 25 % of the world population suffers from health and hygienic problems related to water (Koch 1993). Despite many efforts to provide clean water, many people still have no access to an improved water supply and sanitation. In order to cope with the improvement of water quality, major strategies of water treatment are being advanced and applied chemical treatment of polluted drinking water, surface water and groundwater.

Wastewater discharged from domestic and industrial activity has been a key source of various kinds of pollutants threatening the environment. Therefore, it is essential to build the purification of wastewater to achieve a high quality of drinking water. Furthermore, raising social consciousness and political will to address water quality has induced intensive growth of water purification research

over the last decades. Over the same period, water quality control and regulation against hazardous pollutants also have become stricter in many countries. In addition, the development of analytical methods and technologies to detect, identify, and measure pollutants has not only stimulated a reconceptualization of pollutants, but also has cleared up the impact of very low concentration of pollutants. Specifically, the occurrence of endocrine disrupting compounds (EDCs) in the aquatic environment, has increasingly raised concern in recent years. Because the most hazardous pollutants and EDCs exist as trace materials in the water, the effort to achieve a progressive reduction of pollutants is required.

2. Information on the study compounds

Endocrine disrupting compounds (EDCs) found in everywhere like food, toy, cosmetics, and plastic product cause adverse health effects by either way mimicking a hormone or by blocking humoral effects (Lutz and Kloas 1999). These compounds have been attributed as a suspected compound contributing breast cancer, testicular cancer, hypospadias, and a progressive fall in sperm count (Sharpe and Skakkebaek 1993).

The materials have not been traditionally recognized as a contaminant due to the difficulty in detecting and proving their adverse effect on the environment and health. However, as analytical chemists develop new tools for detecting organic wastewater contaminants, the number of compounds finding in the environment continuously grows. For past several decades, lots of scientists have been endeavoring to solve these problems. The main points of completely solving the matters are to know what chemicals are harmful, to monitor what pollutants exist in aquatic system, to find and develop the methods for removing these chemicals from the environment (Liu et al. 2009).

Bisphenol-A (4-(2-(4-hydroxyphenyl)propan-2-yl)phenol, BPA) and 4-tert-octylphenol (4-(2-methylheptan-2-yl)phenol, t-OP) are the well-known EDCs due to its application and quantity used globally (Dekant and Völkel

2008). BPA is used as a raw material for polycarbonate plastic and epoxy resins which are final products included in food cans, drink packaging applications, bottle tops, and water supply pipes. t-OP is a precursor in the manufacture of nonionic surfactants used in detergents, pesticide formulation, industrial cleaners, emulsifier, and personal care product (Ying et al. 2002). Every year, hundred thousand tons of BPA and t-OP are produced and discharged to aquatic system or sent to wastewater treatment plants (WWTPs), sewage treatment plants (STPs), and water treatment plans (WTPs) (Lyons 1997; Lintelmann et al. 2003; Ning et al. 2007). Table 1 shows the more detail chemical properties of the compounds.

However, the efficiency of elimination of these chemicals was reported less than 55 % at WWTPs (Ito 2008; Körner et al. 2000). Actually 8.8-1000 ng L⁻¹ of BPA and 50-4300 ng L⁻¹ of t-OP were detected at surface water (Vethaak et al. 2005). Even 5 ng L⁻¹ of BPA (Rodriguez-Mozaz et al. 2004) and 2-4.9 ng L⁻¹ of t-OP (Kuch and Ballschmiter 2001) were contained in drinking. Table 2 and 3 shows occurrence and fate of BPA and t-OP. In the view of its presence and low removal efficiency, additional treatment for efficiently eliminating BPA and t-OP is of considerable interest to regulatory authorities.

Table 1. Physical and chemical properties of bisphenol-A and 4-tert-octylphenol

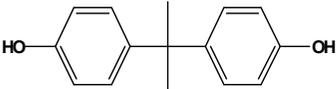
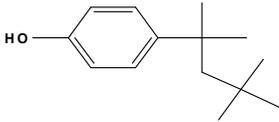
	Bisphenol – A (BPA)	4-tert-octylphenol (t-OP)
Chemical Construction		
Molecular Formula	$C_{15}H_{16}O_2$	$C_{14}H_{22}O$
Molecular Weight	228 g mol ⁻¹	206 g mol ⁻¹
CAS Number	80-05-7	140-66-9
Log K_{ow}	3.32	4.12
Water Solubility	120 mg L ⁻¹ at 21.5 °C	10 mg L ⁻¹ at 23 °C
IUPAC Name	4-(2,4-dihydroxyphenyl)propan-2-ylphenol	4-(2-methylheptan-2-yl)phenol

Table 2. Occurrence BPA and t-OP in various water systems at ng L⁻¹ concentration

Water system	BPA	Reference	t-OP	Reference
Surface water	8.8 – 100	(Vethaak et al. 2005)	50 – 4,300	(Vethaak et al. 2005)
	0.5 - 14	(Kuch et al. 2001)	0.8 - 54	(Kuch et al. 2001)
	n.d - 600	(Hohenblum et al. 2004a)	n.d - 41	(Hohenblum et al. 2004a)
	15 - 29	(Laganà et al. 2004)	0.04 - 1.1	(Beck et al. 2005)
	65 - 295	(Rodriguez et al. 2004)		
	n.d-5.7	(Beck et al. 2005)		
Ground water	n.d - 7	(Laganà et al. 2004)	n.d – 42	(Hohenblum et al. 2004b)
	n.d - 930	(Hohenblum et al. 2004b)		
Drinking water	0.5 - 2.0	(Kuch et al. 2001)	0.2 – 4.9	(Kuch et al. 2001)
	5	(Rodriguez et al. 2004)		

n.d: Not Detected

Table 3. Fate of BPA and t-OP in various water systems at ng L⁻¹ concentration

	WWTPs			Reference
	Influent	Effluent	Removal (%)	
BPA	332 – 339	13 – 36	90	(Laganà et al. 2004)
	250 – 5,620	43 – 4,090	92	(Vethaak et al. 2005)
	720 – 2,376	16 – 1,840	10 – 99	(Clara et al. 2005)
	281 – 3,642	6 – 50	90 – 98	(Drewes et al. 2005)
	88 – 438	11 – 1,054	-58 – 87	(Fernandez et al. 2007)
	450 – 3,300	610 – 710	53 – 55	(Ito 2008)
t-OP	183 – 321	450 – 358	-96 – 13	(Körner et al. 2000)
	270 – 13,000	450 – 1,300	0	(Vethaak et al. 2005)
	300 – 6,704	37.5 – 180	55 – 97	(Drewes et al. 2005)
	n.d – 796	n.d – 240	-11 – 69	(Leusch et al. 2006)

n.d: Not Detected

3. Photolysis

Photolysis decomposes compounds in either way by direct photolysis, which photons generated by UV fluence destruct a chemical, or by indirect photolysis, which highly reactive molecules like hydroxyl-radicals, singlet oxygen or bi/carbonate radicals attack a chemical, or by direct and indirect both ways. If adequately developed, photolysis has advantages to abate pollutions in points of those producing less by-product than chlorination, taking less time than biological process, and requiring no final disposal which is mandatory in adsorption and filtration does (Andreozzi et al. 1999; Robinson and Hellou 2009; Kamoshita et al. 2010). Actually UV induced reaction, UV with other additives, has improved the complete elimination of emerging contaminants such as 1,4-dioxane (Son et al. 2009), carbamazepine (Im et al. 2011), and amoxicillin (Jung et al. 2012). The more information about the advanced oxidation processes (AOPs) are illustrated in Table 4.

However, most of the authors have only concerned to be the fast degradation of pollutions. In other word, the principle influencing factors such as organic compound concentration, UV intensity, and pH have not been paid attention. It should be applied after estimating fundamental information and influencing factors on UV.

Table 4. Research on BPA and t-OP removal by AOPs

Compounds	Media	Treatment process	Operational condition	Analyses	Main conclusions	Reference
BPA	Aqueous solution	O ₃ /UV	C _{O₃} = 15 μmol min ⁻¹ C ₀ = 0.1 mmol L ⁻¹	LC-MS	1) combination of O ₃ and UV could increase the degradation rate and improve removing efficiency. 2) the degradation rate of BPA with O ₃ was fitted with the pseudo-first-order constant.	(Irmak et al. 2005)
BPA	Aqueous solution	Fenton/UV	C ₀ = 10 mg L ⁻¹ T = 25 ± 1°C	GC-MS	1) influence factors of pH, Fe(II) concentration, H ₂ O ₂ concentration and UV strength were studied and in optimal condition, removal of BPA reached above 90% at 9min by oxidation of Fenton/UV; above 90% of BPA could be mineralized to CO ₂ by oxidation of Fenton/UV and degradation mechanism of BPA was proposed. 2) above 90% of BPA could be mineralized to CO ₂ by oxidation of Fenton/UV and degradation mechanism of BPA was proposed.	(Katsumata et al. 2004)
BPA	Aqueous solution	Fenton/UV/Fe(II) Ultrasound/UV/Fe(II)	C ₀ = 118 μmol L ⁻¹	LC-MS	1) BPA could be completely removed after 90min treated by ultrasound, but at least 80% TOC and 50% COD remained in the treated solution. 2) combination of ultrasound with UV or Fe(II) could improve TOC and COD, and combination of Ultrasound/ Fe(II)/UV could attain the best removal result, which was also the most efficient in energy consumption.	(Torres et al. 2007)
BPA	Aqueous solution	UV/H ₂ O ₂	pH 6.8	HPLC	1) removal efficiency could be improved by increasing the strength of UV, and by adding of 15 mg L ⁻¹ H ₂ O ₂ , removal efficiency of EDCs could be increased from 20% to above 90%. 2) apparent second order rate constants were given and a degradation model was also established.	(Rosenfeldt and Linden 2004)

Table 4. Research on BPA and t-OP removal by AOPs (continued)

Compounds	Media	Treatment process	Operational condition	Analyses	Main conclusions	Reference
BPA	Aqueous solution	UV/H ₂ O ₂	C ₀ = 60 μmol L ⁻¹	HPLC YES <i>in vivo</i>	1) BPA could be effectively removed by adding H ₂ O ₂ , removal efficiency could be improved greatly 2) degradation solution of BPA was evaluated by both <i>in vitro</i> assay and <i>in vivo</i> assay, results suggested UV/H ₂ O ₂ was useful for removing of BPA.	(Chen et al. 2006)
BPA	River water	UV/H ₂ O ₂	C ₀ = 0.8–129 nmol L ⁻¹	YES; <i>in vivo</i>	1) degradation of estrogenic activity of solution suggested pseudo-first order rate dynamics, degradation rate of mixed EDCs in water solution was much slower than sole target chemical in water solution; of hydroxyl radical with target EDCs was calculated, data differed from 0.13%–10.71% with different water solution; 2) reaction percentage of hydroxyl radicals with target EDCs was calculated, data differed from 0.13%–10.71% with different water solutions.	(Chen et al. 2007)
t-OP	Aqueous solution	UV/H ₂ O ₂	C ₀ = 5–40 μmol L ⁻¹	HPLC	1) t-OP was degraded effectively at UV/H ₂ O ₂ . However, the extent of mineralization was much weaker. 2) In alkaline solution the degradation rate was slow.	(BŁĘDZKA et al. 2009)
t-OP	Aqueous solution	UV/H ₂ O ₂	C ₀ = 20 μmol L ⁻¹	GC-MS	1) the quantum yield is estimated to be 0.058 ± 0.004 and dimer intermediates of t-OP was detected. 2) the rate of t-OP photo transformation decreased with decreasing oxygen concentration. 3) the second-order rate constant for the reaction of hydroxyl radicals with t-OP was evaluated as 6400 μM ⁻¹ s ⁻¹ .	(Mazellier and Leverd 2003)

4. Additives effects and degradation mechanism

Nitrate (NO_3^-) is considered the one of the principal components of natural water at concentration ranging from 0.2 to 20 mg L^{-1} (Lam et al. 2003). The nitrate could generate various reactive species including $\cdot\text{OH}$, $\text{NO}_2\cdot$, $\text{O}\cdot$ by absorbing solar and ultra violet irradiation (Mack and Bolton 1999). The chemical reaction of the reactive species with organic pollutants possibly causes indirect photolysis and therefore affects its photochemical fate, intermediates and persistence in water. Using this advantage some authors reported the enhancement of degradation efficiency of organic compound (Jacobs et al. 2011; Mao et al. 2011).

The NO_3^- has been the subject of numerous investigations as additive at photolysis. However, no more information was given concerning the photoproducts. Recently, Cheng research team (2010) investigated the degradation of pentachlorophenol induced by the photolysis of nitrate in aqueous solution and identified some nitro-intermediates. But it is still little known about the influence of these species on the photoreaction behavior of BPA and t-OP.

5. Objectives

Although many studies about the photo-oxidation of BPA and t-OP have been undertaken, the principle influencing factor such as organic compound concentration, UV intensity, pH, NO_3^- and photodegradation mechanism present with nitrate have not been sufficient. This is the fundamental and basic information on understanding the advanced oxidation processes.

Therefore, in order to better understand and predict the behavior of BPA and t-OP photodegradation at aqueous, the objectives of this study are to examine the effects of initial concentrations, UV intensity, pH, and NO_3^- concentrations on the photodegradation of BPA and t-OP in aqueous solution and to identify intermediate products in photolysis of BPA and t-OP with NO_3^- .

Our results can be helpful to understand the kinetics and removal mechanisms of BPA and t-OP by photolysis in the treatment process and in the natural water environment containing nitrate ions.

II. Materials and Methods

1. Chemicals

Bisphenol-A ($C_{15}H_{16}O_2$, 99 %), 4-tert-octylphenol ($C_{14}H_{22}O$, 97 %), potassium nitrate (KNO_3 , 99 %), 1,10-phenanthroline monohydrate ($C_{12}H_8N_2 \cdot H_2O$, 99 %), hydrochloric acid (HCl, 37 %), and sodium hydroxide (NaOH, 98 %) were purchased from Sigma Aldrich. Potassium trioxalato ferrate(III) trihydrate ($Fe(C_2O_4)_3 \cdot 3H_2O$) was supplied by Alfa Aesar. The BPA and t-OP concentration conducted in the experiment was 2 mg L^{-1} except the initial concentration experiment. All stock solution was prepared in deionized water ($R = 18.2 \text{ M}\Omega \text{ cm}^{-1}$, Milli-Q). All chemicals used in this experience were reagent grade and use as received.

2. Intensity and quantum yield

Intensities according to various numbers of lamps were measured by ferrioxalate actionmetry method (Ahmed 2004). The method is that one Fe^{3+} ion

produces one Fe^{2+} ion as the photo process preceding. Thus, by monitoring of the Fe^{2+} formation and employing Eq. (1), intensities were calculated.

Quantum yield, defined as the number of moles of product formed or reactant removed per Einstein of photons absorbed, was calculated using Eq. (2) (Lin et al. 2004).

$$I_{\lambda} = \frac{d[Fe^{2+}]/dt}{\phi_{Fe^{3+}}} N_A \quad (1)$$

$$\phi = \frac{k_1}{2.0303 I_{\lambda} E_{\lambda} l} \quad (2)$$

where, I is UV intensity (Einstein $L^{-1} \text{ min}^{-1}$), $d[Fe^{2+}]/dt$ is a rate of formation of $[Fe^{2+}]$. ϕ is quantum yield (mol Einstein $^{-1}$); 1.21 is employed for $\phi_{Fe^{3+}}$ (Hatchard and Parker 1956), k_1 is the pseudo-first-order rate constant (min^{-1}), E is absorbance coefficient ($M^{-1} \text{ cm}^{-1}$), l is the distance of the reaction column from UV source (cm), and N_A is the Avogadro number ($6.022 \times 10^{23} \text{ mol}^{-1}$).

3. Photoreactor

The experiment was performed in a circulating photo reactor system consisting of a stirred reservoir, UV lamp (20W, 254 nm , San-kyo electrics, Electrics Co., Kyoto, Japan), photoreaction chamber, and a peristaltic pump (Master Flex model 7518-00, Cole-Parmer Instrument, Vernon Hills, USA) for circulating solution. Teflon tube was used for connecting each quartz column (10 mm diameter, 650 mm length). The reactor around the quartz columns was covered with aluminum foil for UV safety and energy consideration. The reaction solutions were continuously re-circulated with a rotary pump at a flow rate of 1 L min⁻¹. The distance from a UV lamp to a quartz column was 40 mm. UV intensity was controlled by adjusting number of UV lamps.

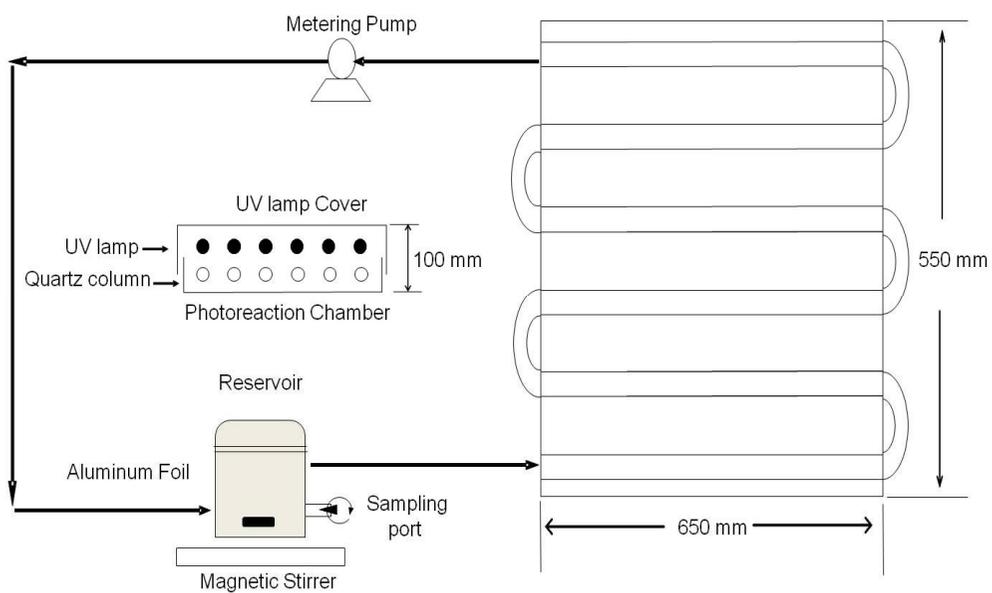


Fig. 1. Schematic diagram of the photolysis reactor.

4. Analytical method

All samples taken at selected time were filtered with 0.2 μm PTFE filter (Advantec MFC Inc. Dublin, USA) to remove particle suspensions prior to analysis. The concentration of BPA and t-OP were quantified using high performance liquid chromatography (HPLC, Ultimate-3000, Dionex Co., Sunnyvale, USA) with an absorbance detector (VWD-3100) and C-18 silica column (25 cm \times 4.6 mm i.d., 5 μm particles, Supelco Park, Bellefonte, USA). Detection wavelength was 278 nm and mobile phase was acetonitrile and water (5:5, V/V) at a flow rate 0.8 mL min⁻¹ for BPA and detection wavelength was 230 nm, mobile phase was acetonitrile and water (62:38, V/V) for t-OP at a flow rate is 0.8 mL min⁻¹.

Intermediates were identified with ultra performance liquid chromatography (UPLC, NEXERA, Shimadzu Co., Kyoto, Japan) equipped with API 4000 (AB Sciex, Foster, Canada). Mass spectrometer was operated in the negative ion mode [M-H]. The mobile phase was acetonitrile and water (5:5, V/V) at a flow rate 0.2 mL min⁻¹ for BPA and acetonitrile and water (8:2, V/V) at a flow rate 0.3 mL min⁻¹ for t-OP. The peak separation was conducted with a Luna C18(2) column (150 mm \times 20 mm i.d., 3 μm particles, phenomenex, Torrance, Canada).

The formation of Fe^{2+} was measured using ultraviolet-visible spectrophotometer (Biomate 3, Thermo Fisher Science, Inc., Waltham, USA) at 510 nm. Solution pH was determined using a pH meter (Model 52A, Orion, Reno, USA).

III. Results and Discussion

1. The initial concentration influence

The amount of pollutants in aqueous exists with substantial different level depending on place and time. Therefore, it is instructive information to study the photodegradation kinetics of BPA and t-OP based on its initial concentration.

Eq. (3) can be used to calculate degradation kinetics (Jin et al. 2010). Eq. (4) and (5) were formulated for BPA and t-OP removal efficiency and the pseudo-first-order rate constant (k_1) by integration of Eq. (3).

$$rate = -\frac{d[C]}{dk_1} = t C \quad (3)$$

$$\frac{C_t}{C_0} = e^{-k_1 t} \quad (4)$$

$$k_1 = -\ln\left(\frac{C_t}{C_0}\right)t^{-1} \quad (5)$$

In these equations, C is concentration of an organic compound (mg L^{-1}), t is time (Drewes et al.), and k_1 is the pseudo-first-order rate constants (min^{-1}) for direct photolysis.

By using those equations, the effects of initial BPA and t-OP concentration on photodegradation were investigated. Fig. 2 and 3 depict a plot of the pseudo-first-order rate constant for BPA and t-OP photodegradation as a function of initial concentration of organic chemicals. These organic compounds were removed 86, 82, 74, 65, 59 % at 240 min for BPA and 90, 84, 78, 75, 67% for t-OP with the initial concentration of those chemical increasing. The pseudo-first-order rate constants of BPA and t-OP were decreased from 8.5×10^{-3} to $3.7 \times 10^{-3} \text{ min}^{-1}$ and from 8.96×10^{-2} to $3.28 \times 10^{-2} \text{ min}^{-1}$, respectively, as the initial concentrations were increased. The photodegradation of both chemicals were significantly affected by initial concentration.

The possible reasons of this result are inner filter effect and the scattering effect. As initial concentrations were increased, light did not much penetrate the solution. Some other authors reported the similar effect on additives that at a certain quantity of additives added resulted in decreasing the pseudo-first-order rate constants (Neamtu and Frimmel 2006; Wu and Linden 2010). As the same as scattering effect of additives, increased BPA and t-OP concentration should scatter the more light. Also complete absorption of the incident photon flux by higher initial t-OP concentration over shorter path length and the lower

transmission of the samples at higher concentration of t-OP should affect the decreased pseudo-first-order rate constant.

In order to predict the pseudo-first-order rate constants (k_1) of BPA and t-OP according to the initial concentration, k_1 in Eq. (4) can be converted to be $b + aC_0$ as described in Eq. (6).

$$\frac{C_t}{C_0} = e^{-(b + aC_0)t} \quad (6)$$

where C and t are the same as mentioned before, b and a are the y-intercept and the slope in Fig. 2 (b), and Fig. 3 (b), respectively. As described in Fig. 2 (b) and Fig. 3 (b), these calculated values which are estimated to be $0.00859 - 1.28 \times 10^{-3} C_0$ for BPA and $0.0821 - 1.00 \times 10^{-2} C_0$ for t-OP with Eq. (6) can be used in predicting the required time to eliminate various initial concentrations of BPA and t-OP.

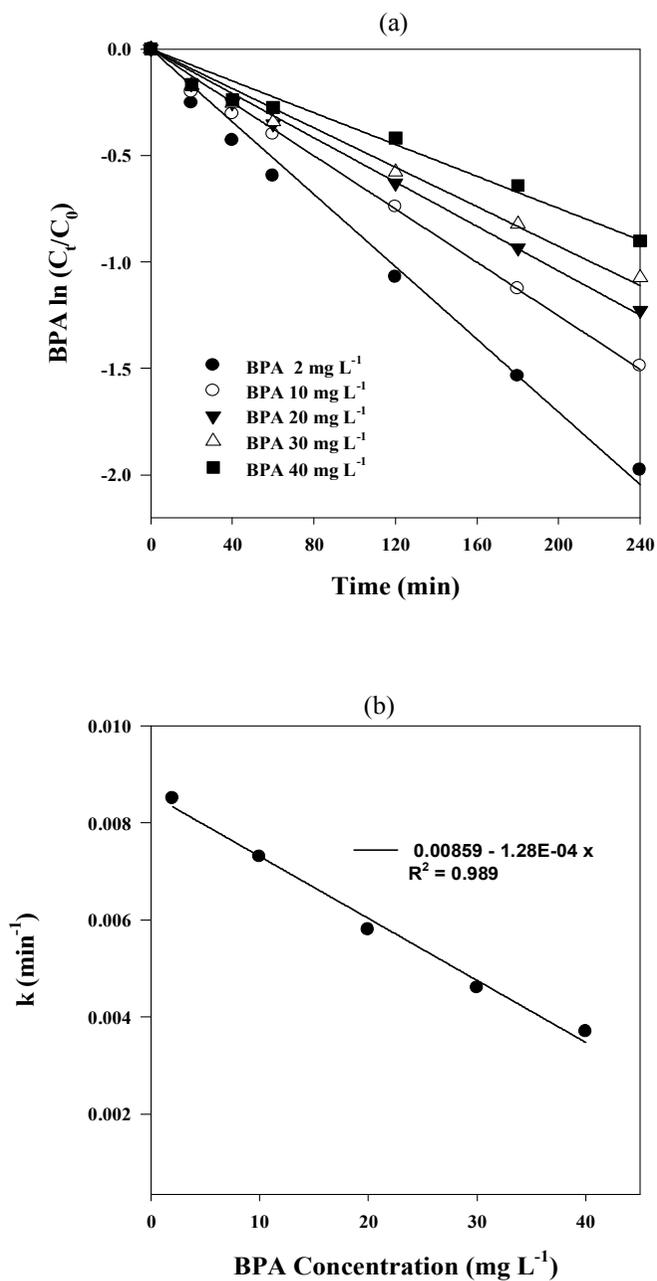


Fig. 2. Direct photodegradation of BPA with various initial concentrations (a) and the pseudo-first-order rate constants as a function for initial BPA concentration (b).

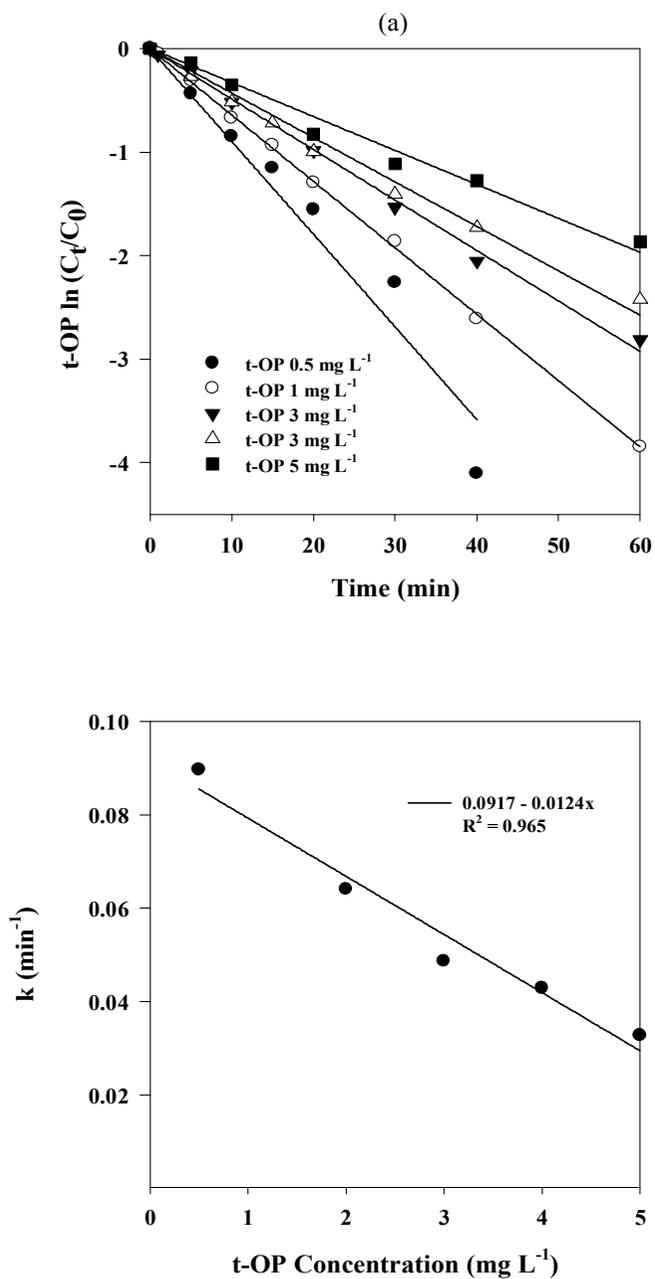


Fig. 3. Direct photodegradation of t-OP with various initial concentrations (a) and the pseudo-first-order rate constants as a function for initial t-OP concentration (b).

2. UV intensity effects on direct photolysis

The time taken to remediate pollutants is of importance at WWTPs, SWTPs, and WTPs in the terms of planning, cost, and operation. With no doubt, the UV is the one of most important factor affecting remediation time. BPA and t-OP photolysis and quantum yield were investigated with various UV intensities to study the pseudo-first-order rate constants and to know more information about photodegradation of BPA and t-OP.

As shown in Fig. 4 and 5, BPA and t-OP photodegradation removal efficiencies and pseudo-first-order rate constants were gradually promoted by increasing UV intensity. The pseudo-first-order rate constants increased from 5.74×10^{-3} to $14.50 \times 10^{-3} \text{ min}^{-1}$ for BPA and from 5.06×10^{-2} to $12.07 \times 10^{-2} \text{ min}^{-1}$ for t-OP when UV intensity increased from 3.65×10^{-5} to $9.68 \times 10^{-5} \text{ Einstein L}^{-1} \text{ min}^{-1}$. As well as pseudo-first-order rate constants increase, the removal efficiencies were increased from 72 to 96 % for BPA and from 80 to 97 % for t-OP as UV intensity was stronger.

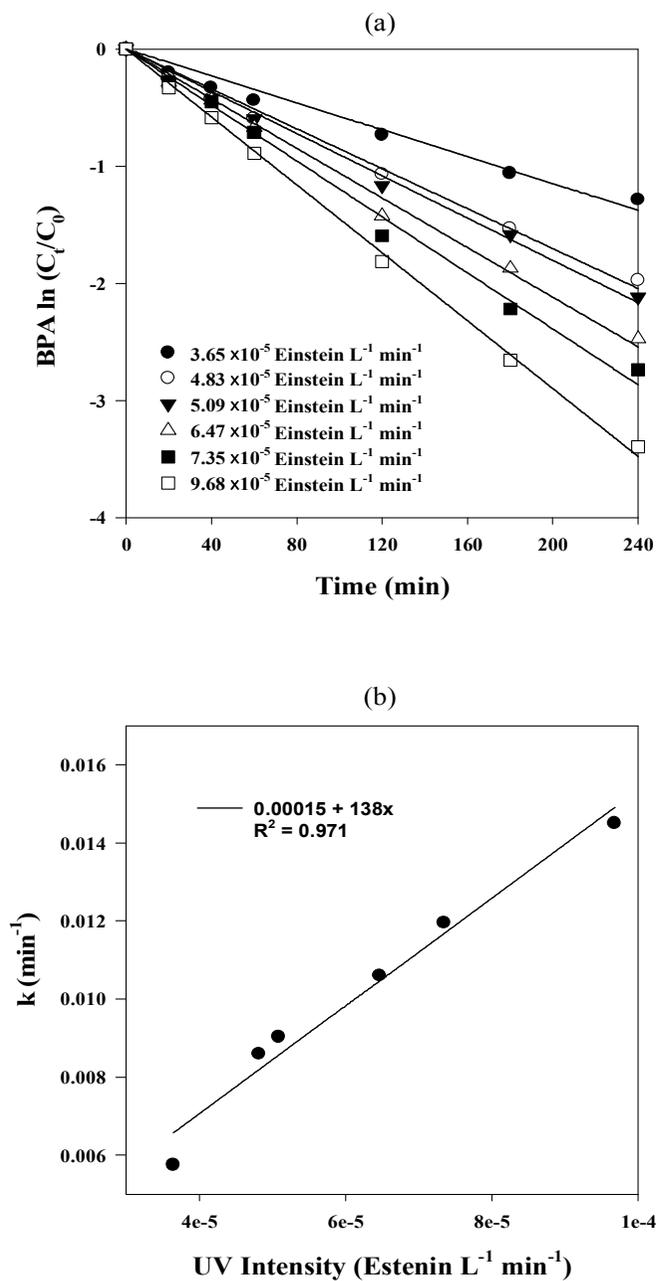


Fig. 4. Direct photodegradation of BPA with various UV intensities (a) and the pseudo-first-order rate constants as a function for UV intensities (b).

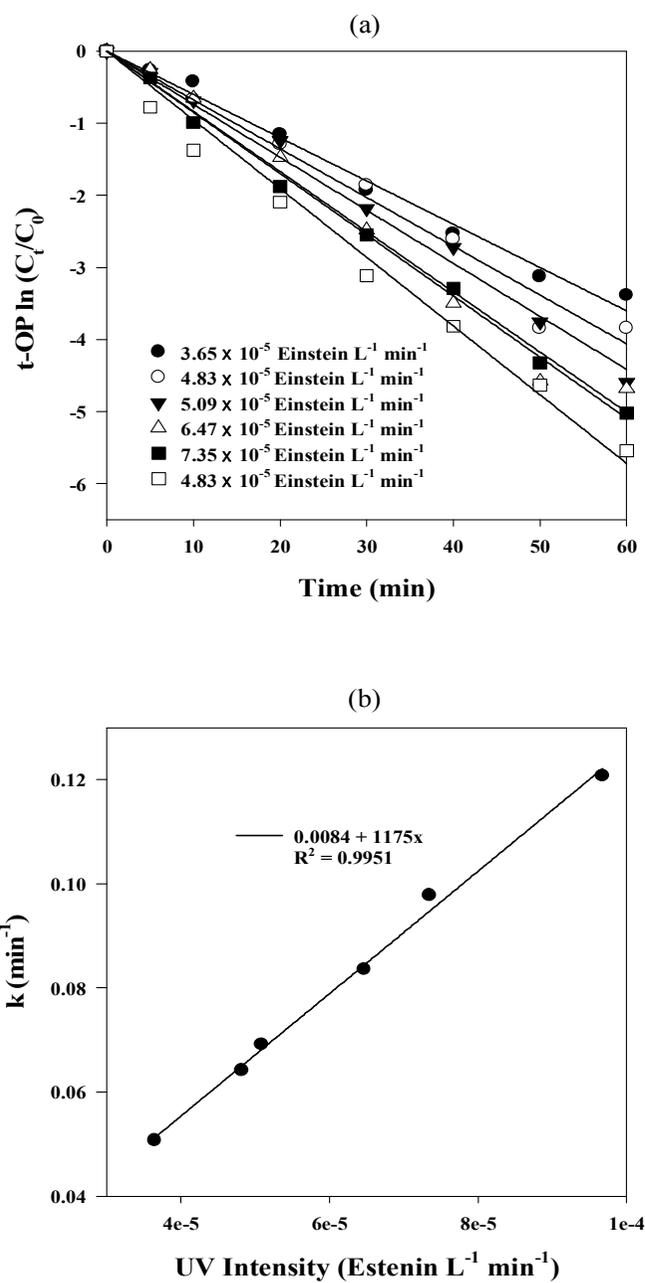
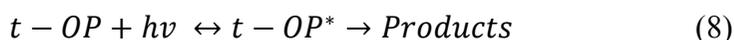
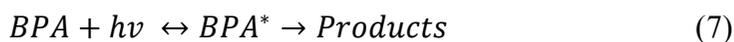


Fig. 5. Direct photodegradation of t-OP with various UV intensities (a) and the pseudo-first-order rate constants as a function for UV intensities (b).

The increased efficiencies were probably due to the fact that the photons make chemicals excited (Schwarzenbach et al. 2003). In other words, the more photons generated by UV are absorbed in compounds, the more chemicals are transitioned like $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$. This excited electronic orbital state develops chemical destruction. In here, the stronger UV intensity moved more BPA to BPA* and t-OP to t-OP*. The results caused pseudo-rate-order rate constants to increase. It could be also expressed as Eq. (7) and Eq. (8).



When BPA and t-OP have been excited to BPA* and t-OP*, the amount that is changed to product or is returned to BPA and t-OP determine the quantum yield. This is why compounds having a similar absorption coefficient show different degradation kinetic. The value can be calculated using ferrioxalate actinometry method as mentioned above (Lin et al. 2004). The average quantum yields were estimated to be $0.0364 \text{ mol Einstein}^{-1}$ for BPA and $0.409 \text{ mol Einstein}^{-1}$ for t-OP (Table 2 and 3).

The absorbance coefficients showed $680 \text{ M}^{-1} \text{ cm}^{-1}$ for BPA and $350 \text{ M}^{-1} \text{ cm}^{-1}$ for t-OP at pH 7. However, the quantum yields of BPA and t-OP showed

significantly difference. Even the absorbance coefficient of BPA was almost 2 times higher than t-OP, the quantum yield of BPA was more than 10 times lower than t-OP. Therefore, it is certain that the quantity of excited state of BPA should be two times higher than t-OP but t-OP* is more readily to change to product while BPA* prefer to return BPA (ground state).

Also, there are interesting results on photolysis pattern. Photodegradation of t-OP is much more sensitive than BPA, which as influencing factors like initial concentration and UV intensity change the pseudo-first-order rate constant of t-OP are sharply altered. However, we can not sure the definite answer in the present. Therefore further research is required.

Table 5. Photolysis of BPA at various intensities

UV Intensity (Einstein L⁻¹ min⁻¹)	Removal efficiency (%)	k₁ (min⁻¹)	Quantum yield (mol Einstein⁻¹)
3.65×10^{-5}	72.39	5.74×10^{-3}	0.0348
4.82×10^{-5}	80.07	8.58×10^{-3}	0.0394
5.09×10^{-5}	85.97	9.02×10^{-3}	0.0392
6.47×10^{-5}	89.36	10.59×10^{-3}	0.0362
7.35×10^{-5}	93.52	11.95×10^{-3}	0.0359
9.68×10^{-5}	96.65	14.50×10^{-3}	0.0331

Table 6. Photolysis of t-OP at various intensities

UV Intensity (Einstein L⁻¹ min⁻¹)	Removal efficiency (%)	k₁ (min⁻¹)	Quantum yield (mol Einstein⁻¹)
3.65×10^{-5}	80.47	5.06×10^{-2}	0.4291
4.82×10^{-5}	84.49	6.41×10^{-2}	0.4122
5.09×10^{-5}	87.68	6.91×10^{-2}	0.4204
6.47×10^{-5}	91.64	8.35×10^{-2}	0.4001
7.35×10^{-5}	93.67	9.77×10^{-2}	0.4123
9.68×10^{-5}	97.42	12.07×10^{-2}	0.3866

The BPA value estimated in our experiment is different from Rosenfeldt and Linden (2004) and Rivas et al. (2009) estimated which are 0.0085 and 0.045 mol Einstein⁻¹, respectively (Rosenfeldt and Linden 2004; Rivas et al. 2009). This probably came from a different experimental design. Our experiment was conducted at recycling system that solution passes a thin quartz tube while the others performed at batch system. As well, using a petri dish (Rosenfeldt and Linden 2004) and making vigorous agitation (Rivas et al. 2009) make the difference quantum yield.

The different quantum yield of t-OP was reported by (BŁĘDZKA et al. 2009). There are also some differences in operation conditions. In the work, t-OP photolysis was experimented the same condition as BPA photolysis. However, the aforementioned author used a different setup arrangement with batch system and no agitation. The different values indicate that it should be calculated each different experimental design and that more information should be gathered for the exact quantum yield at different experimental designs.

3. The effect of pH

The pH effects on photolysis BPA and t-OP were studied using the 4.82×10^{-5} Einstein $L^{-1} \text{ min}^{-1}$ of UV intensity. Solution pH 4, 7, and 11 were selected based on its pK_a which is 10.2 for BPA (Kosky et al. 1991) and 10.33 for t-OP (BŁĘDZKA et al. 2009). Because we assumed that the different species changed by pH should affect the photodegradation.

Fig. 6 (a) and 7 (a) show that photolysis of BPA and t-OP are strongly dependent on its pK_a values. During 240 min reaction time, BPA was completely removed at pH 11 while the removal efficiencies were 80% and 86% at pH 4 and 7. As the same as BPA, at pH 11 t-OP was completely removed during 30 min reaction time but just 81 % and 84 % were removed at pH 4 and 7, respectively. All of these were degraded well fitted to first-order reaction. The pseudo-first-order rate constants of BPA and t-OP at pH 11 were several times higher than at pH 4 and 7. However, the difference of the pseudo-first-order rate constants between pH 4 and 7 were negligible. It is clearly showed that the increase rate constant was rapidly changed at pH 11.

Fig. 5 (b) and 6 (b) illustrate the absorption coefficients of BPA and t-OP at pH 4, 7, and 11. The absorption coefficients were 500, 680, and 4143 $M^{-1} \text{ cm}^{-1}$ for BPA and 309, 350, and 3280 $M^{-1} \text{ cm}^{-1}$ for t-OP at pH 4, 7, and 11,

respectively. As the same as the pseudo-first-order rate constants increase, the absorption coefficients at pH 11 were remarkably increased compare to the solution pH 4 and 7. In addition, the absorption coefficients between pH 4 and 7 showed almost similar value.

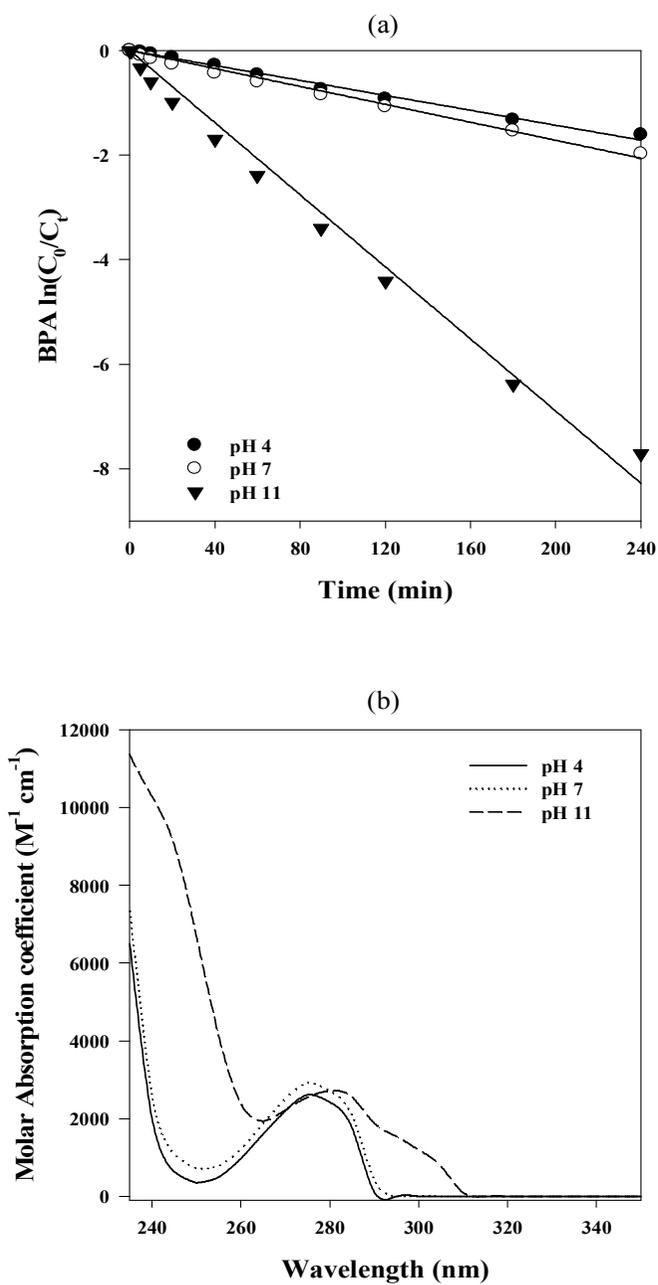


Fig. 6. The effect of solution pH on BPA photodegradation (a) and on the BPA molar absorption coefficient (b) at pH 4, 7 and 11.

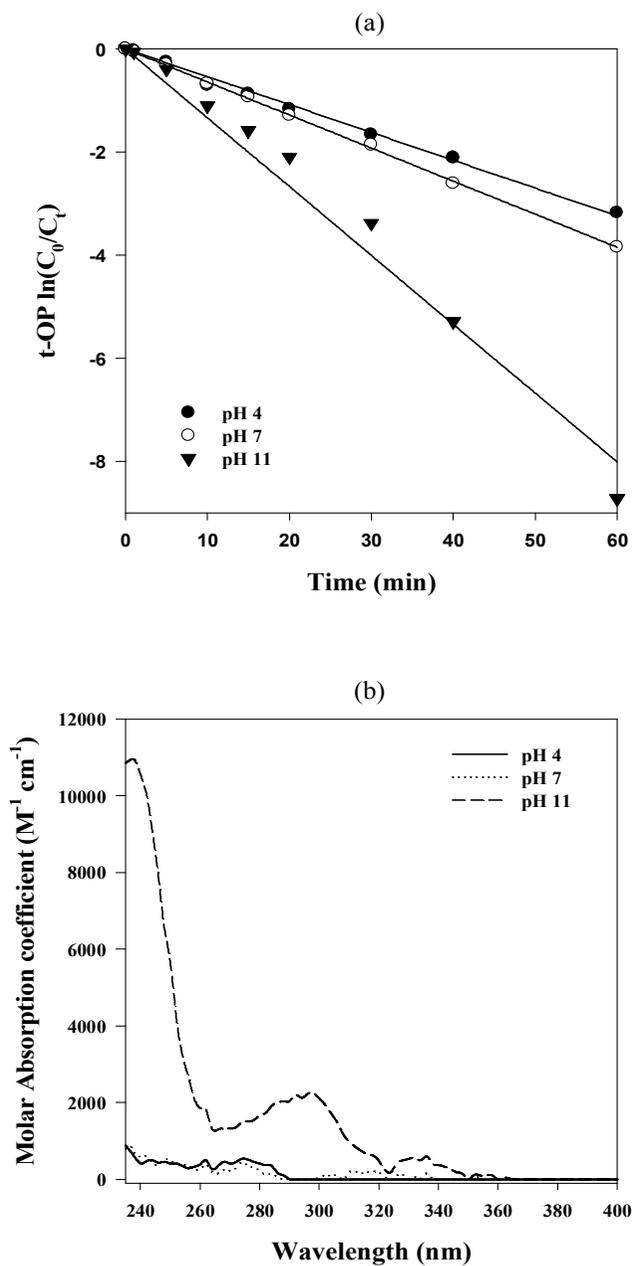


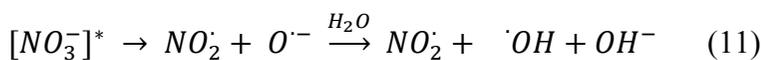
Fig. 7. The effect of solution pH on t-OP photodegradation (a) and on the t-OP molar absorption coefficient (b) at pH 4, 7 and 11.

The sudden absorption increase at pH 11 is due to the fact that the effect of substituents with unshared electrons which the length of π -system is increased by non-bonding electrons through resonance (Ungnade 1953). In other words, when BPA and t-OP became deprotonated form, where solution pH is bigger than its pK_a , BPA and t-OP absorb more photons than protonated form. Those two experimental results, absorption coefficient and photodegradation efficiency, obviously confirm that the deprotonated form of BPA and t-OP changed by pH caused the effect of substituents with unshared electrons and this effect led absorption coefficient to increase. This rising coefficient results in rapid change of the pseudo-first-order rate constant at pH 11. Also, the radicals such as $\cdot\text{CH}_3$ or $\cdot\text{H}$ are generated in photolysis of BPA and t-OP (Peltonen et al. 1986). These radicals are more active with the deprotonated form of BPA ($-\text{O}^-$) and t-OP ($-\text{O}^-$) than the hydroxyl substituent due to the electrophilic characteristic of radicals. Therefore, BPA and t-OP were degraded much faster by the radicals like $\cdot\text{CH}_3$ and $\cdot\text{H}$ at solution pH 11, where BPA and t-OP have been changed to deprotonated form.

These two reasons explain why the pseudo-first-order rate constants and the absorption coefficients of BPA and t-OP were dramatically changed at pH 11 and stayed almost the same values at solution pH 4 and 7. For the same reason, the EDCs photolysis could be significantly increased by changing solution pH condition slightly higher than its pK_a value.

4. The effect of NO_3^-

As mentioned before, nitrate generates OH radical, which are powerful and reactive with organic pollutants, by absorbing photons through Eq. (9) ~ (11) (Mack and Bolton 1999).



The highest absorption coefficient of nitrite is UV-C (200 ~ 290 nm) range (Fig. 8). Therefore, when exploiting nitrate as a source of radicals UV-C is the most suitable application.

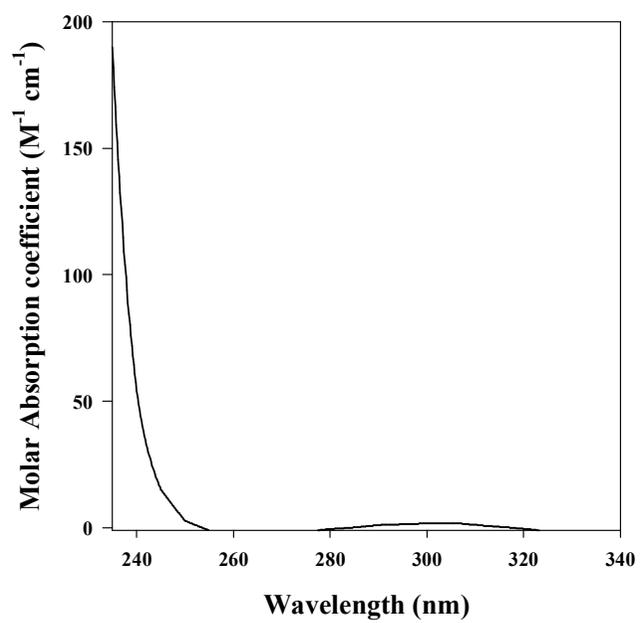


Fig. 8. The UV-visible absorption spectra of nitrate.

In order to investigate efficiencies of BPA and t-OP degradation affected by nitrate dosage, photolysis was conducted at various nitrate concentrations. All experiments that were placed with NO_3^- in a solution showed that removal efficiencies of BPA and t-OP increased as compared to no addition (Fig. 9 and 10). These results indicate that the radicals are generated by nitrate reacted with the pollutants and contributed to destruct the pollutants. All degradation kinetics were fitted well with pseudo-first-order reaction having $R^2 > 0.991$. However, as shown in Fig. 9 (b) and 10 (b) the pseudo-first-order rate constants were not consistently increased with increasing nitrate dosage. The greatest pseudo-first-order rate constants (k_1) of BPA was achieved at 40 mg L^{-1} nitrate dosage with $1.37 \times 10^{-2} \text{ min}^{-1}$. However, the degradation efficiencies became smaller with more addition than 40 mg L^{-1} nitrate. In the case of t-OP photodegradation, the highest pseudo-first-order rate constants (k_1) was shown to be 0.109 min^{-1} at 30 mg L^{-1} nitrate dosage and diminished with the more addition of nitrate.

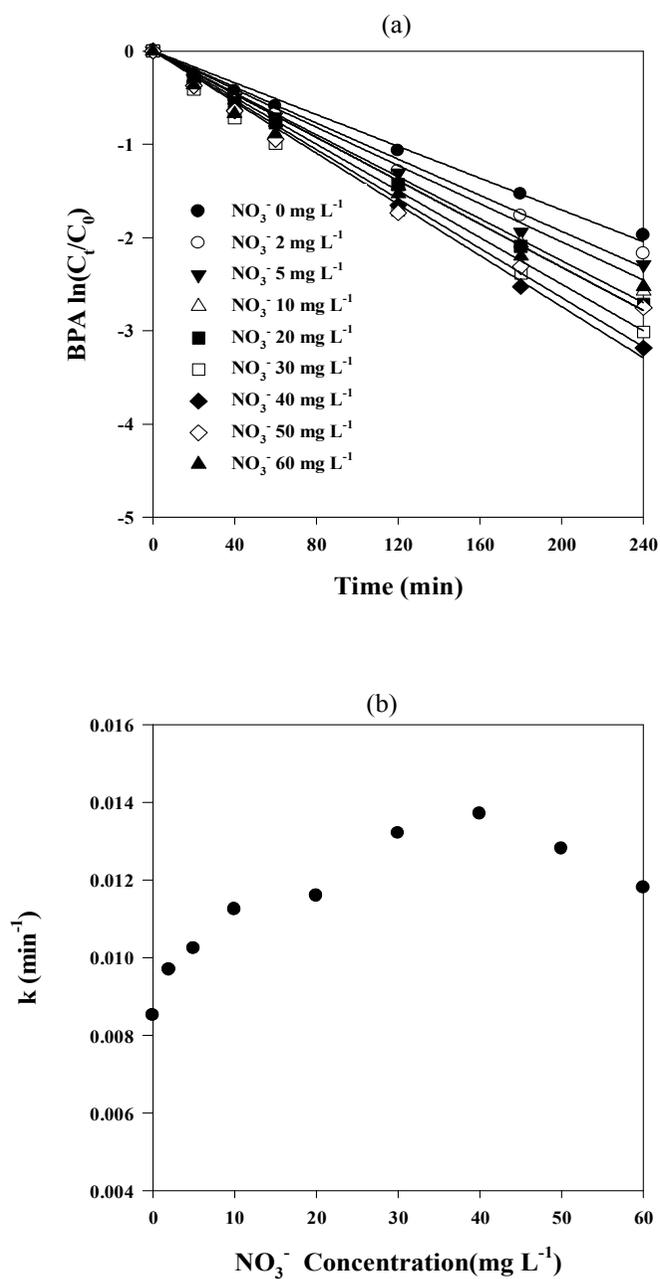


Fig. 9. The pseudo-first-order rate constants for BPA (a) and apparent pseudo-first-order rate constants for BPA photodegradation (b) at different NO_3^- concentrations.

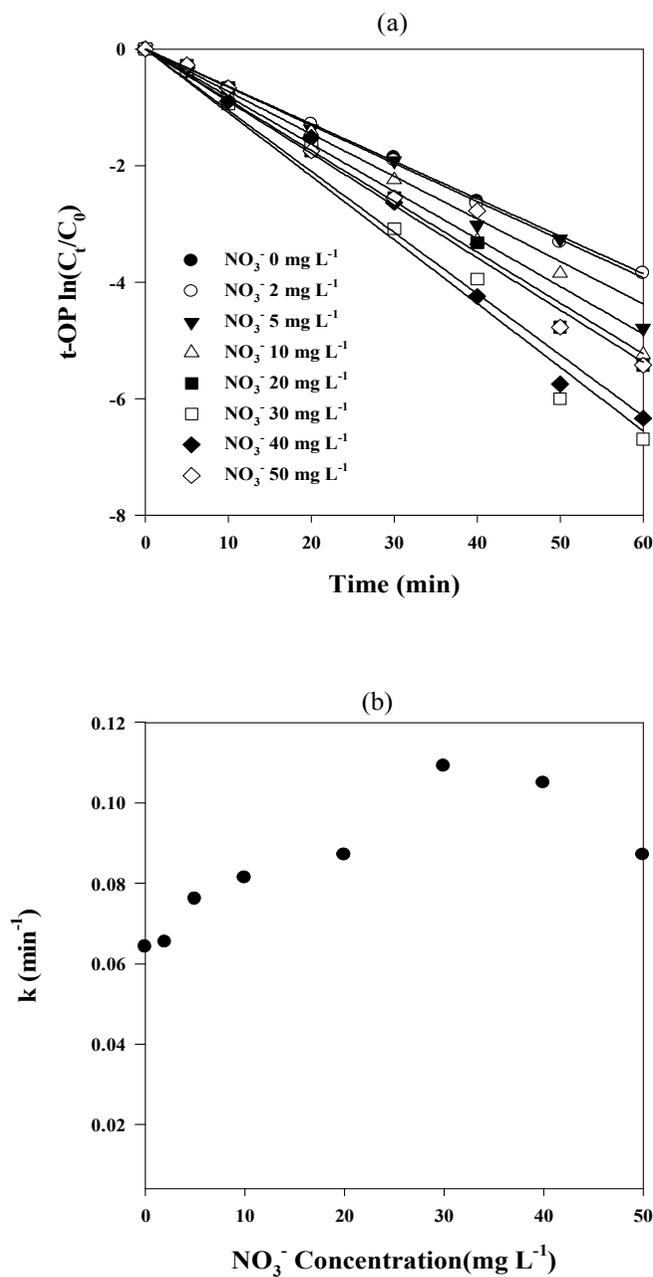
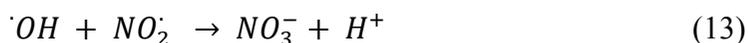
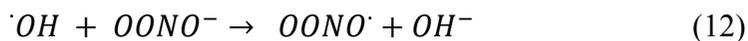


Fig. 10. The pseudo-first-order rate constants for t-OP (a) and apparent pseudo-first-order rate constants for t-OP photodegradation (b) at different NO_3^- concentrations.

It might be explained by those equation expressed below (Gonzalez and Braun 1995; Mark et al. 1996; Mack and Bolton 1999).



OH radical reacts not only with BPA and t-OP but also with nitrate. It is, however, certain that an excess quantity of nitrate resulted in the pseudo-first-order rate constants decrease by scavenging of OH radical. Also light attenuation according to nitrate dosage might affect the decrease.

Although it is the source of radicals, nitrate existing higher than 40 mg L⁻¹ for BPA and 30 mg L⁻¹ for t-OP are inefficient for photodegradation. The result informed us of the possibility of nitrate as photolysis additive to remove EDCs and the negative effect of nitrate with excess of quantity.

5. Intermediates

Intermediates of BPA and t-OP generated during photolysis in solution with nitrate were studied using LC-MS/MS. In the HPLC analysis with flow injection the m/z 227 ion for BPA and the m/z 205 ion for t-OP were observed as the principal peak as shown Fig. 11 and Fig. 12, respectively.

Deprotonated form of BPA (m/z 227) is explained by characteristic cleavage of the O-H bond in the hydroxyl group and a fragment ion at m/z 212, resulting from a cleavage of one of the CH_3 groups is observed (Fig. 11). Also, deprotonated form of t-OP (m/z 205) is explained by characteristic cleavage of the O-H bond in the hydroxyl group and a fragment ion at m/z 113, indicating from a cleavage of one of the $\text{CH}_2\text{CC}_3\text{H}_9$ group (Fig. 12).

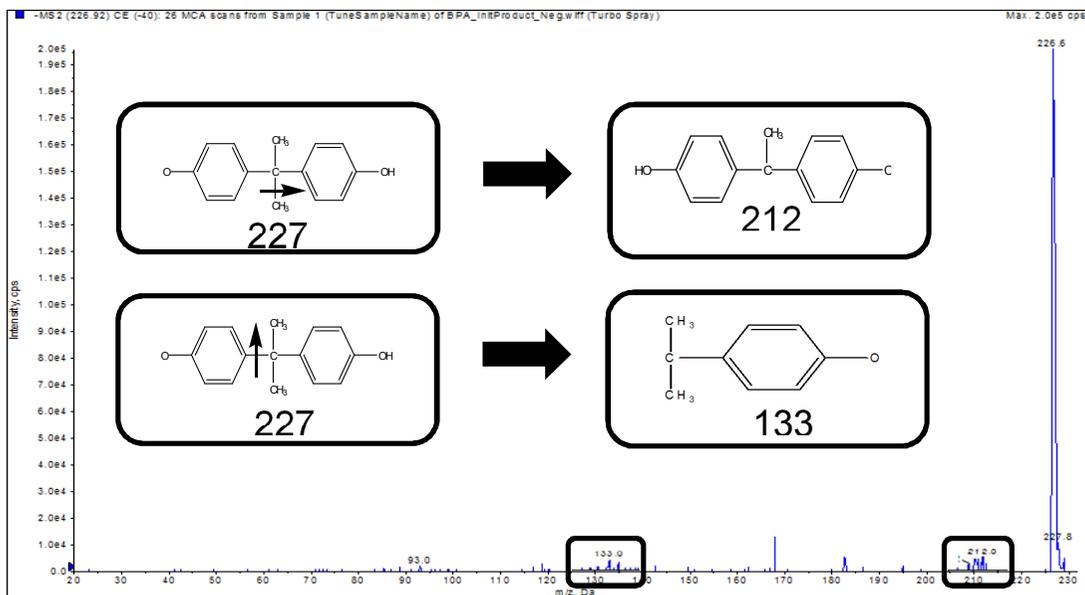


Fig. 11. LC/MS/MS spectrum of BPA.

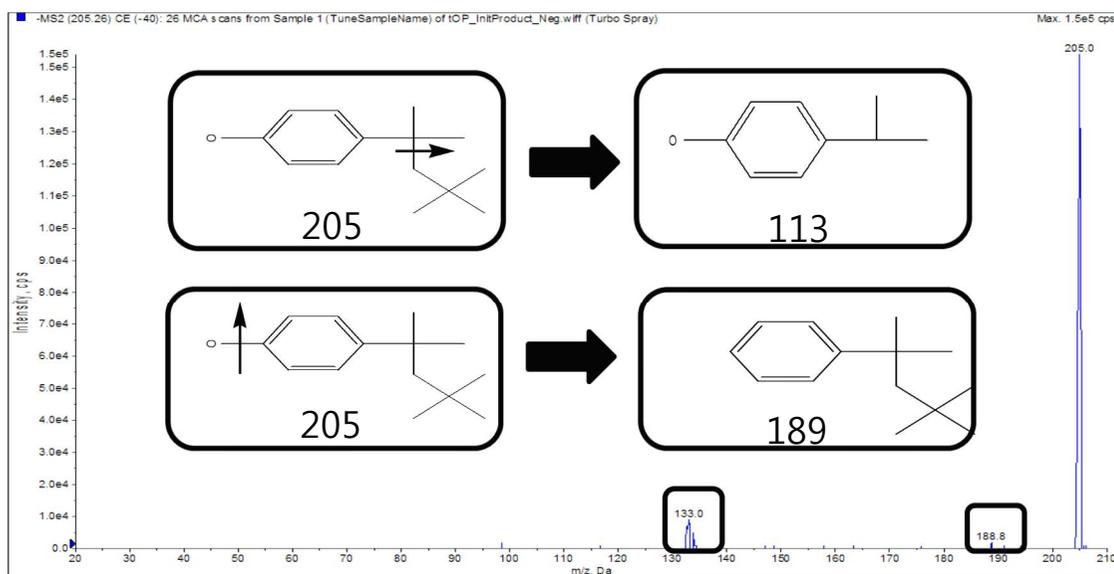


Fig. 12. LC/MS/MS spectrum of t-OP.

As Table 4 and 5 summarized, the retention time, ion pairs (m/z), and intermediates for BPA and t-OP were identified in negative ion mode (M-1) of LC-MS/MS. These intermediates were verified by interpretation of LC-MS/MS data obtained. For example, in Table 4 the first peak identified as 2-(4-hydroxyphenyl)-2-methylpropanal exhibits a parent peak at m/z 163 (M-1) with fragment ion peaks 134 (M-1-29) which is losses of CHO and 92 (M-1-29) which is losses of CCH_3CH_3CHO . Likewise, it is proposed that the second peak in Table 4 is 4-hydroxybenzaldehyde based on a parent peak at m/z 122 (M-1) with fragments at m/z 92 and 77. These fragments indicate the loss of CHO (M-1-29) and O CHO (M-1-45), respectively. Rests of intermediate are calculated by using the same calculation method.

Eight intermediates were identified at the BPA photodegradation with nitrate such as 2-(4-hydroxyphenyl)-2-methylpropanal, 4-hydroxybenzaldehyde, 1-(4-hydroxyphenyl)ethanone, 4-nitrophenol, 4-(2-(4-hydroxyphenyl)propan-2-yl)benzene-1,2-diol, 4-(2-nitropropan-2-yl)phenol, 4-(2-(4-hydroxy-3-nitrophenyl)propan-2-yl)benzene-1,2-diol, and 4-(2-(4-hydroxy-3-nitrophenyl)propan-2-yl)phenol.

In the case of t-OP, five intermediates were detected at the t-OP photolysis with nitrate such as 1-(4-hydroxyphenyl)ethanone, 3-(4-hydroxyphenyl)but-3-en-2-one, 4-(4-methylpenta-1,4-dien-2-yl)phenol, 2-(3,4-dihydroxyphenyl)2,4,4-trimethylpentan-3-one, and 4-(2,4,4-trimethylpentan-2-yl)benzene-1,2-diol.

Table 7. Structures and mass spectral data for BPA and postulated transformation products, as determined from LC/MS/MS

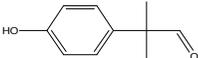
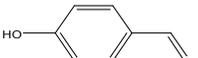
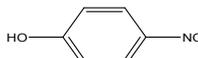
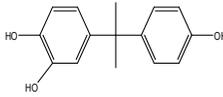
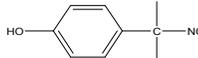
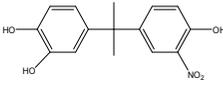
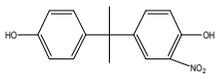
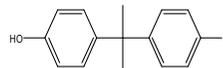
Peak	Retention Time (min)	Molecular Weight	ESI(-) MS, m/z	ESI (-) MS/MS, m/z	Possible Intermediates
1	1.51	164	163	134, 92	
2	2.17	122	121	92, 77	
3	2.31	136	135	92, 104	
4	2.65	139	138	122, 77	
5	2.99	244	243	226, 228, 150	
6	3.08	181	180	134, 92	
7	3.31	289	288	242, 150, 225	
8	4.04	273	272	226, 134, 209	
9	4.26	228	227	212, 133	

Table 8. Structures and mass spectral data for t-OP and postulated transformation products, as determined from LC/MS/MS

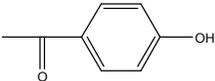
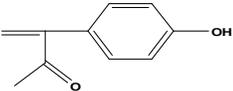
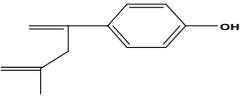
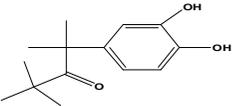
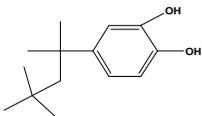
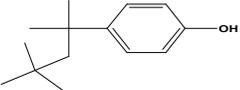
Peak	Retention Time (min)	Molecular Weight	ESI(-) MS, <i>m/z</i>	ESI (-) MS/MS, <i>m/z</i>	Possible Intermediates
1	1.25	136	135	92, 77	
2	2.02	162	161	146, 92, 77	
3	2.90	174	173	159, 132, 92	
4	4.27	236	235	178, 150	
5	4.57	222	221	205, 150	
6	5.00	206	205	113, 189	

Fig. 13 shows the formation and decomposition of the BPA photodegradation intermediates by chromatogram peak. Since the peaks 5, 7, and 8 are formed prevailing over the other intermediates formation until 200 min of reaction time, indicating that $\cdot\text{OH}$ or $\text{NO}_2\cdot$ generated by nitrate were added to BPA in the earlier stage of the reaction. With further increase of reaction time, however, the peaks 5, 7, and 8 decomposed to smaller molecular.

Also, the formation and decomposition of the t-OP photodegradation intermediates are shown in Fig. 14. The OH radical added intermediates, peak 4 and 5, were appeared and disappeared in the early stage of reaction. As time goes far smaller molecular such as peak 1, 2, and 5 were formed. Since t-OP has bigger quantum yield than BPA, the time taking to decompose to smaller molecular was shorter than BPA. The nitro-intermediates were not identified at photodegradation of t-OP. This reason why nitro-intermediates were not found in t-OP photolysis could not find out in the present state. Therefore, further study should be conducted.

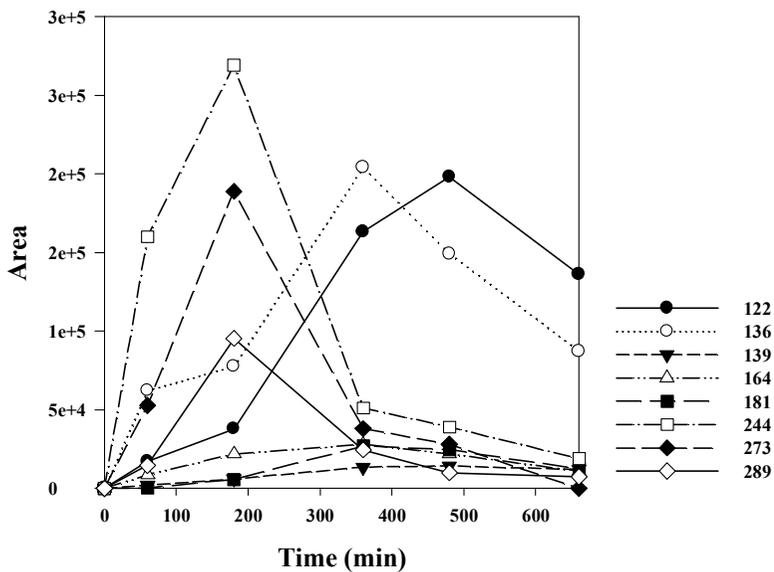


Fig. 13. BPA intermediates products change during photolysis.

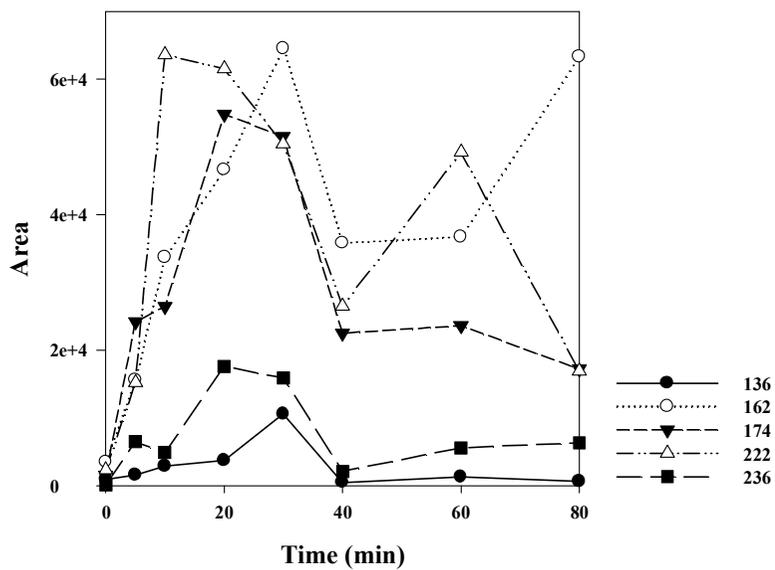


Fig. 14. t-OP intermediates products change during photolysis.

It is notable that the nitrate induced the formation of intro-intermediates such as peak 4, 6, 7 and 8 in BPA photolysis. Since nitrate is the one of the principle components in natural water, nitro-intermediates are inevitable degradation product for BPA photolysis not only photo-treatment process but also in the environment. Therefore, it is important to investigate how intro-intermediates are generated and how they are toxic when BPA is degraded in the presence with nitrate.

In order to know more detail about the degradation behavior of BPA with NO_2^\bullet in water, the degradation of BPA at $\text{H}_2\text{O}_2/\text{UVC}$ process which generates relatively much high amount of $^\bullet\text{OH}$ was conducted and compared to NO_3^-/UVC process. Intermediates such as peak 1, 3, 4 and 6 were also found in $\text{H}_2\text{O}_2/\text{UVC}$ process but the nitro-intermediates were not detected in $\text{H}_2\text{O}_2/\text{UVC}$. Therefore, It was conformed that nitrate induced the formation of intro-intermediates. When BPA was degraded by NO_3^-/UVC , the formation of added intermediates and decomposition into smaller molecular showed a time lag (Fig. 13). Since NO_3^- quantum yields of OH ($\Phi_{\text{OH}}=0.09$) and NO_2^- ($\Phi_{\text{NO}_2^-}=0.1$) were small (Mark et al. 1996), it took a few time to decomposed into smaller molecular intermediates from added intermediates. At $\text{H}_2\text{O}_2/\text{UVC}$ process, however, most of intermediates were produced and decomposed at the similar time (Fig.14) because of its high productivity of OH radical ($\Phi_{\text{OH}}=1.17$) (Goldstein et al. 2007).

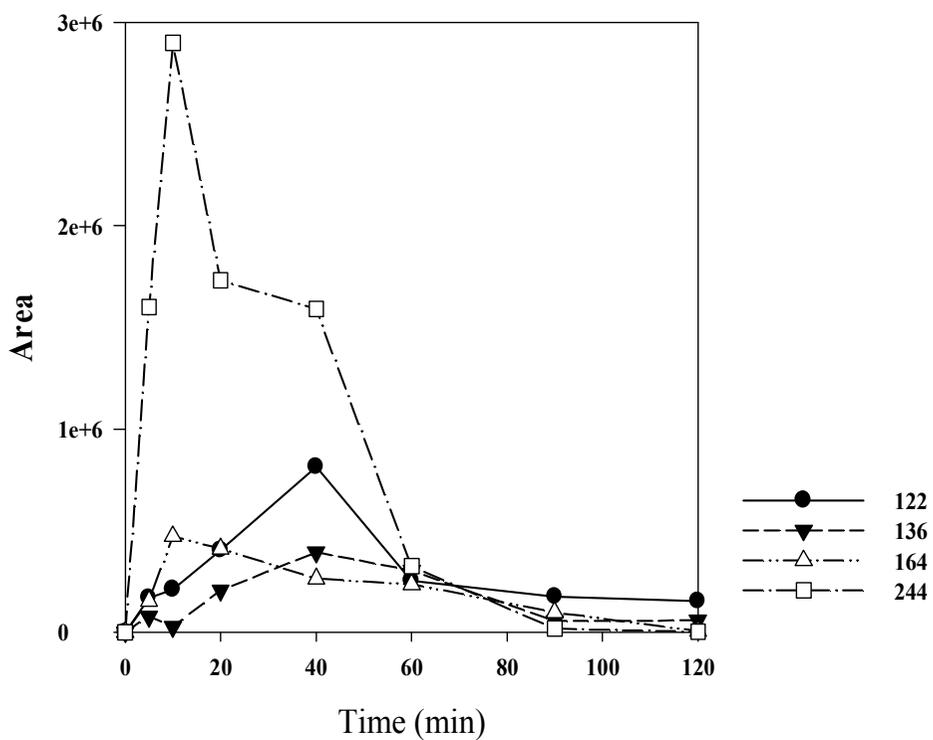


Fig. 15. Intermediates products change during BPA photolysis with H₂O₂.

Fig. 15 illustrates the proposed mechanism of BPA photolysis at $\text{H}_2\text{O}_2/\text{UVC}$ and at NO_3/UVC based on the results so far. It seems like that the degradation of BPA at NO_3/UVC process involves all of the mechanism as suggested time sequencing in Fig. 15 but BPA might be degraded in the path peak 5 and then 1 eventually peak 2 and 3 in $\text{H}_2\text{O}_2/\text{UVC}$ process.

Fig. 16 illustrates the proposed mechanism of t-OP photolysis at NO_3/UVC based on the result. The degradation pattern is different from BPA because it has no nitro-intermediates. Therefore, it is suspected that the nitrate does not affect t-OP photolysis products.

The estrogen activity of BPA photolysis intermediates of peak 3 and 8 are approximately 10 and 100 times less than BPA (Nakagawa and Suzuki 2001; Chen et al. 2002). However, the acute toxicity of LD_{50} dermal of peak 1 and 5 are 6 and 3 time higher than BPA (MSDS 2012). The other intermediates are not studied about their toxicity or estrogen activity. Therefore, further study should be conducted to ascertain the toxicity of the other intermediates for the efficient mineralization of BPA and t-OP.

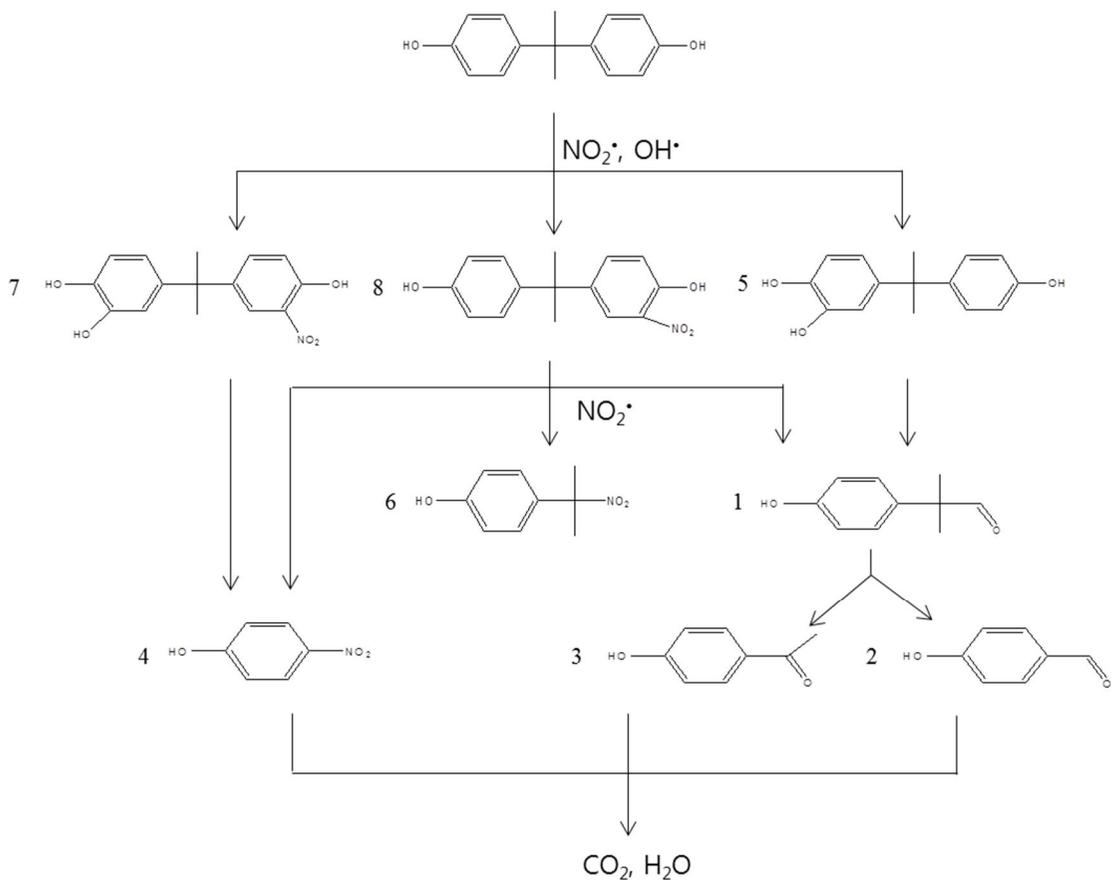


Fig. 16. The proposed photodegradation reaction pathway of BPA in NO_3^-/UVC process.

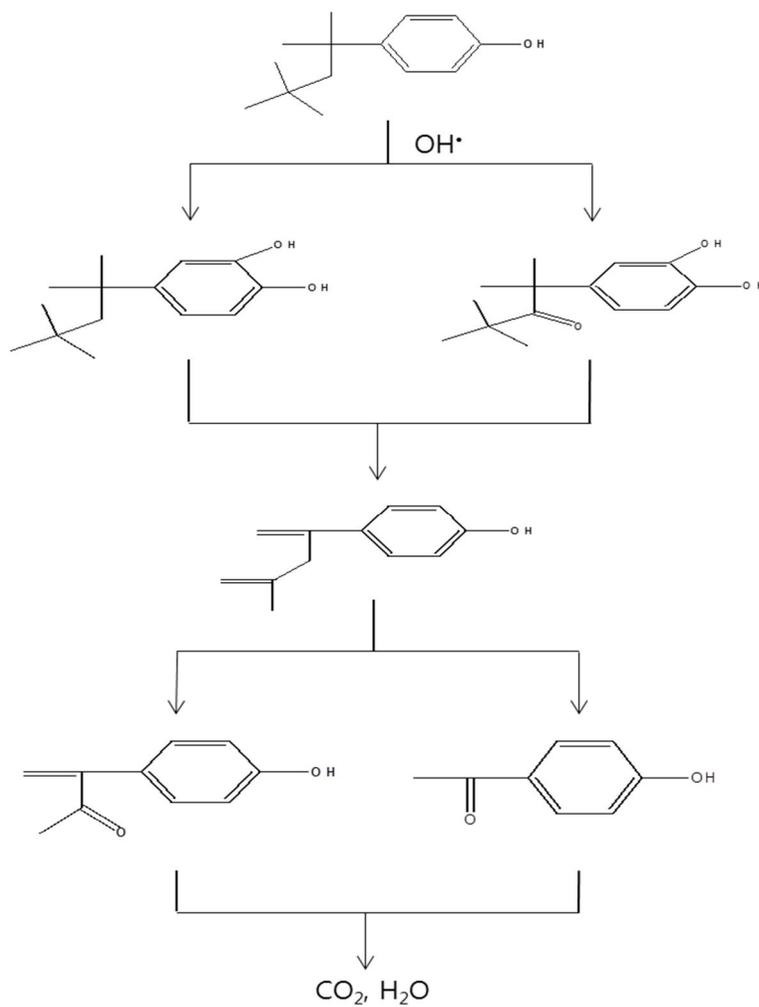


Fig. 17. The proposed photodegradation reaction pathway of t-OP in NO_3^-/UVC process.

IV. Conclusions

This paper investigated the effects of initial concentration, UV intensity, solution pH, and nitrate dosage on photodegradation of BPA and t-OP in a circulating photo reactor system with UV-C (254 nm) lamp. All photodegradation kinetics were well fitted to pseudo-first-order reaction. The higher initial concentration caused low degradation efficiency of BPA and t-OP probably because of its complete absorption of the incident photon flux by higher initial t-OP concentration and scattering effect. The stronger UV intensity led the pseudo-first-order rate constants (k_1) of BPA and t-OP to increase by making more chemical moved like $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$. The BPA and t-OP quantum yield was estimated to be 0.0354 and 0.409 mol Einstein⁻¹, respectively. It is notable that photodegradation of BPA and t-OP were enhanced remarkably when pH solution was higher than its pK_a. Nitrate in photolysis of BPA and t-OP increased the pseudo-first-order rate constants due to its availability of generating OH and NO₂ radicals. Intermediates in the photolysis of BPA and t-OP were identified by using LC/MS/MS. Photolysis of BPA in UV/H₂O₂ and UV/NO₃⁻ process, intermediates were found to be 4-hydroxybenzaldehyde, 1-(4-hydroxyphenyl) ethanone, 2-(4-hydroxyphenyl)-2-methylpropanal, and 4-(2-(4-hydroxyphenyl)propan-2-yl)benzene-1,2-diol in common. Interestingly, however,

4-nitrophenol, 4-(2-nitropropan-2-yl)phenol, 4-(2-(4-hydroxy-3-nitrophenyl)propan-2-yl)-benzene-1,2-diol, and 4-(2-(4-hydroxy-3-nitrophenyl)propan-2-yl)phenol were only identified in UV/NO₃⁻ process. In photolysis of t-OP with NO₃⁻ process five intermediates were identified such as 1-(4-hydroxyphenyl)ethanone, 3-(4-hydroxyphenyl)but-3-en-2-one, 4-(4-methylpenta-1,4-dien-2-yl)phenol, 2-(3,4-dihydroxyphenyl)-2,4,4-trimethylpentan-3-one, and 4-(2,4,4-trimethylpentan-2-yl)benzene-1,2-diol without nitro-intermediates.

In this paper the interaction effects of each influencing factor are not studied. As discussed in direct photodegradation section, it seems to have relative each influencing factor. Therefore, further research about each factors on BPA and t-OP photolysis are required.

These results can be helpful to understand the kinetics and removal mechanism of BPA and t-OP photodegradation in the water.

References

Ahmed, S. (2004) Photo electrochemical study of ferrioxalate actinometry at a glassy carbon electrode. *Journal of Photochemistry and Photobiology A: Chemistry* 161(2-3), 151-154.

Andreozzi, R., Caprio, V., Insola, A. and Marotta, R. (1999) Advanced oxidation processes (AOP) for water purification and recovery. *Catalysis today* 53(1), 51-59.

Beck, I.C., Bruhn, R., Gandrass, J. and Ruck, W. (2005) Liquid chromatography–tandem mass spectrometry analysis of estrogenic compounds in coastal surface water of the Baltic Sea. *Journal of Chromatography A* 1090(1), 98-106.

BŁĘDZKA, D., Gryglik, D. and Miller, J.S. (2009) Photolytic degradation of 4-tert-octylphenol in aqueous solution. *Environment Protection Engineering* 35(3), 235-247.

Chen, M.Y., Ike, M. and Fujita, M. (2002) Acute toxicity, mutagenicity, and estrogenicity of bisphenol-A and other bisphenols. *Environmental toxicology* 17(1), 80-86.

Chen, P.J., Linden, K.G., Hinton, D.E., Kashiwada, S., Rosenfeldt, E.J. and Kullman, S.W. (2006) Biological assessment of bisphenol A degradation in water following direct photolysis and UV advanced oxidation. *Chemosphere* 65(7), 1094-1102.

Chen, P.J., Rosenfeldt, E.J., Kullman, S.W., Hinton, D.E. and Linden, K.G. (2007) Biological assessments of a mixture of endocrine disruptors at environmentally relevant concentrations in water following UV/H₂O₂ oxidation. *Science of the Total Environment* 376(1), 18-26.

Cheng, R., Qi, D., Dong, W. and Wang, J. (2010) Effect of nitrate on degradation of pentachlorophenol in water with iron nanoparticles. *Journal of Tsinghua University Science and Technology* 50(6), 877-880.

Clara, M., Kreuzinger, N., Strenn, B., Gans, O. and Kroiss, H. (2005) The solids retention time--a suitable design parameter to evaluate the capacity of

wastewater treatment plants to remove micropollutants. *Water research* 39(1), 97-106.

Dekant, W. and Völkel, W. (2008) Human exposure to bisphenol A by biomonitoring: methods, results and assessment of environmental exposures. *Toxicology and applied pharmacology* 228(1), 114-134.

Drewes, J.E., Hemming, J., Ladenburger, S.J., Schauer, J. and Sonzogni, W. (2005) An assessment of endocrine disrupting activity changes during wastewater treatment through the use of bioassays and chemical measurements. *Water environment research* 77(1), 12-23.

Fernandez, M.P., Ikonomou, M.G. and Buchanan, I. (2007) An assessment of estrogenic organic contaminants in Canadian wastewaters. *Science of the Total Environment* 373(1), 250-269.

Gonzalez, M. and Braun, A. (1995) VUV photolysis of aqueous solutions of nitrate and nitrite. *Research on chemical intermediates* 21(8), 837-859.

Hatchard, C. and Parker, C. (1956) A new sensitive chemical actinometer. II. Potassium ferrioxalate as a standard chemical actinometer. *Proceedings of the*

Royal Society of London. Series A. Mathematical and Physical Sciences
235(1203), 518-536.

Hohenblum, P., Gans, O., Moche, W., Scharf, S. and Lorbeer, G. (2004)
Monitoring of selected estrogenic hormones and industrial chemicals in
groundwaters and surface waters in Austria. *Science of the Total Environment*
333(1-3), 185-193.

Im, J.K., Cho, I.H., Kim, S.K. and Zoh, K.D. (2011) Optimization of
carbamazepine removal in O₃/UV/H₂O₂ system using a response surface
methodology with central composite design. *Desalination*.

Irmak, S., Erbatur, O. and Akgerman, A. (2005) Degradation of 17β-estradiol
and bisphenol A in aqueous medium by using ozone and ozone/UV techniques.
Journal of hazardous materials 126(1), 54-62.

Ito, M. (2008) Occurrence and fate of estrogen and androgen in municipal
wastewater treatment by combination of chemical analyses and bioassay. Master
essay Osaka: Osaka City University.

Jacobs, L.E., Weavers, L.K., Houtz, E.F. and Chin, Y.P. (2011) Photosensitized degradation of caffeine: Role of fulvic acids and nitrate. *Chemosphere*.

Jin, J., El-Din, M.G. and Bolton, J.R. (2010) Assessment of the UV/Chlorine process as an advanced oxidation process. *Water research*.

Jung, Y.J., Kim, W.G., Yoon, Y., Kang, J.W., Hong, Y.M. and Kim, H.W. (2012) Removal of amoxicillin by UV and UV/H₂O₂ processes. *Science of the Total Environment*.

Kamoshita, M., Kosaka, K., Endo, O., Asami, M. and Aizawa, T. (2010) Mutagenic activities of a chlorination by-product of butamifos, its structural isomer, and their related compounds. *Chemosphere* 78(4), 482-487.

Katsumata, H., Kawabe, S., Kaneco, S., Suzuki, T. and Ohta, K. (2004) Degradation of bisphenol A in water by the photo-Fenton reaction. *Journal of Photochemistry and Photobiology A: Chemistry* 162(2), 297-305.

Koch, E. (1993) *Global Trend 93/94*. Fischer Taschenbuchverlag, Frankfurt 305.

Körner, W., Bolz, U., Süßmuth, W., Hiller, G., Schuller, W., Hanf, V. and Hagenmaier, H. (2000) Input/output balance of estrogenic active compounds in a major municipal sewage plant in Germany. *Chemosphere* 40(9-11), 1131-1142.

Kosky, P.G., Silva, J.M. and Guggenheim, E.A. (1991) The aqueous phase in the interfacial synthesis of polycarbonates. Part 1. Ionic equilibria and experimental solubilities in the BPA-sodium hydroxide-water system. *Industrial & Engineering Chemistry Research* 30(3), 462-467.

Kuch, H.M. and Ballschmiter, K. (2001) Determination of endocrine-disrupting phenolic compounds and estrogens in surface and drinking water by HRGC-(NCI)-MS in the picogram per liter range. *Environmental science & technology* 35(15), 3201-3206.

Laganà, A., Bacaloni, A., De Leva, I., Faberi, A., Fago, G. and Marino, A. (2004) Analytical methodologies for determining the occurrence of endocrine disrupting chemicals in sewage treatment plants and natural waters. *Analytica Chimica Acta* 501(1), 79-88.

Lam, M.W., Tantuco, K. and Mabury, S.A. (2003) PhotoFate: A new approach in accounting for the contribution of indirect photolysis of pesticides and

pharmaceuticals in surface waters. *Environmental science & technology* 37(5), 899-907.

Leusch, F.D.L., Chapman, H.F., van den Heuvel, M.R., Tan, B.L.L., Gooneratne, S.R. and Tremblay, L.A. (2006) Bioassay-derived androgenic and estrogenic activity in municipal sewage in Australia and New Zealand. *Ecotoxicology and environmental safety* 65(3), 403-411.

Lin, Y.J., Teng, L.S., Lee, A. and Chen, Y.L. (2004) Effect of photosensitizer diethylamine on the photodegradation of polychlorinated biphenyls. *Chemosphere* 55(6), 879-884.

Lintelmann, J., Katayama, A., Kurihara, N., Shore, L. and Wenzel, A. (2003) Endocrine disruptors in the environment. *Pure and Applied Chemistry* 75(5), 631-681.

Liu, Z., Kanjo, Y. and Mizutani, S. (2009) Removal mechanisms for endocrine disrupting compounds (EDCs) in wastewater treatment--physical means, biodegradation, and chemical advanced oxidation: A review. *Science of the Total Environment* 407(2), 731-748.

Lutz, I. and Kloas, W. (1999) Amphibians as a model to study endocrine disruptors: I. Environmental pollution and estrogen receptor binding. *The Science of the total environment* 225(1-2), 49-57.

Lyons, G. (1997) *Substances in the Marine Environment (SIME)*. World Wide Fund for Nature.

Mack, J. and Bolton, J.R. (1999) Photochemistry of nitrite and nitrate in aqueous solution: a review. *Journal of Photochemistry and Photobiology A: Chemistry* 128(1-3), 1-13.

Mao, L., Meng, C., Zeng, C., Ji, Y., Yang, X. and Gao, S. (2011) The effect of nitrate, bicarbonate and natural organic matter on the degradation of sunscreen agent *p*-aminobenzoic acid by simulated solar irradiation. *Science of the Total Environment*.

Mark, G., Korth, H.G., Schuchmann, H.P. and von Sonntag, C. (1996) The photochemistry of aqueous nitrate ion revisited. *Journal of Photochemistry and Photobiology A: Chemistry* 101(2-3), 89-103.

Mazellier, P. and Leverd, J. (2003) Transformation of 4-tert-octylphenol by UV irradiation and by an H₂O₂/UV process in aqueous solution. *Photochem. Photobiol. Sci.* 2(9), 946-953.

MSDS (2012) Material Safety Data Sheet

<http://www.sigmaaldrich.com/catalog/DisplayMSDSContent.do>

Nakagawa, Y. and Suzuki, T. (2001) Metabolism of bisphenol A in isolated rat hepatocytes and oestrogenic activity of a hydroxylated metabolite in MCF-7 human breast cancer cells. *Xenobiotica* 31(3), 113-123.

Neamtu, M. and Frimmel, F.H. (2006) Degradation of endocrine disrupting bisphenol A by 254 nm irradiation in different water matrices and effect on yeast cells. *Water research* 40(20), 3745-3750.

Ning, B., Graham, N.J.D. and Zhang, Y. (2007) Degradation of octylphenol and nonylphenol by ozone-Part I: Direct reaction. *Chemosphere* 68(6), 1163-1172.

Peltonen, K., Zitting, A., Koskinen, H. and Itkonen, A. (1986) Free radicals form photodecomposition of bisphenol-A. *Photochemistry and photobiology* 43(5), 481-484.

Rivas, F.J., Encinas, A., Acedo, B. and Beltrán, F.J. (2009) Mineralization of bisphenol A by advanced oxidation processes. *Journal of Chemical Technology and Biotechnology* 84(4), 589-594.

Robinson, B.J. and Hellou, J. (2009) Biodegradation of endocrine disrupting compounds in harbour seawater and sediments. *Science of the Total Environment* 407(21), 5713-5718.

Rodriguez-Mozaz, S., Lopez de Alda, M.J. and Barceló, D. (2004) Monitoring of estrogens, pesticides and bisphenol A in natural waters and drinking water treatment plants by solid-phase extraction-liquid chromatography-mass spectrometry* 1. *Journal of Chromatography A* 1045(1-2), 85-92.

Rosenfeldt, E.J. and Linden, K.G. (2004) Degradation of endocrine disrupting chemicals bisphenol A, ethinyl estradiol, and estradiol during UV photolysis and advanced oxidation processes. *Environmental science & technology* 38(20), 5476-5483.

Schwarzenbach, R.P., Gschwend, P.M. and Imboden, D.M. (2003) *Environmental organic chemistry*, Wiley Online Library.

Sharpe, R.M. and Skakkebaek, N.E. (1993) Are oestrogens involved in falling sperm counts and disorders of the male reproductive tract? *The Lancet* 341(8857), 1392-1396.

Son, H.S., Im, J.K. and Zoh, K.D. (2009) A Fenton-like degradation mechanism for 1, 4-dioxane using zero-valent iron (Fe⁰) and UV light. *Water research* 43(5), 1457-1463.

Torres, R.A., Pétrier, C., Combet, E., Moulet, F. and Pulgarin, C. (2007) Bisphenol A mineralization by integrated ultrasound-UV-iron (II) treatment. *Environmental science & technology* 41(1), 297-302.

Ungnade, H.E. (1953) The effect of solvents on the absorption spectra of aromatic compounds. *Journal of the American Chemical Society* 75(2), 432-434.

Vethaak, A.D., Lahr, J., Schrap, S.M., Belfroid, A.C., Rijs, G.B.J., Gerritsen, A., de Boer, J., Bulder, A.S., Grinwis, G. and Kuiper, R.V. (2005) An integrated assessment of estrogenic contamination and biological effects in the aquatic environment of The Netherlands. *Chemosphere* 59(4), 511-524.

Wu, C. and Linden, K.G. (2010) Phototransformation of selected organophosphorus pesticides: Roles of hydroxyl and carbonate radicals. *Water research* 44(12), 3585-3594.

Ying, G.G., Williams, B. and Kookana, R. (2002) Environmental fate of alkylphenols and alkylphenol ethoxylates--a review. *Environment International* 28(3), 215-226.

국문초록

광분해를 이용한 비스페놀-A 와 4-tert-옥틸페놀의 분해속도와

메커니즘 연구

강영민

서울대학교 보건대학원

환경보건학과 환경보건 전공

지도교수 조 경덕

내분비장애물질(endocrine disrupting compounds)로 알려진 비스페놀-A와 4-tert-옥틸페놀은 기존 하·폐수처리장에 분해효율이 낮고, 인체에 들어와 유방암, 경련, 그리고 고환암 등의 건강영향을 일으키기 때문에 시급한 처리가 필요하다. 광분해는 적절히 적용된다면 기존 처리방법과 달리 오염물을 완전히 무기화(mineralization) 시킬 수 있기 때문에 내분비계장애물질처리에 가장 적합한 처리 방법이다. 하지만 분해에 영향을 미치는 인지와 분해중간체(intermediate)를 제대로 파악하지 않고 처리 공정에 도입하면 설계, 비용, 운전측면에서 문제가

야기될 수 있고, 심지어 방류시 본 물질보다 높은 독성 물질이 배출되어 생태계 뿐만 아니라 인간에도 해로운 영향을 미칠 수 있다.

따라서 본 연구의 목적은 초기농도, UV 강도, pH, 그리고 질산염 (NO_3^-)이 비스페놀-A 와 4-tert-옥틸페놀의 광분해의 속도에 미치는 영향과 분해부산물을 규명하는 것이다.

비스페놀-A 의 초기농도가 $2 - 40 \text{ mg L}^{-1}$ 그리고 4-tert-옥틸페놀의 초기농도가 $0.5 - 5 \text{ mg L}^{-1}$ 로 증가함에 따라 비스페놀-A 와 4-tert-옥틸페놀의 유사일차속도상수(k_1)는 각각 8.5×10^{-3} 에서 $3.7 \times 10^{-3} \text{ min}^{-1}$ 으로 그리고 7.72×10^{-2} 에서 $3.28 \times 10^{-2} \text{ min}^{-1}$ 으로 감소하였다. UV 강도가 3.65×10^{-5} 에서 $9.68 \times 10^{-5} \text{ Einstein L}^{-1} \text{ min}^{-1}$ 로 증가함에 따라 더 많은 유기물이 $\pi \rightarrow \pi^*$ 혹은 $n \rightarrow \pi^*$ 상태가 되어 비스페놀-A 의 일차속도상수는 5.74×10^{-3} 에서 $14.50 \times 10^{-3} \text{ min}^{-1}$ 으로 그리고 4-tert-옥틸페놀은 5.06×10^{-2} 에서 $12.07 \times 10^{-2} \text{ min}^{-1}$ 증가되었다. 두 물질은 비슷한 흡광도를 가졌지만 비스페놀-A 와 4-tert-옥틸페놀의 quantum yield 는 각각 0.035 와 $0.409 \text{ mol Einstein}^{-1}$ 이었다. 비스페놀-A 와 4-tert-옥틸페놀의 광분해는 용액의 pH 를 유기오염물의 pKa (비스페놀-A(10.2) 4-tert-옥틸페놀(10.33))보다 높게 조절함에 따라 상당히 상승하였다. 이는 비결합 전자가 공명에 의해 π -system 의 길이를 증가시킨 결과 흡광도가 증가된 결과이다. 질산염은 빛과 반응하여 OH 와 NO_2 라디칼을 발생시켜 유기오염물의 광분해를 빠르게 하였다. 하지만 일정량 이상이 첨가되면 일차속도상수는 오히려 점차적으로 감소하였다. LC/MS/MS 를 이용한 분해부산물 검출결과 질산염이 공존하는 광분해에서 비스페놀-A 는 8 개의 분해부산물이, 4-

tert-옥틸페놀은 5 개의 분해부산물이 검출되었다. 질산염은 비스페놀-A 의 광분해에서 nitro-intermediate 발생을 유발하였다. 반면, 4-tert-옥틸페놀은의 광분해에서 질산염은 nitro-intermediate 를 발생하지 않았다.

본 연구는 하·폐수처리장과 질산염이 들어있는 자연수의 광분해에 의한 비스페놀-A 와 4-tert-옥틸페놀의 광분해속도와 분해 메커니즘을 이해하는데 도움이 될 것이다.

주요어: 광분해, 질산염, pH, 분해중간체, 부산물, 라디칼, nitro-intermediate

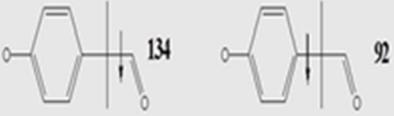
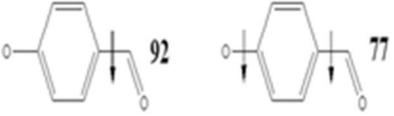
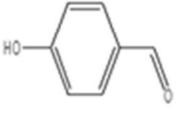
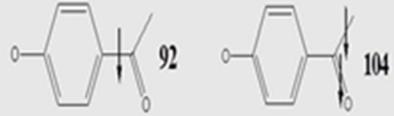
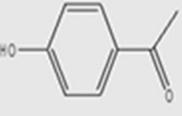
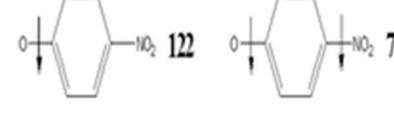
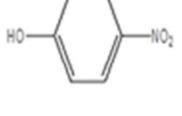
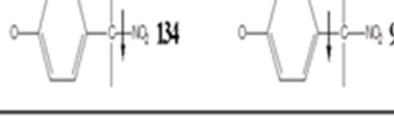
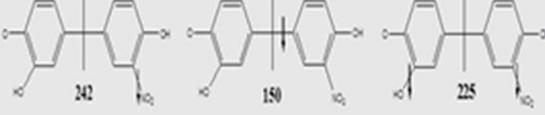
학번: 2010-23779

Appendix

t-OP calculation method determined from LC/MS/MS

Retention Time	Molecular Weight	Single MS	MS / MS Fragment	The way how to being calculated	Possible Intermediate
1.25	136	135	92, 77	 92 77	
2.02	162	161	146, 92, 77	 146 92 77	
2.90	174	173	159, 132, 92	 159 132 92	
4.57	236	235	178, 150	 178 150	
4.27	222	221	205, 150	 205 150	
5.00	206	205	113, 189	 113 189	

BPA calculation method determined from LC/MS/MS

Retention Time	Molecular Weight	Single MS	MS / MS Fragment	The way how to being calculated	Possible Intermediate
1.51	164	163	134, 92		
2.17	122	121	92, 77		
2.31	136	135	92, 104		
2.65	139	138	122, 77		
2.99	244	243	226, 228, 150		
3.08	181	180	134, 92		
3.31	289	288	242, 150, 225		
4.04	273	272	226, 134, 209	