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Degradation kinetics and mechanism of bisphenol A in vacuum ultraviolet photolysis

진공자외선 공정에서의 비스페놀 A의 분해 특성과 메커니즘에 관한 연구

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최예림

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Abstract

Degradation kinetics and mechanism of bisphenol A in vacuum ultraviolet photolysis

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Bisphenol A (BPA) is a compound classified as an EDC that is mainly used for the production of polycarbonates and epoxy resins. In this study, the kinetics and degradation mechanism of BPA during vacuum ultraviolet (VUV) treatment were examined. BPA was completely degraded within 60 minutes of VUV treatment, following the pseudo-first-order kinetics (k_{obs} = 6.75 × 10^{-2} min^{-1}). The degradation kinetics of one the BPA alternatives, BPAF, was observed in parallel for the comparison with BPA. The k_{obs} of BPAF was 5.49 × 10^{-2} min^{-1} which was slightly slower than that of BPA. The influencing factors on BPA degradation were observed at different pH levels, as well as the presence of dissolved organic matter (DOM) and inorganic anions, bicarbonate (HCO_3^-), and nitrate (NO_3^-). The k_{obs} of BPA was the fastest at pH 6.0 and it gradually decreased with the increasing pH. The radical contribution during VUV reaction was also observed using TBA for competition kinetics with BPA. It was found out that •OH contributed to 82.6%, 71.4%, 49.65%, and 43.36% at pH 6, 7, 8, and 9, respectively, which explains the retardation of k_{obs} with increasing pH. The influence of DOM and HCO_3^- were insignificant at low concentrations, whereas the presence of NO_3^- hindered BPA degradation. Approximately 91% of BPA was mineralized within 12 hours of VUV reaction, and

a total of seven organic transformation products were identified (TP 243, TP 241, TP 257, TP 259, TP 181, TP 104). The acute toxicity was observed by the inhibition rate of bioluminescence of *Vibrio fischeri*. The toxicity decreased about 20% after the reaction, indicating that VUV treatment could potentially diminish the toxicity of BPA.

Keywords: Bisphenol A; Endocrine Disrupting Compounds; VUV; degradation kinetics; byproducts; degradation pathway

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1. Introduction

1.1. Study Background

As the world's industrial market develops, the demand for the production of new materials also increases. As a consequence of increased demand for such materials, various chemicals are produced for manufacturing purposes (Muhamad et al., 2016). Due to such reasons, the chemicals that are used for manufacturing are introduced to the environment, in which the impact on the environment and the ecosystem may cause potential danger afterward. Even though the used chemicals undergo water treatment processes in wastewater treatment plants (WWTPs), some of the refractory chemicals are released to the environment without complete degradation. Numerous types of organic contaminants that are frequently detected in the environment include pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting compounds (EDCs), which are considered as contaminants of rising concern. Especially, the EDCs are the prime municipal driven contaminants released to the environment mainly through the discharge of industrial and municipal wastewater (Huang and Huang, 2009). When these contaminants are released to surface water without complete degradation, they may potentially pose detrimental effects not only on the aquatic ecosystem but also to humans (Ming et al., 2021; Qin et al., 2018; Kong et al., 2019).

Bisphenol A (BPA), one of the well-known EDCs, is widely used as a raw material for manufacturing purposes (Hunge et al., 2021) for the productions of polycarbonates, epoxy resins, polyesters, etc. (Allsop et al., 2019). BPA is used for the production of products that are used in everyday life, such as plastic cups and bottles, thermal papers, medical devices, vehicle parts, etc. (Muhamad et al., 2016). Every year, 5 million tonnes of BPA is produced, and it is reported that production increases every year (Vandenber et al., 2007). The problem is that BPA is detected at several μg L^{-1} levels to thousands of ng L^{-1} in sewage water treatment effluents and even in drinking water (Man et al., 2018; He et al., 2017; Fan et al., 2013; Zhang et al., 2019). It has been revealed that BPA potentially could cause neurotoxicity, cardiovascular disease, breast cancer, reproductive disorder (Rochester 2013;

Almeida et al., 2019). Ever since the detrimental effect of BPA has been reported, the use of BPA has been restricted as BPA alternatives were introduced.

As the restriction on BPA usage increased, the demand for BPA alternatives has increased in return. The BPA analogues include BPS, BPF, BPB, and etc. (Qiu et al., 2019), which are substituted in products that claim to be BPA free (Zhang et al., 2018). As the demand for BPA alternatives increased for BPA substitutes, they have been detected not only in water bodies but also in sediments. However, because the BPA alternatives have analogous molecular structure to that of BPA, the BPA analogues have similar endocrine disrupting property (Lu et al., 2019). Therefore, further studies on efficient degradation of such BPA alternatives need to be fulfilled. Among the BPs however, BPA has been and is still most frequently detected in various water sources in different countries (Table 1). Therefore, efficient removal of BPA in water is essential to reduce the risk on human health and aquatic ecosystems.

Even though several methods for organic pollutant treatment exist, including biological treatment, adsorption, and oxidation, these conventional treatment methods are not as effective as advanced oxidation processes (AOPs) (Du et al., 2016; Hunge et al., 2021;). AOP is an oxidative degradation technique that is efficient for removing refractory organic compounds (Gmurek et al., 2017). Ever since the introduction of AOP, it has been receiving much interest for its efficacy and practicality, especially the UV-based AOPs consist of a UV lamp and an oxidant is one of the best known AOPs (e.g., H_2O_2, $S_2O_8^{2-}$, etc.) (Chong et al., 2010; Wang et al., 2019a). In the UV/oxidant reaction, the UV photolysis converts the oxidant into highly reactive species, such as hydroxyl radical (•OH) and sulfate radical (•SO_4) that are in charge of target compound degradation (Hossaini et al., 2014). However, the so-called efficient photochemical processes need additional chemicals.

Among the aforementioned AOPs, vacuum ultraviolet (VUV) photolysis is considered as a green method that does not require additional chemicals as oxidants but still produces plenty of reactive species through activation of water molecules (Xie et al., 2018; Gonzalez et al., 2004). The VUV radiation covers wavelength from 100- 200 nm in which the photons homolyze and ionize water molecules to produce powerfully-oxidizing species; •OH, though Eq. (1) and (2) (Zoschke et al., 2014).

$$H_2O + hv_{185nm} \rightarrow \bullet\mathrm{OH} + \mathrm{H}\bullet \quad (1)$$

$$H_2O + hv_{185nm} \rightarrow \bullet\mathrm{OH} + \mathrm{H} + +e_{aq}^{-} \quad (2)$$

Even without additive chemicals and simple reaction equipment, the VUV process has the advantages of high efficiency for organic pollutants degradation (Imoberdorf and Mohseni, 2012; Wu et al., 2021). Hence, since the VUV treatment is a technology that does not require auxiliary chemical oxidant, it is considered as an environmentally sustainable process (Bagheri and Mohseni (2015)), which does not require post treatment of residual oxidant. Through VUV photolysis, organic pollutants are degraded rapidly, and the toxicity decrease was remarkable compared to other treatments such as chlorination (Yang et al., 2018; Wu et al., 2021). Previous studies of BPA degradation in the AOP are listed in Table 2.

Table 1. Occurrence of BPA in various water media (unit: ng L^{-1})

	Country	Concentration	Reference
Sewage water effluent	China	2,980	Sun et al. (2014)
	Australia	17 - 165	Ying et al (2016)
	France	109 - 791	Tran et al. (2015)
	USA	6.48 - 4700	Santos et al., (2016)
Surface water	South Korea	4.6 - 272	Yamazaki et al. (2015)
	Japan	ND - 431	Yamazaki et al. (2015)
	India	40 – 4,460	Chakraborty et al. (2021)
	Mexico	39.1 – 174.6	Calderón-Moreno et al. (2019)
Drinking water	China	34.9 - 128	Zhang et al. (2019); Fan et al. (2013)
	Malaysia	3.5 – 59.8	Santhi et al. (2012)
	Serbia	7.3	Čelić et al. (2020)

Table 2. Previous studies on degradation of BPA in AOP

Process	Kinetics	Removal %	Byproduct	Reference
UV/H_2O_2	O	89	X	Zhang and Li (2014)
VUV/H_2O_2	O	97.6	X	Moussavi et al. (2018)
VUV/PMS	O	96.7	O	Sharma et al. (2015)
Ozonation	O	-	O	Kusvuran and Yildirim (2013)
Granular Activated carbon(GAC)	X	100	X	Moura et al. (2018)

Objective

As mentioned earlier, numerous AOP methods for BPA removal have been carried out, but there are minimal studies on BPA using VUV treatment. Because of such unique property of the VUV process of producing reactive species through the activation of water molecules that are in charge of the pollutant degradation, more research needs to be fulfilled. Therefore, the main objective of this study is to not only observe the efficacy and performance of the VUV reaction on BPA degradation, but also figure out the impact of the degraded/ transformed BPA after the treatment.

2. Materials and methods

2.1. Chemicals

Bisphenol A (BPA, 99% ≥) and bisphenol AF (BPAF, analytical standard) were purchased from Sigma Aldrich (St. Louis, MO, USA), and the physicochemical properties are listed in Table 3. Potassium phosphate monobasic (NaH_2PO_4), humic acid, potassium phosphate dibasic (Na_2HPO_4), sodium bicarbonate ($NaHCO_3$), sodium nitrate ($NaNO_3$), and tert-butanol (TBA), were purchased from Sigma Aldrich (St. Louis, MO, USA). Acetonitrile was purchased from Thermo Fischer Scientific (Waltham, MA, USA) at HPLC grade, which was used as the mobile phase for HPLC analysis.

Table 3. Physicochemical property of bisphenol A

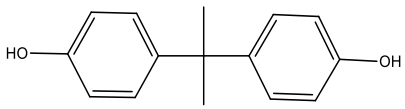
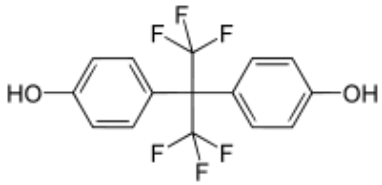
Structure	Properties	
	Chemical formula	$C_{15}H_{16}O_2$
	Molecular weight	228.29 g mol^{-1}
	Water solubility	120 mg L^{-1}

Table 4. Physicochemical property of bisphenol AF

Structure	Properties	
	Chemical formula	$C_{15}H_{10}F_6O_2$
	Molecular weight	336.233 g mol^{-1}
	Water solubility	240 mg L^{-1}

2.2. Experimental procedure

2.2.1. Degradation kinetics

The degradation kinetics of BPA in VUV photolysis was conducted using a dual jacketed batch type photo-reactor (600 mL) equipped with a 6-W low-pressure VUV mercury lamp (185 nm/254 nm, Sankyo Electric Co., Tokyo, Japan) (Figure 1.). All of the experiments were conducted in duplicate. The stock solutions were prepared by dissolving the chemicals in deionized water. The high stock BPA was prepared by dissolving powdered form of BPA, and it was kept in the dark and cold condition in the refrigerator.

For the removal kinetics, pH was first adjusted by spiking in 1M phosphate buffer into 600 mL of deionized water and stirring with a magnetic bar on a stirring plate. Then the BPA stock was spiked into the reactor to adjust to the initial concentration of 22 μM (5 mg L^{-1}). Finally, a VUV lamp was inserted into the batch reactor, in which the reaction started as soon as the lamp was ignited. The temperature of the reaction solution was maintained at 20.0 ± 0.1 ℃ during the reaction by circulating cooling water in the jacket to minimize the heat emitted from the UV lamp.

The influence of pH and the presence of inorganic anions and dissolved organic matter (DOM) on BPA degradation were observed during the VUV reaction. For the pH effect, pH was adjusted to 6, 7, 8, and 9 using phosphate buffer. Also, for the effect of water components, bicarbonate and nitrate ions were used as inorganic anions, and humic acid (HA) was used as DOM, at concentrations 0 mg L^{-1}, 1 mg L^{-1}, 10 mg L^{-1}, and 30 mg L^{-1}.

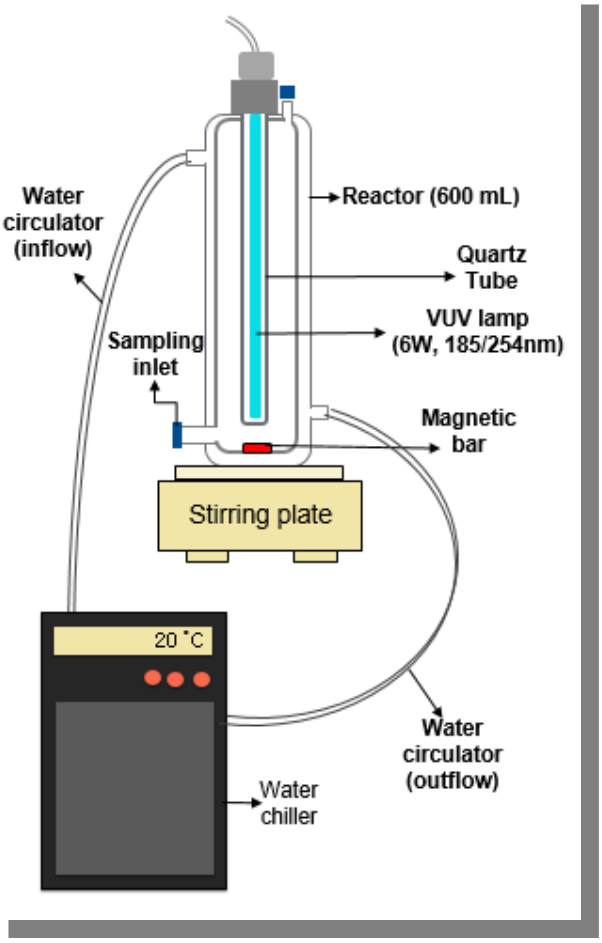


Figure 1. The schematic diagram of the batch type reactor system.

2.2.2. Toxicity test

Acute toxicity test was fulfilled to examine the change in toxicity of BPA after the VUV treatment using Microtox Model 500 Toxicity Analyzer. The luminescence intensity was measured using bioluminescent bacteria *Vibrio Fischeri*. For the experiment, the pH of the sample was not adjusted and VUV reaction was done with BPA concentration of 22 μM and the reaction time of 3 hours.

2.3. Analytical method

2.3.1. Analysis of BPA

BPA was analyzed using high-performance liquid chromatography (HPLC) (UltiMate- 3000, Dionex, Sunnyvale, CA, USA) equipped with a Luna C18 (2) column (2.0 mm × 150 mm i.d., 3-μm particles; Phenomenex, Torrance, CA, USA). The UV detector was set at 278 nm wavelength, and acetonitrile and deionized water were used as the mobile phases (A) and (B), with the flow rate of 0.8 mL min-1 in isocratic mode (A: B = 5:5). The injection volume was set to 100 μL, and the column was thermostated at 40 ℃.

2.3.2. Mineralization of BPA

Total organic carbon (TOC) was employed to observe the mineralization of BPA during the VUV process by using a TOC analyzer (TOC 5000, Shimadzu, Japan).

2.3.3. Analysis of transformation products (TPs)

In order to identify the organic transformation products (TPs) of BPA during the VUV reaction, ultra-performance liquid chromatography quadrupole time-of-flight mass spectrometry (UPLC-qTOF/MS) (Acquity UPLC Synapt G2-Si, Waters, USA) equipped with Waters Acquity UPLC BEH C18 column (2.1 mm × 100 mm, 1.7 μm). As for the HPLC condition, (A), acetonitrile, and (B) deionized water were used for the UPLC-qTOF/MS mobile phase. The flow rate was set to 0.3 mL min-1, and the samples were analyzed in the isocratic mode of 50% of (B), under negative ESI mode. After UPLC-qTOF/MS analysis, the data were analyzed with UNIFI software (Waters, Milford, MA, USA) to identify transformation products.

2.3.4. Radical contribution

The radical concentrations at each pH were determined using tertiary butanol (TBA) for the calculation of the contribution of •OH during VUV reaction. Since TBA is a •OH probe and reacts with •OH while it does not react with other radicals, the contribution of reactive species can be calculated using competition kinetics.

3. Results and discussion

3.1. Degradation kinetics of BPA during VUV photolysis

The degradation of BPA in VUV and UV-C photolysis is shown in Fig. 2, in which the VUV reaction was shown to be much more efficient than that of UV-C reaction. The BPA removal reached 99.5% removal within 1 hour while UV-C treatment reached only 15.4% removal given the same amount of time. Even though UV-C also contributed to slight BPA degradation, it requires a longer reaction time than the VUV reaction, which can be considered inefficient.

The degradation of BPA during VUV and UV-C photolysis reaction both followed the pseudo-first-order reaction kinetics (k_{obs}) of 6.71×10^{-2} min^{-1} (R^2 = 0.99), and 2.66×10^{-3} min^{-1} (R^2 = 0.99), respectively in the same condition at pH 7.0. The k_{obs} of VUV treatment was 25 times faster than the UV-C reaction. This may be because UV-C photolysis is not a radical mediated reaction, which does generate any reactive species. Rather, the 254 nm wavelength directly photolyzes the target compound with photons. Since the role of photons is minimal in BPA degradation, UV-C degradation may not have contributed to efficient BPA degradation. In contrast, the VUV reaction led to effective degradation of BPA via indirect oxidation by the formation of •OH via activation of water.

In order to compare the effectiveness of VUV treatment in BPA degradation, one of the BPA analogues, BPAF was compared in parallel in kinetic-wise. The degradation kinetics of BPAF is illustrated in figure 2b, in which the k_{obs}) of BPAF at pH 7.0 was 5.49×10^{-2} min^{-1} (R^2 = 0.99). Compared to BPA degradation at the same condition, BPAF tends to have slower degradation kinetics. Because BPAF has two trifluromethyl groups attached on the center of two phenols, it may have slower degradation efficiency compared to that of BPA. However, since BPA and BPAF have analogous molecular structures, they tend to have similar degradation kinetics.

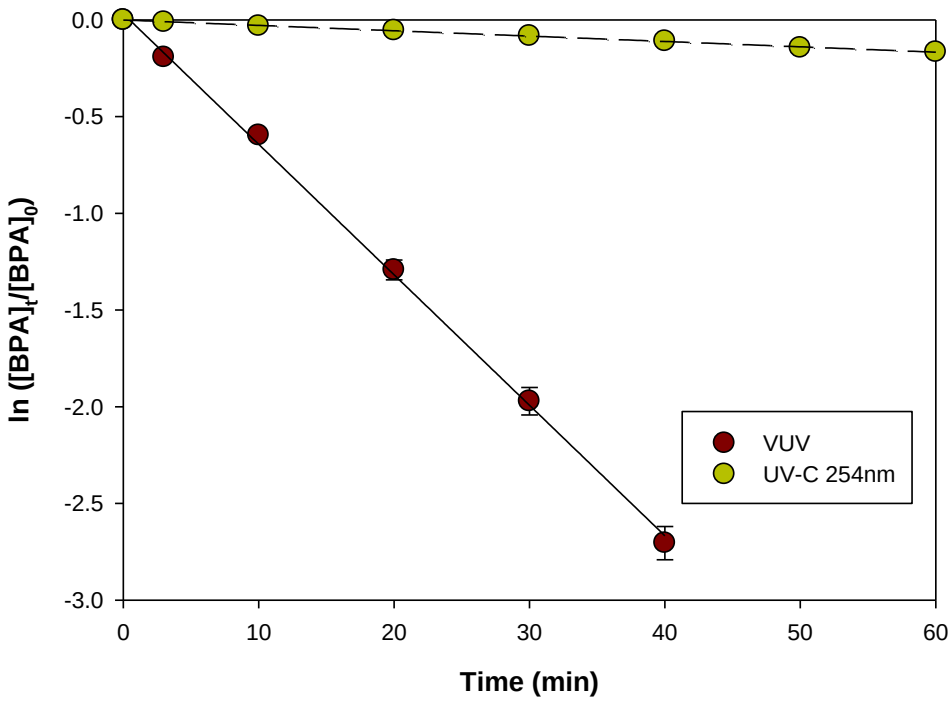


Figure 2a. Degradation kinetics of BPA by VUV and UV-C photolysis. ($[BPA]_0$ = 23 μM; pH = 7.0, (6 W), The error bars indicate standard deviation (SD) of duplicate experiments)

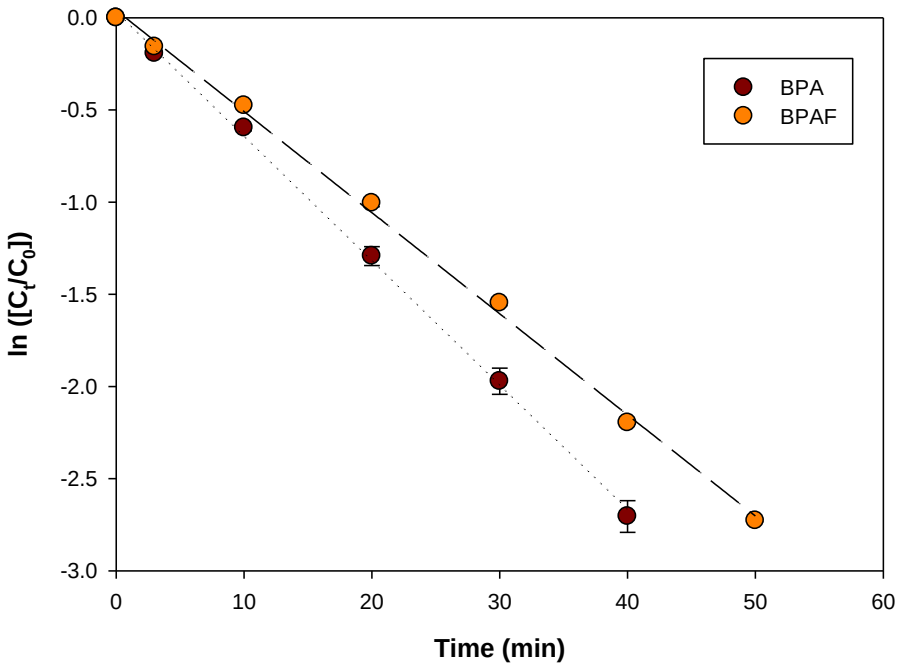


Figure 2b. Degradation kinetics comparison of BPA and BPAF during VUV treatment ($[BPA]_0 = [BPAF]_0 = 23$ μM; pH = 7.0, (6 W), The error bars indicate SD of duplicate experiments)

3.2. Influencing factors

In water treatment processes, numerous factors influence the removal of pollutants. Among those factors, the solution's pH, water components, and the temperature of water play significant roles in the target pollutant degradation. Therefore, it is necessary to observe the target compound degradation under various pH ranges and during the presence of inorganic anions and dissolved organic matters.

3.2.1. Effect of pH

For most cases, the pH of the solution often plays a significant impact on target compound degradation. The pH of the solution affects the oxidation potential and the production rate of •OH (Yang and Zhang 2019). The k_{obs} of BPA decreased as the pH of the solution increased from 6 to 9 (Fig. 3). The k_{obs} at pH 6 was the fastest, with the value of 8.76×10^{-2} min^{-1}. The k_{obs} gradually decreased to 5.08×10^{-2} min^{-1}

as the solution leaned to a more alkaline condition. Since the oxidation potential of •OH decreases from 2.59 V at pH 0 to 2.18V at pH 7, the removal efficiency has slowed down (Koppenol and Liebman (1984)). As a result, the k_{obs} of BPA declined due to a decrease in abundance of •OH, which played as the key factor in the retardation of BPA degradation.

According to a previous study of VUV degradation on organic pollutants, a higher production rate of H_2O_2 was observed under acidic conditions, which favored the production of •OH, following Eq. (3) (Yang et al. 2018).

$$H_2O_2 + hv \rightarrow 2 \bullet \mathrm{OH} \quad (3)$$

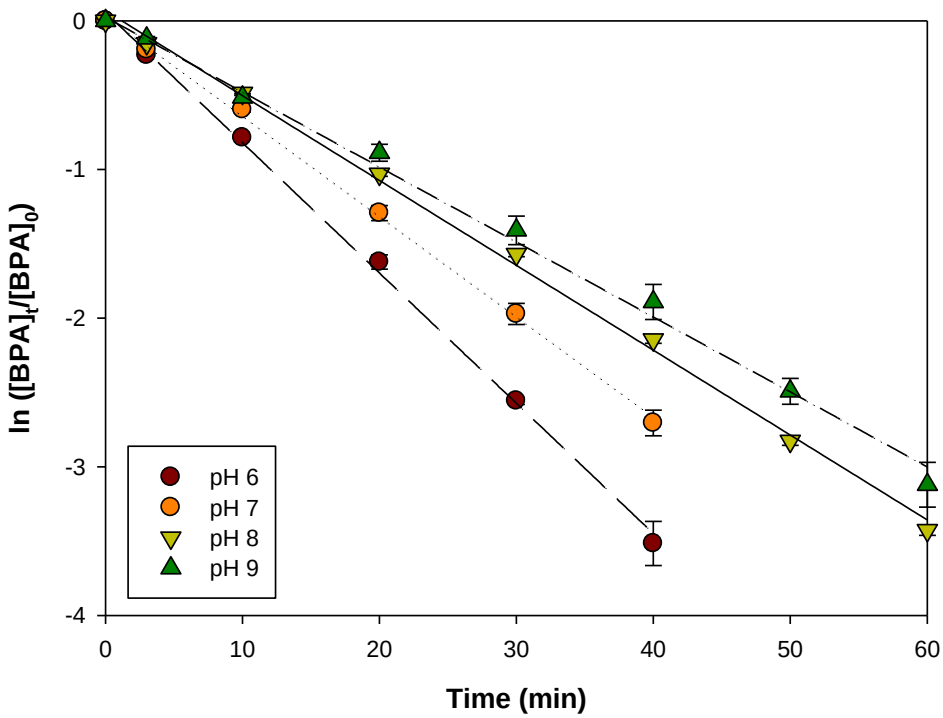


Figure 3. Degradation kinetics of BPA in different pH values. ($[BPA]_0$ = 23 μM; pH = 7.0, (6 W), The error bars indicate the SD of duplicate experiments)

Table 5. Pseudo-first-order kinetics and coefficients of different pH values

pH	6	7	8	9
k_{obs} (min^{-1})	0.0876	0.0675	0.0571	0.0516
R^2	0.998	0.999	0.998	0.995

3.2.2. Effect of DOM and inorganic anions

Dissolved organic matter (DOM) and inorganic anions are also significant factors that influence target compound degradation. Various anions and DOM are present in every water sources, they should not be neglected since they are known to inhibit the degradation efficiency of oxidation processes by scavenging the reactive radicals (Chen, 2019; Duca et al., 2016). Therefore, the effects of water components on BPA degradation in the VUV reaction should be considered. Humic acid (HA) was used as the reference DOM, which is known to perform as a photosensitizer, light filter, and radical quencher (Dhaka et al., 2017). Bicarbonate (HCO_3^-) and nitrate (NO_3^-) were used as the anions, for they are the most common constituents present in water bodies. The results on the effect of DOM, HCO_3^- and NO_3^- at concentrations of 1, 10, and 30 mg L^{-1} are shown in Fig. 4.

As shown in Fig. 4, the removal percentage of BPA in the presence of 1, 10, and 30 mg L^{-1} HA was 99.6%, 98.7%, and 94.7%, respectively. Compared to 99.5% removal in the absence of HA. At HA concentration at 1 and 10 mg L^{-1}, the degradation efficiency of BPA slightly improved and almost had no effect, while concentration at 30 mg L^{-1} slightly inhibited BPA degradation. The observed k_{obs} were 7.07×10^{-2} min^{-1}, 6.73×10^{-2} min^{-1}, and 4.58×10^{-2} min^{-1} for concentrations 1 mg L^{-1}, 10 mg L^{-1}, and 30 mg L^{-1}, respectively. Compared to k_{obs} of 0 mg L^{-1} of HA, which was 6.75×10^{-2} min^{-1}, the presence of 1mg L^{-1} surely enhanced the BPA degradation. This may be due to the formation of photo-oxidant species by the reaction between HA and contaminants (Rebeiro et al., 2019; Ngouyap Mouamfon et al., 2010). Moreover, it has been revealed that low concentrations of HA can promote the degradation of target compound when photons excite HA into a triplet state and generate various reactive oxygen species (ROS) are produced (Sharma et al., 2015a; Kang et al., 2018). However, at HA concentration of 30 mg L^{-1}, the observed k_{obs} slowed down, in which HA conducted as a radical scavenger (Zhang et al., 2019).

The presence of anions in water could either boost the degradation of target compounds via the generation of reactive species or hinder the degradation efficiency by scavenging reactive species in AOPs (Moussavi et al., 2019; Zhang et al., 2019; Acero et al., 2019). According to Fig. 4, the different concentrations of 1

mg L^{-1}, 10 mg L^{-1}, and 30 mg L^{-1} of HCO_3^- did not alter the degradation efficiency of BPA. The percent removal of BPA reached above 99% for all concentration levels within 60 min of reaction in the HCO_3^- existence. Also, kinetic-wise, the observed k_{obs} of BPA rather slightly increased at the presence of 10 mg L^{-1} of HCO_3^- of 7.71 × 10^{-2} min^{-1} (R^2 = 0.99) compared to k_{obs} of the absence of HCO_3^-. Since the reaction rate constant of HCO_3^- is very slow, its inhibition on BPA degradation was insignificant. This may be explained by the fact that CO_3^- radical, •CO_3^-, is produced by the reaction with •OH (Duca et al., 2017), which is less reactive than •OH. Because the produced •OH is converted into •CO_3^-as shown in Eq. (3), the degradation of BPA has remained unchanged.

$$\bullet \mathrm{OH} + \ HCO_3^- \rightarrow H_2O + \ \bullet CO_3^- \qquad (3)$$

In contrast, the presence of NO_3^- ions hindered the removal efficiency during VUV reaction where the observed k_{obs} in the presence of NO_3^- anions were 6.66 × 10^{-2} min^{-1} (R^2 = 0.99), 4.15 × 10^{-2} min^{-1} (R^2 = 0.99), and 3.60 × 10^{-2} min^{-1} (R^2 = 0.99) for 1 mg L^{-1}, 10 mg L^{-1}, and 30 mg L^{-1} NO_3^- respectively. At 1 mg L^{-1} of NO_3^-, there was almost no change on the degradation kinetics when compared to 0 mg L^{-1} NO_3^- condition. However, at concentrations of 10 and 30 mg L^{-1}, the degradation This can be explained by the fact that NO_3^- acted as an inner filter for the photon absorption at 185 nm (Duca et al., 2017), which absorbed 185 nm photons and inhibited the homolysis of water molecule. As a result, the formation of •OH drastically decreased, and retarded the degradation of BPA.

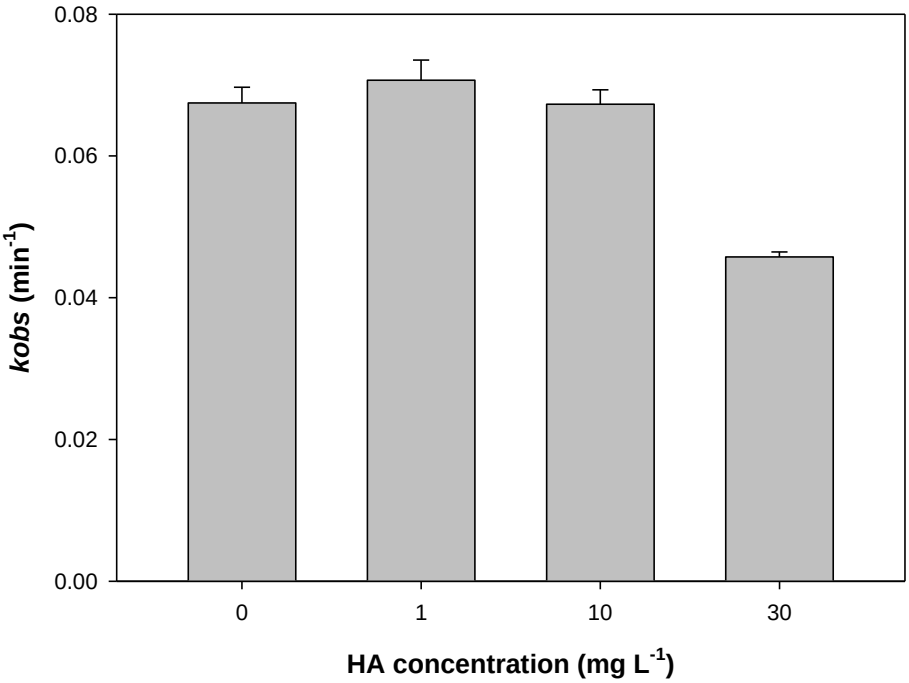
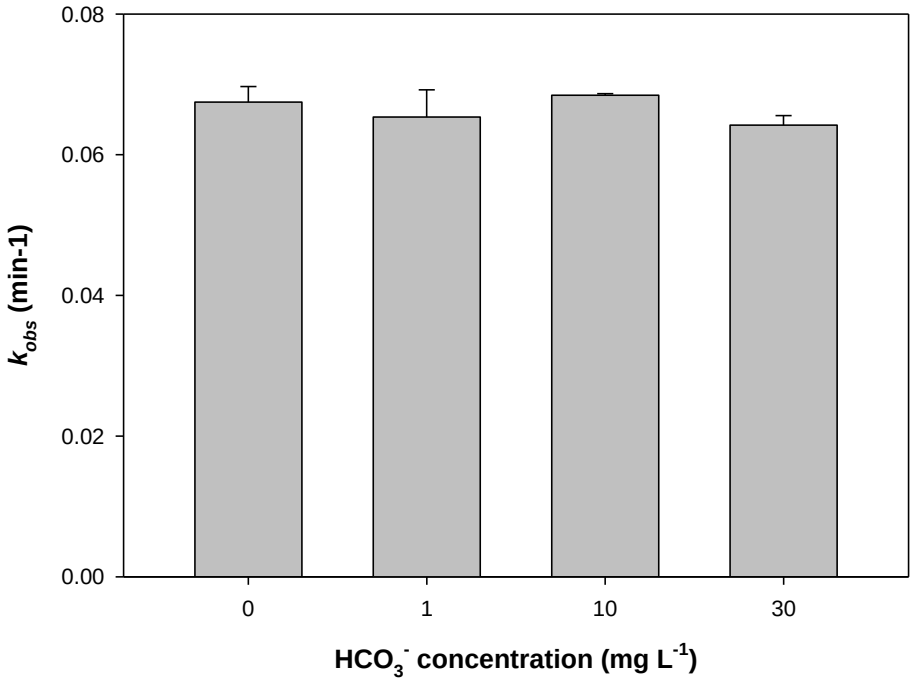


Figure 4. Degradation of BPA in the presence of HA during VUV reaction. ($[BPA]_0$ = 23 μM; pH = 7.0, (6 W). The error bars indicate the SD of duplicate experiments)



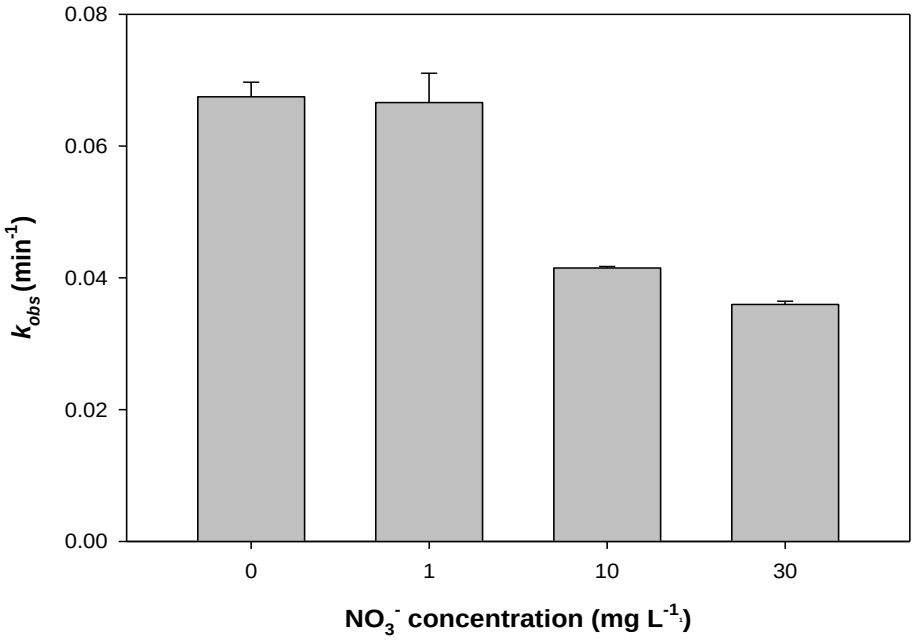


Figure 5. Degradation of BPA in the presence of HCO_3^- and NO_3^- during VUV reaction. ($[BPA]_0$ = 23 μM; pH = 7.0, (6 W), The error bars indicate the SD of duplicate experiments)

3.3. Mineralization and transformation products

3.3.1. TOC mineralization of BPA

The mineralization of BPA was observed through the decrease in TOC during the 12 hours VUV reaction time. As illustrated in Fig. 6, while BPA was completely degraded within 60 min of reaction, only about 14% of mineralization of BPA was achieved during 1 hour of reaction. It subsequently increased to 40% after 2 hours and further reached to 91% mineralization at the final point. The fact that 92% mineralization of BPA was attained within 12 hours indicates that a longer reaction would completely mineralize BPA. Moreover, the decrease in TOC of BPA during VUV reaction designates the aromatic ring opening of the BPA molecule, and it is further broken down into smaller molecules.

3.3.2. Identification of TPs

A total of seven organic TPs of BPA during the VUV reaction were identified with UPLC-qTOF/MS (TP 243, TP 241, TP 257, TP259, TP181, TP 104). The time-peak area profile and degradation pathway of the identified BPA are illustrated in Fig. 7 and 8, respectively. The degradation pathway of BPA was deduced by examining the time-peak area profile, which provides examples of identified byproducts.

According to the degradation pathway illustrated in Fig. 7 and 8, the very first transformation product formed was expected to be TP 243, which was driven by the attachment of an OH adduct on BPA ($[M-H]^-$ = 227.1085). It can be inferred that TP 243 formation initiated the further formation of other TPs for they appeared after the formation of TP 243. After the TP 243, the structure further transformed to TP 167 in which one of the phenol rings of the BPA structure was torn off by the •OH attack, and simultaneous followed the attachment of another OH bond. Then TP 241 was produced when OH on each side of TP 243 was oxidized, which then further transformed into TP 259 which is formed by another hydroxylation on the meta position of the meta position of the previous structure. Moreover, TP 257 was produced by the transformation of methyl to carboxylic acid, which was then transformed into TP181, which is also known as benzophenone.

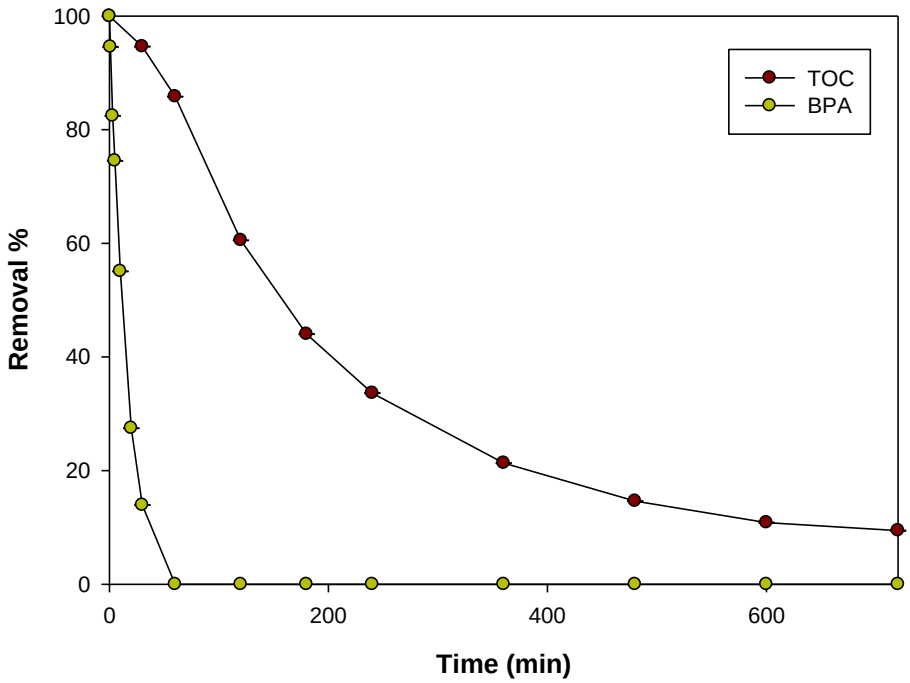


Figure 6. Decrease in TOC of BPA during VUV process. ($[BPA]_0$ = 23 μM; pH = 7.0, (6 W). The error bars indicate the SD of duplicate experiments)

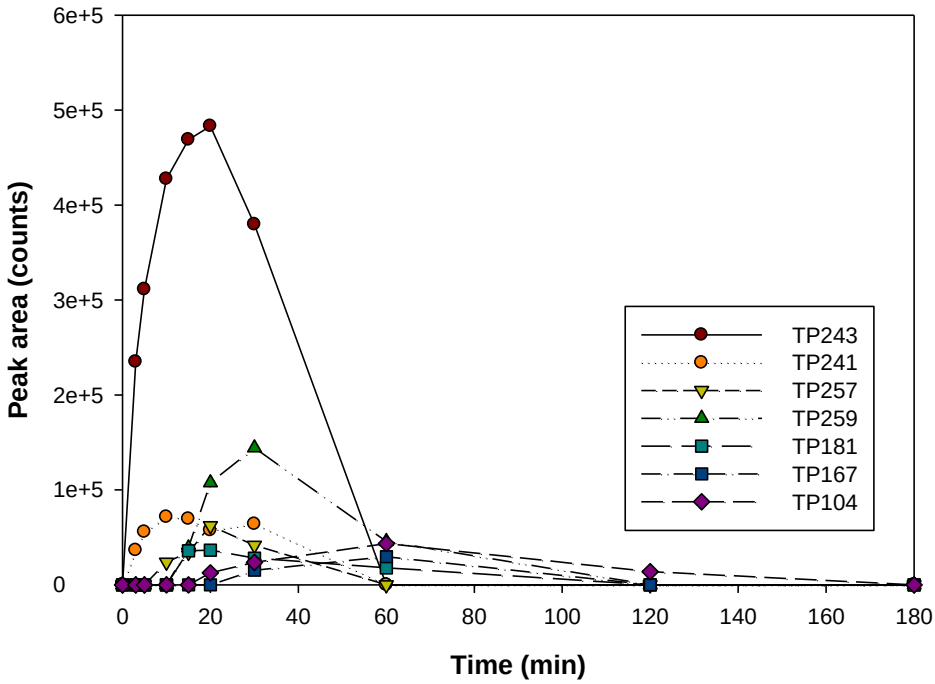


Figure 7. Time peak-area profile of TPs formed during VUV process. ($[BPA]_0$ = 23 μM; initial pH = 5.67, final pH = 4.81, (no buffer was used for the identification of TPs); (6 W))

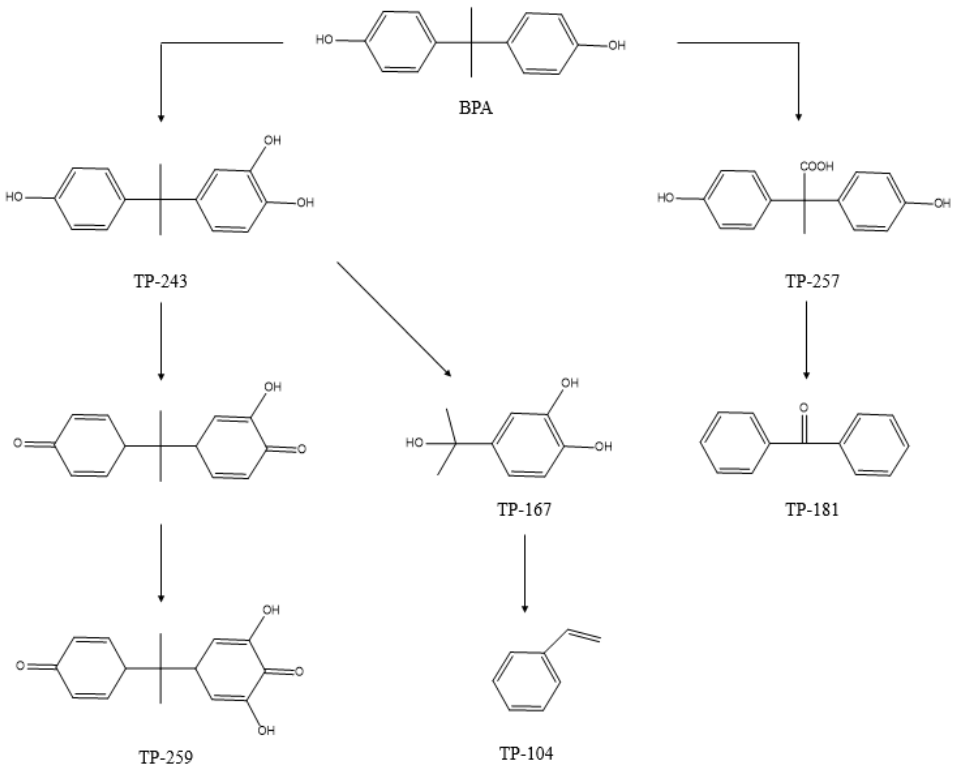
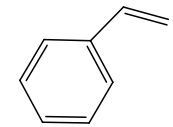
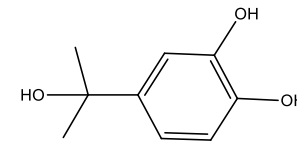
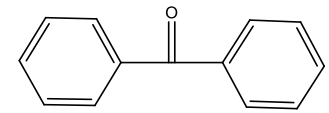
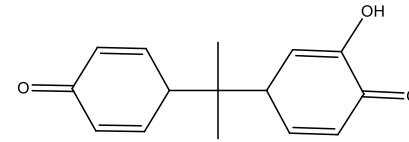
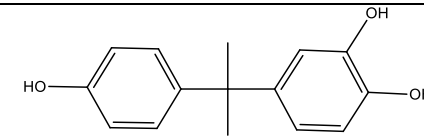
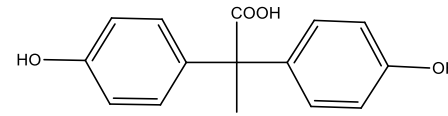
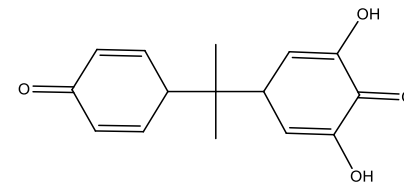


Figure 8. Proposed degradation pathway of BPA during VUV process.

Table 7. Identified degradation products of BPA during VUV process

Component	Formula	Observed m/z	Mass error	RT	Structure
TP104	C_8H_8	104.0629	2.63	0.91	
TP167	$C_9H_{12}O_3$	167.0717	0.33	0.91	
TP181	$C_{13}H_{10}O$	181.0728	-0.26	1.28	
TP241	$C_{15}H_{15}O_3$	241.0860	0.49	1.28	

TP243	$C_{15}H_{16}O_3$	243.1016	0.39	1.28	
TP257	$C_{15}H_{11}O_4$	257.0822	1.36	1.16	
T259	$C_{15}H_{14}O_4$	259.0989	-0.41	1.09	

3.4. Toxicity

In order to examine the ecological risk of BPA and its TPs during the VUV reaction, acute toxicity test was assessed using Microtox and bioluminescent bacteria *V. fischeri*. The luminescence of the bacteria is used as an index for the observation of change in toxicity. The higher the luminescence of *V. fischeri* gets, the less toxic the samples are. For the acute toxicity assessment, *V. fischeri* was exposed to VUV treated samples. Unlike the effective degradation of BPA within 40 min of VUV reaction, there was no dramatic change in luminescence. However, as illustrated in Fig. 7, the luminescence inhibition decreased about 20% after 60 min, and maintained until 180 min of the reaction. The increased luminescence indicates that VUV treatment could potentially decrease the toxicity of BPA after the treatment. Hence, the results indicate that the residual byproduct are less toxic than BPA.

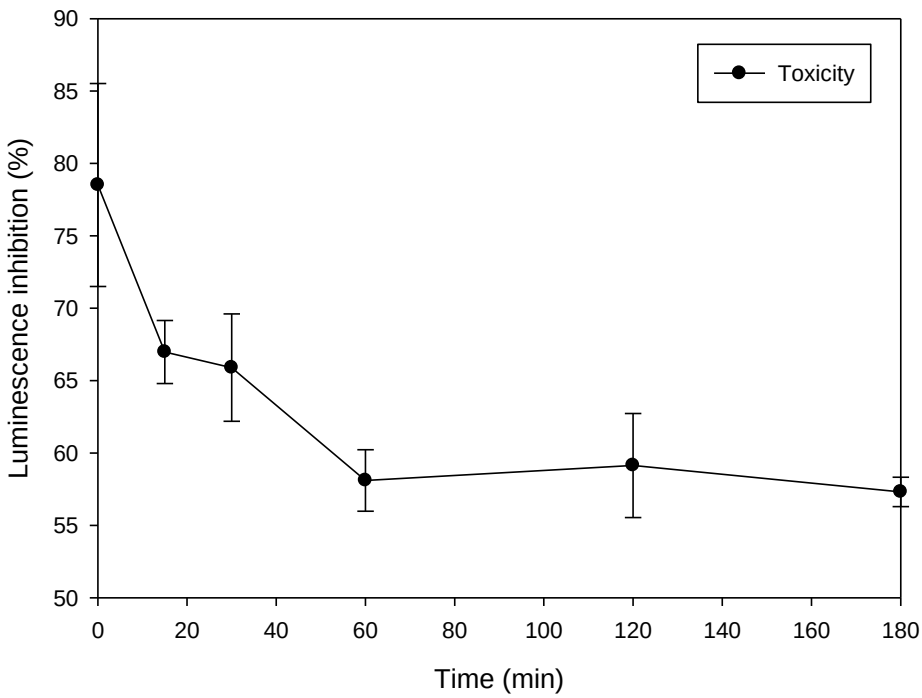


Figure 9. Luminescence inhibition of *V. fischeri*. ([BPA]$_0$ = 23 μM; pH = 7.0, (6 W). The error bars indicate the SD of duplicate experiments)

3.5. Radical Contribution

The contribution of dominant radical species that is in charge of BPA degradation during the VUV treatment was investigated using a radical scavenger, tertiary butanol (TBA). During the VUV reaction, •OH, •H, and e^-_{aq} are produced, and among these reactive species, •OH plays a major role in target pollutant degradation, for it has the highest oxidation potential. Since •OH is the main contributor of BPA degradation in the VUV reaction, TBA, which is a powerful •OH scavenger was used to figure out the •OH contribution. The contribution of •OH at pH 6, 7, 8, and 9 were evaluated in the presence of 23 μM TBA adopting a competition kinetics method under different pH conditions (6, 7, 8, and 9) to determine the second-order rate constants of BPA with •OH ($k_{\bullet OH\text{-}TBA}$). The $k_{\bullet OH\text{-}TBA}$ is known to have a rate constant of 6.0×10^8 $M^{-1}s^{-1}$ (Buxton et al., 1988), and $k_{\bullet OH\text{-}TBA}$ can be obtained via degradation kinetics of TBA, which was analyzed using GC-MS. Therefore, $[\bullet OH]_{ss}$ can be determined using Eq. (4). The k'_{TBA} was calculated to be 5.45×10^{-3}, 3.4×10^{-3}, 4.08×10^{-3}, and 4.21×10^{-3} min^{-1} at pH 6, 7, 8, and 9, respectively, and $[\bullet OH]_{ss}$ is shown was calculated to be 1.51×10^{-13}, 9.28×10^{-14}, 1.13×10^{-13}, and 1.17×10^{-13} M at pH 6, 7, 8, and 9, respectively. As for $k_{\bullet OH\text{-}BPA}$ in Eq. (5), it has been reported previously (1.7×10^{10} $M^{-1}s^{-1}$) (Sanchez-Polo et al., 2013).

$$k'_{TBA} = k_{\bullet\mathrm{OH-TBA}} \times [\bullet\ \mathrm{OH}]_{ss} \quad (4)$$

$$k'_{\bullet\mathrm{OH-BPA}} = k_{\bullet\mathrm{OH-BPA}} \times [\bullet\ \mathrm{OH}]_{ss} \quad (5)$$

The contribution of •OH ($k'_{\bullet OH\text{-}BPA}$) to BPA degradation during the VUV reaction at different pH values can be calculated using Eq. (5). The results show that •OH contributed to 82.6%, 71.4%, 49.65%, and 43.36% at pH 6, 7, 8, and 9, respectively. Since the degradation kinetic was the fastest at pH 6 and gradually decreased with rising pH, the contribution of •OH also decreased as pH increased.

4. Conclusion

This study investigated the degradation kinetics, influencing factors, transformation products, and toxicity during the removal of BPA during VUV reaction. The BPA degradation reached 99.5% removal with VUV reaction within 1 hr. Based on the experimental results, the VUV process exhibited a higher efficiency for BPA removal than that of the UV process. The BPA was degraded with k_{obs} of 6.75×10^{-2} min^{-1} for VUV reaction, whereas the k_{obs} of UV-C process was 25 times slower. Also, the solution pH played a significant role in BPA degradation in which BPA degraded faster in acidic conditions than alkaline conditions. During the VUV reaction, approximately 92% of BPA was mineralized, and seven organic transformation products were identified. With the identified TPs, the degradation pathway of BPA was proposed. Based on the VUV reaction, acute toxicity test was assessed with *V. fischeri* in which the luminescence inhibition rate decreased, indicating the toxicity decrease of BPA after the treatment. Through the calculation of radical contribution, it was revealed that the contribution of •OH gradually decreased as pH increased. These results imply that the VUV process can be one of the alternative options in water treatment plants in removing organic pollutants.

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Supplementary materials

Figure S1. Extracted ion chromatogram (XIC) and ion spectrum of BPA.

Figure S2. XIC and ion spectrum of TP104.

Figure S3. XIC and ion spectrum of TP167.

Figure S4. XIC and ion spectrum of TP181.

Figure S5. XIC and ion spectrum of TP241.

Figure S6. XIC and ion spectrum of TP243.

Figure S7. XIC and ion spectrum of TP257.

Figure S8. XIC and ion spectrum of TP259.

Figure S1. Extracted ion chromatogram (XIC) and ion spectrum of BPA.

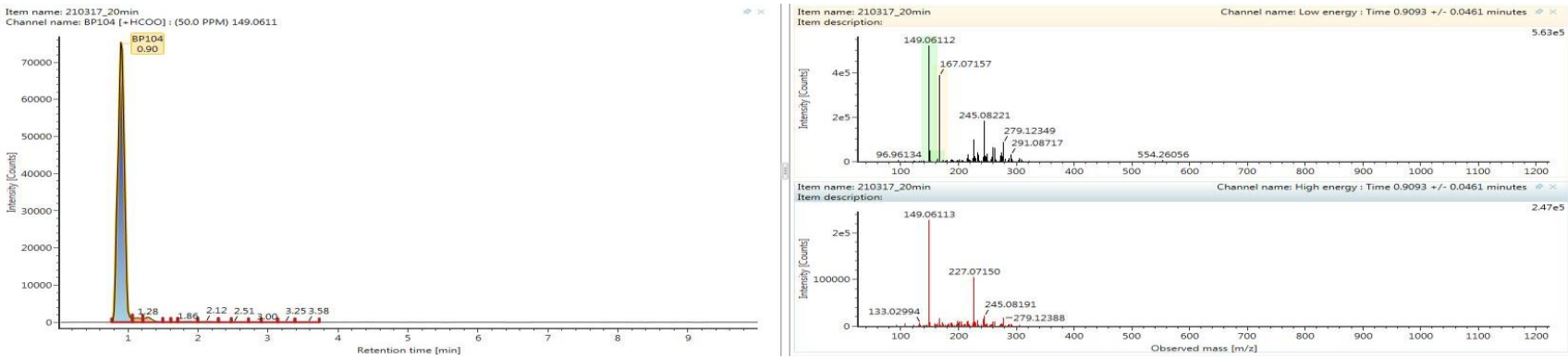

Figure S2. XIC and ion spectrum of TP104.

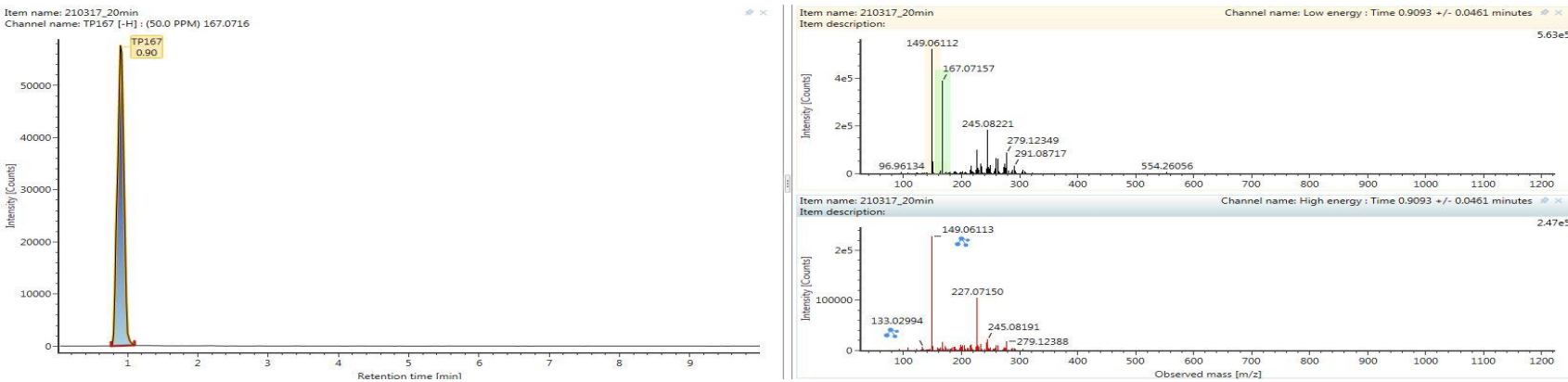

Figure S3. XIC and ion spectrum of TP104.

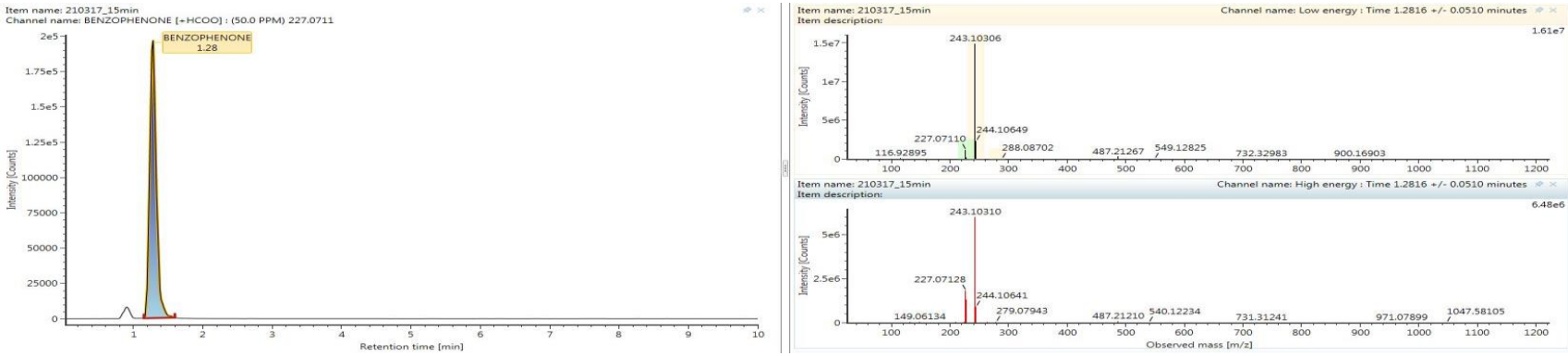

Figure S4. XIC and ion spectrum of TP181.

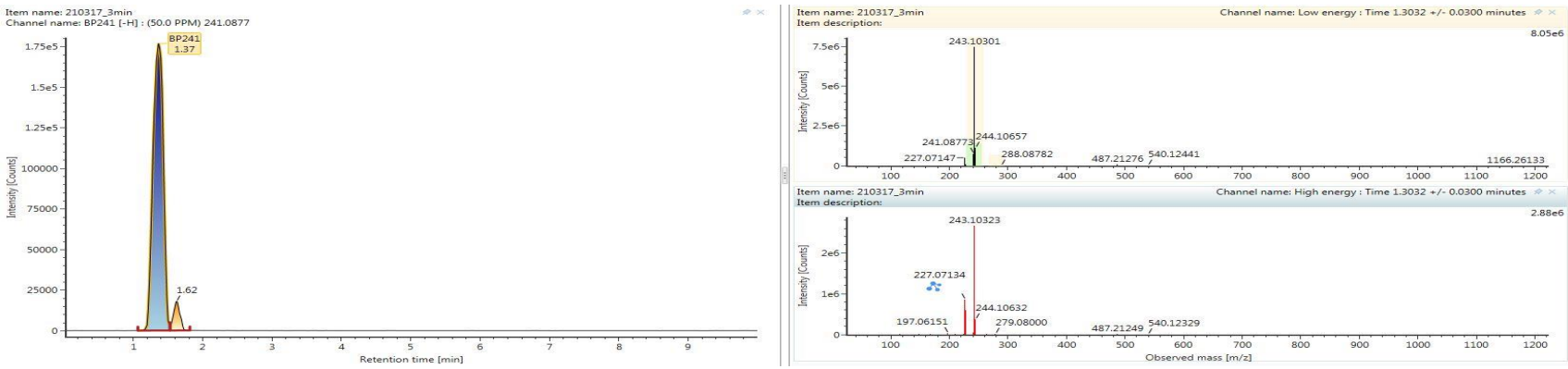

Figure S5. XIC and ion spectrum of TP241.

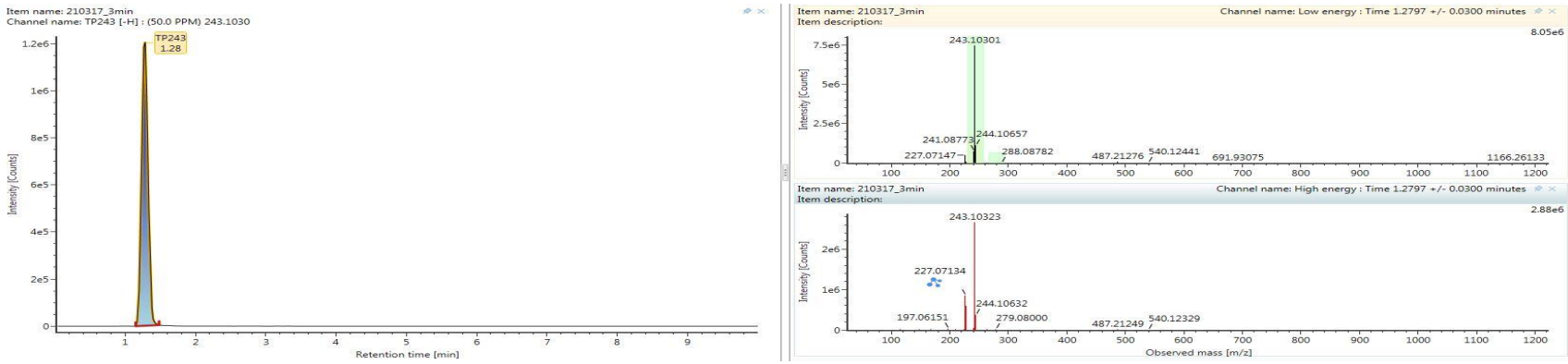

Figure S6. XIC and ion spectrum of TP243.

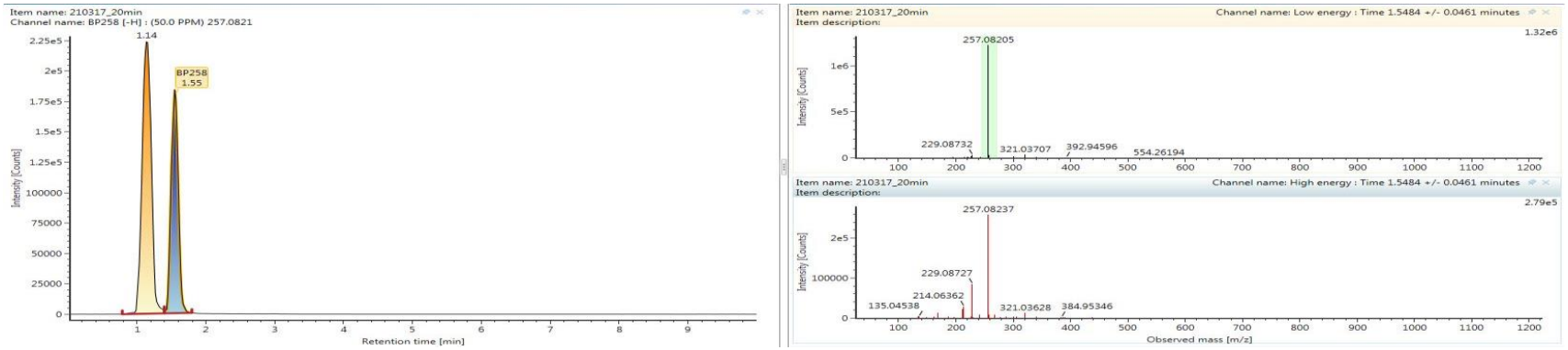

Figure S7. XIC and ion spectrum of TP257.

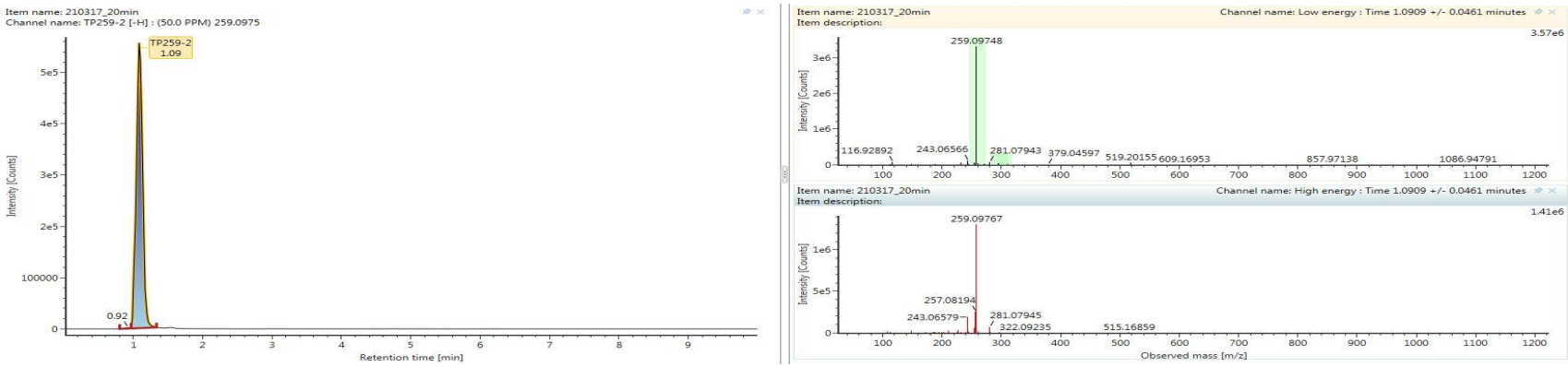

Figure S8. XIC and ion spectrum of TP259

국문 초록

진공자외선 공정에서의 비스페놀 A의 분해 특성과 메커니즘에 관한 연구

최예림

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환경보건학과 환경보건학 전공

비스페놀 A(BPA)는 인간과 수생 생태계에 해로운 건강 영향을 줄 수 있는 물질로써 내분비계 장애물질(EDC)로 분류 되어있다. BPA 는 주로 폴리카보네이트와 에폭시 수지의 생산에 사용되는 화학 화합물로 플라스틱 컵이나 식품포장용기, 의료기기 등 여러 분야에 필요한 물품을 만드는데 사용되는 물질이다. BPA 가 체내에 쌓이게 되면 신경 독성, 심혈관 질환, 생식 장애, 각종 암 등의 건강 영향을 끼칠 수 있다고 알려져 있는데, 이에 따른 건강 영향에 대한 정보가 알려지기 시작하면서 최근 10 년동안 전 세계 국가별 BPA 사용에 대한 제한이 있지만 여전히 산업물품 제조에 활발히 쓰이고 있다. 그러나 아직까지 전 세계의 다양한 수계에서 BPA 의 검출사례가 발생하고 있는다. 수처리 시설에서 완전히 제거가 되지 않는 잔여 BPA 는 방류수 속에 포함되어 환경 중으로 배출이 되어 지표수뿐만이 아니라 음용수에서도 검출이 되어 이것의 효과적으로 제거하기 위한 공정의 연구가 필요하다. 따라서 본 연구에서는 BPA 의 효율적인 제거 방법을 제시하고자 VUV 공정을 이용한 실험을 진행하였다. VUV 공정을 통하여 BPA 는 60 분 이내로

99.5%의 높은 제거율로 처리되었으며 유사 1 차 반응을 따르는 제거 양상을 보였다 (kobs = 6.75 × 10^{-2} min^{-1}). 제거 반응에 영향을 줄 수 있는 pH, 용존 유기물, 음이온의 영향을 관찰하였고, pH 가 산성 조건일 때 BPA 의 제거율이 알칼리 조건일때보다 더 빠른 것을 확인 하였다. 그리고 용존유기물과 중탄산염이온의 영향에 영향이 미흡한 반면 질산염에 의한 BPA 의 제거율이 저해하는 것을 확인하였다. 12 시간의 VUV 반응으로 약 92%의 BPA 가 무기화 되었고 BPA 구조의 벤젠 고리가 열리면서 무기화가 진행되고 이로인해 부산물이 생성되는 것을 확인하였다. 총 7 가지의 유기 부산물을 (TP 243, TP 241, TP 257, TP 259, TP 181, TP 104) 규명하였으며 이를 통해 BPA 의 분해 경로를 제시하였다. VUV 공정으로 BPA 를 처리할 때 *Vibrio fischeri* 의 발광 저해율이 감소하는 것을 통하여 BPA 의 독성이 감소하는 것을 확인하였다.

주요어: 비스페놀 A; 내분비계장애물질; VUV; 제거 속도상수; 부산물; 분해경로

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