

## Proposal degradation pathway of BPA during ozone reaction Propuesta de ruta de degradación del BPA durante la reacción del ozono

Ramiro Vallejo Rodríguez <sup>1</sup> <sup>(1)</sup> - Roberto E. San Juan Farfán <sup>2</sup> <sup>(1)</sup> - Elizabeth León Becerril <sup>1</sup> <sup>(1)</sup> Valeria Ojeda Castillo <sup>3</sup> <sup>(0)</sup> - Daryl Osuna Laveaga <sup>4</sup> <sup>(1)</sup> - Valentín Flores Payán <sup>1,5</sup> <sup>(1)</sup>  $\boxtimes$ 

<sup>1</sup> Centro de Investigación y Asistencia en Tecnología y Diseño del Estado de Jalisco (CIATEJ), Área de Ingeniería Ambiental. Guadalajara, Jalisco, México

<sup>2</sup> Centro Universitario de Ciencias Exactas e Ingenierías (CUCEI), Departamento de Ingeniería Química. Guadalajara, Jalisco, México

<sup>3</sup> Universidad, de Guadalajara. Guadalajara, Jalisco, México

<sup>4</sup> Universidad Autónoma de Guadalajara, Departamento de Ciencias Biotecnológicas y Ambientales. Zapopan Jalisco, México

<sup>5</sup> Universidad de Guadalajara, Centro Universitario de Tonalá, Departamento de Ciencias Básicas. Tonalá, Jalisco, México

☑ Correspondence author: valentin.flores@academicos.udg.mx

Recepción: 25-07-2022 / Aceptación: 02-03-2023 © Nova Scientia, bajo licencia Creative Commons / ISSN 2007-0705

## Abstract

Endocrine-disrupting compounds (EDC) are present in surface water bodies that supply water to the population. One of them is bisphenol A (BPA), which is listed as a carcinogen. This research addresses its degradation through the ozone reaction and presents a likely pathway established by analyzing products and degradation products using gas chromatography-mass spectrometry (GC-MS). BPA degradation was carried out under pseudo-first-order conditions, where liquid phase ozone was the limiting reactive, in doses of  $\approx 2.29 \times 10^{-4}$  M and BPA doses of  $1.25 \times 10^{-4}$ ,  $17.5 \times 10^{-4}$ , and  $35.0 \times 10^{-4}$  M, looking to have molar ratios [BPA]> [O<sub>3</sub>]; the oxidation reaction was carried out in a stopped-flow system that allows obtaining results in the order of seconds. The degradation pathway obtained shows the rupture of one of the benzene rings, decreasing the phenolic toxicity of the BPA compound. The proposed pathway can contribute to the understanding of the degradation of BPA in the environment and tertiary treatment processes with the use of ozone. Likewise, it is intended to contribute with new data to the issues of drinking water treatment to offer safe water to the population.

**Keywords:** bisphenol A; stopped-flow; degradation pathway; ozonation; GC-MS; compounds; ozone; degradation

# Resumen

Los compuestos disruptores endocrinos (CDE) están presentes en algunas masas de agua superficiales que suministran agua a la población. Uno de ellos es el bisfenol A (BPA), el cual está enlistado como carcinógeno. Esta investigación aborda su degradación a través de la reacción del ozono y presenta una vía probable establecida mediante el análisis de productos y subproductos por cromatografía de gases y espectrometría de masas (GC-MS, por sus siglas en ingles). La degradación del BPA se llevó a cabo en condiciones de pseudo primer orden, donde el ozono en fase líquida fue el reactivo limitante, en dosis de  $\approx 2.29 \times 10^{-4}$  M y dosis de BPA de 1.25  $\times 10^{-4}$ , 17.5  $\times 10^{-4}$  y 35.0  $\times 10^{-4}$  M, buscando relaciones molares [BPA] > [O<sub>3</sub>]; la reacción de oxidación se llevó a cabo en un sistema de flujo detenido que permite obtener resultados en el orden de segundos. La vía de degradación obtenida muestra la ruptura de uno de los anillos de benceno, disminuyendo la toxicidad fenólica del compuesto BPA. La vía propuesta puede contribuir a la comprensión de la degradación del BPA en el medio ambiente y los procesos de tratamiento terciario con el uso del ozono. Asimismo, se pretende contribuir con nuevos datos a los temas de tratamiento de agua potable para ofrecer agua segura a la población.

Palabras clave: bisfenol A; flujo-detenido; vías de degradación; ozonación; GC-MS; compuestos; degradación

#### 1. Introduction

Endocrine-disrupting compounds (EDCs) have been defined as exogenous agents, which interfere with the function, synthesis, secretion, transport, or elimination of natural hormones in the human body (USEPA, 1997). EDCs can be natural compounds such as steroids secreted by animals and humans or anthropogenic compounds, such as natural and synthetic hormones, agricultural or industrial chemicals (bisphenol A, alkylphenols, pesticides, phthalates, etc.) (Deborde*et al.*, 2008).

Due to the manufacturing of plastic polycarbonate and epoxy resin (Vandenberg et al., 2009) bisphenol A, (also named 2,2-bis-(4-hydroxyphenyl)propane or 4,4-isopropylidenediphenol) have been found in effluents of water treatment plants. Bisphenol A (BPA) is one of the most produced EDCs generated in the world. It is estimated that about 2.5 million tons are produced worldwide, of which approximately 100 tons are annual discharged into the environment (Umar *et al.*, 2013) BPA is sold as crystals, pills, or flakes under environmental conditions. BPA is melted at elevated temperatures during manufacturing (melting point = 150-155 °C). The water solubility of BPA has been reported at 120-300 mgL<sup>-1</sup> (CDHFINECHEMICAL, 2020; Handbook of Environmental 2020). The US Environmental Protection Agency (USEPA, 1997) cites an unlisted reference stating that BPA has greater solubility at alkaline pH values due to its disassociation constants, pKa 9.6 a 10.2 (Kosky*et al.*, 1991; Staples *et al.*, 1998).

The biological processes of water treatment hardly degrade BPA in water due to the two aromatic phenyl groups, which gives stability and persistence to biologic degradation (Benotti*et al.*, 2009). Nevertheless, the presence of BPA in the aqueous medium represents a public health risk; concentrations of 0.64 and 1.49 ng mL<sup>-1</sup> of BPA have been found in the blood of older adults (Takeuchi *et al.*, 2002), whose origin can be multifactorial, among those being the food or water consumed.

For this reason, alternative EDC degradation processes have been developed, such as advanced oxidation processes (AOPs), which allow the degradation of this type of pollutants present in the environment, especially in water (Vallejo-Rodríguez *et al.*, 2014; López-López *et al.*, 2007; López-López *et al.*, 2016; Hubert *et al.*, 2003).

BPA degradation by ozone (O<sub>3</sub>) in the liquid phase follows a second-order reaction (López-López *et al.*, 2007; Hoigné and Bader 1983; Jabesa *et al.* 2022; Zhang *et al.* 2020). This reaction can be carried out utilizing direct reaction (molecular pathway, or also called, non-radial pathway) where the molecular ozone attacks double bonds of compounds, and this pathway is favored at pH<7 (Hoigné and Bader 1983; Lee *et al.*, 2002; Zhang *et al.* 2020; Jabesa *et al.* 2022). Furthermore, the BPA degradation can also happen by indirect reaction (radical pathway) through the hydroxyl radicals (•OH), which are formed by the ozone decomposition into the water by secondary oxidants (radical species). This reaction is favored at pH>7, but when the reaction occurs at pH $\approx$ 7 (von Gunten and Laplanche 2000; Jabesa *et al.* 2022; Zhang *et al.* 2020), both pathways (molecular and radical) can interact at the same time.

Degradation of BPA by ozone, whether molecular, radical, or both, is a fast reaction (in a matter of seconds), making it difficult to determine the reaction kinetics and to know its degradation mechanisms. The by-products of the BPA reaction with O<sub>3</sub> can help to establish a BPA degradation pathway. Then, its main by-product tracking and quantification are required (Deborde*et al.*, 2008). It can also help identify any risk compounds formed in the final reaction or if the mineralization degree was reached.

Some authors have degraded BPA in aqueous solutions by ozonation. For example, Garoma *et al.*, (2010) reported BPA degradation and the generation of by-products in a semi-continuous reactor with stream of ozone gas (10 mgL<sup>-1</sup>) for 5 minutes, with 51  $\mu$ M of initial concentration. The degradation products observed were resorcinol, catechol, acetone, and formaldehyde within the first minutes of degradation. Deborde *et al.*, (2008) worked with a batch reactor (laboratory scale) of 125 mL at 20 ± 2 °C with an initial pH  $\approx$  6.5 to remove BPA using ozone in spiked solution through the molecular and radical pathways. The degradation products reported by the authors were catechol, orthoquinone, muconic acid, benzoquinone, and 2-(4hidroxiphenyl)-propanol-2-ol, finding the kinetic constants reaction values of 1.68×10<sup>4</sup> M<sup>-1</sup>s<sup>-1</sup> for the molecular pathway and 1.06×10<sup>9</sup> M<sup>-1</sup>s<sup>-1</sup>, 1.11×10<sup>9</sup> M<sup>-1</sup>s<sup>-1</sup> for the radical pathway. Lee *et al.*, (2002) reported the BPA ozonation in water

by molecular pathway, using a ratio of tert-butanol/BPA> 300 and by radical pathway, with different hydrogen peroxide concentrations. The kinetic constants degradation values obtained were  $1.3 \times 10^4$  M<sup>-1</sup>s<sup>-1</sup> at pH 2 and  $1.6 \times 10^9$  M<sup>-1</sup>s<sup>-1</sup> at pH 12 using the competitive kinetic method, adding phenol as a reference compound under heterogeneous conditions semi-continuous reactor. Jabesa *et al.* (2022) removed BPA from aqueous medium by ozone microbubbles with efficiencies from 41 to 98% within 600 s at pH from 3 to 7. The reported reaction rate constants were 294.1, 1365.3, and 2477.7 L mol-1 s-1, for three stages of ozonation, 0–0.6, 0.6–2.5, and 2.5–3.0 ks, respectively. On the other hand, Zhang *et al.* 2020 assayed an ozonation process with catalyst (Fe<sub>3</sub>O<sub>4</sub>–MnO<sub>2</sub>) that reached 97.0% at initial solution pH 7 with a flow rate of O<sub>3</sub> of 100 mL/min and dose of Fe<sub>3</sub>O<sub>4</sub>–MnO<sub>2</sub> of 100 mg/L. A degradation pathways of BPA were proposed by the authors.

The identification of BPA degradation products by ozone is a key stage and it has been carried out by different chromatographic methods. Garoma *et al.* (2010) have searched the BPA degradation products using in a liquid chromatograph equipped with a UV detector at 275 nm. Deborde *et al.* (2008) analyzed the degradation products by liquid chromatography coupled to UV spectrometry at 270 nm and mass spectrometry with a Kromasil reverse phase column of C18 (4.6 x 250 mm). On others hand, the degradation products have been identified by Lee *et al.* (2002) using a liquid chromatography equipment with a capillary column (HP5, 30 m x 0.32 mm ID x 0.25  $\mu$ m) coupled to UV/VIS at 230 nm. Quantitative analyses of the concentrations of BPA, catechol, and hydroquinone of the experiments done by Jabesa *et al.* (2022) were made by an ultra-fast liquid chromatograph (UFLC) (LC-20AD, Shimadzu, Japan) equipped with UV detector, using a C18 column (Hypersil ODS, 250 mm x, 4.6 mm ID, 5 m).

The by-products identified by Lee *et al.*, allowed them to define the BPA degradation and transformation pathway, estimate the reaction progress, determine the risked compounds formation, or know whether the reaction is in mineralization status. Flores-Payan *et al.*, (2017) developed a novel real-time method to evaluate the BPA degradation kinetics by molecular ozone and radical pathway using the stopped-flow technique. They determined the second-order kinetics under pseudo-first-order conditions for the molecular pathway by the absolute rate constant method and the radical pathway involving the hydroxyl radical and ozone ratio. BPA degradation by ozone was performed and evaluated at a pH of 2 to 10. The method permits the determination of kinetic parameters for chemical reactors.

The aim of this study is addressed the BPA degradation through the ozone reaction and presents a likely pathway established by analyzing products and by-products using gas chromatography-mass spectrometry (GC-MS). Likewise, it is necessary to understand the degradation mechanisms of BPA at the laboratory level to understand what happens to this compound in nature, so that the water supplied to the population must be safe.

# 2. Methods, techniques, and instruments *Materials*

BPA (99%) was purchased from Sigma Aldrich (USA). Sodium hydroxide to prepare buffer solution to pH 7, 8, and 9 and tert-butyl alcohol, used as a scavenger of •OH radical in the experiments, were acquired from Sigma–Aldrich (USA) with a chemical purity greater than 97% and without further purification. All solvents were chromatographic grade; dichloromethane was obtained from Tedia (USA), methanol from JT Baker (USA). The ozone was generated from oxygen in an ozone generator (Pacific Ozone G11). The ozone saturation and the standard solution were performed utilizing deionized water obtained from an Elix III model Mili-Q, with a resistivity average of 18 M $\Omega$ .

## **BPA standard solution**

BPA solutions were prepared with deionized water by agitation in a hotplate stirrer at 21°C for 24 hours without contact with sunlight to ensure the total dissolution of the reagent and avoid the BPA degradation by radicals present in the UV spectrum. To assure molar ratios [BPA]> $[O_3]$  in the experiments, BPA concentrations in the

solutions were fixed at 1.25 × 10<sup>-4</sup>, 17.5 × 10<sup>-4</sup>, and 35.0 × 10<sup>-4</sup> M. O<sub>3</sub> was the limiting reactive in the reaction and consumed quickly, avoiding it to continue reacting with the by-products generated in this first reaction.

## Analytical method

Residual BPA and by-products were detected by chromatographic analysis was carried out using a method adapted from Tay *et al.* (2012); an Agilent model 6890N chromatograph coupled to an Agilent 5975 mass spectrometry detector (electron impact) and a quadruple mass filter with a model 7683 autosampler was used. An Agilent (USA) capillary column model HP-5MS 30 m x 0.250 mm with a stationary phase of 5% phenyl and 95% dimethyl polysiloxane, and 0.25  $\square$ m film thickness was used under the following operating conditions: Injection volume 0.50 µL, injection temperature of 300°C, initial temperature of 280 °C maintaining it for 10 min, with a carrier gas flow of helium at 1.10 mL/min. The injection port and the transfer line were set at 290 °C and 300 °C, respectively. The detection was in SCAN mode in the range of 50-600 uma at 1.5 sec./scan to analyze the mass/charge ratios (m/z) resulting from the reaction between BPA and ozone. Ozone concentration in the liquid phase was determined by indigo colorimetric method 4500 (Eaton, 2005). Degradation products were identified or confirmed using the NIST/EPA/NIH Mass Spectra Library v. 2.0.

## By-products identification of BPA-O3 reaction

Mixed solutions at the end of the BPA and  $O_3$  were recovered in a  $C_{18}$  cartridge previously conditioned with 5 mL of methanol and 5 mL of water at the exit of the stopped-flow chamber equipment module. Each  $C_{18}$  cartridge was dried at 13-18 in Hg for 15 minutes in a vacuum system. Then, the cartridges were eluted with 10 mL of dichloromethane. Next, the extracted solvent was collected in a 10 mL ball flask. Followed, the volume was reduced to 500  $\mu$ L using a rotary evaporator IKA model RV 10 with water bath at 35°C, 120 rpm of stirring a vacuum of 4.5 in Hg. Once the extract was reduced, it was transferred to a 2 mL silanized amber vial, where the volume was subjected to dryness using a gentle nitrogen stream (N<sub>2</sub>). Finally, the sample was resuspended with 200  $\mu$ L of dichloromethane for chromatographic analysis (see Analytical method section).

## **Ozonation system**

Deionized water was saturated with ozone at 20 °C and pH 7 in an instrumented and controlled ozonation system, reaching a liquid ozone concentration of  $\approx 11 \text{ mgL}^{-1}(2.29 \times 10^{-4} \text{ M})$  (figure 1). The system included an oxygen (extra dry and 99% purity) cylinder (1), whose gas was fed to an ozone generator G11 Pacific Ozone<sup>TM</sup> (2) with an experimental production of 16.9 g/h. The ozonation system was operated utilizing a temperature control (B&C Electronics TR-7615) (3), pH control (B&C Electronics pH 7685) (4), stirring control (5); the residual ozone was destroyed with a thermal ozone destroyer unit (Pacific Ozone<sup>TM</sup>) (6); the gas phase was measured with an ozone meter (Teledyne Instruments 465H) (7); the gas flow was controlled by electrovalve system (8); the reactor was stirred with an agitation motor (9); a stirred tank reactor (ApplikonBiotechnology<sup>TM</sup>) with an operation volume of 4L and a ratio height diameter (H:D) equal to 1.5, where ozone saturation in deionized water was performed (10); voltage supply for the control (11); the ozone in liquid phase was measured with a meter (ATI<sup>TM</sup>) model Q45H/64, utilizing a sensor which was introduced into an acrylic cell filled with the fluid extracted from the reactor by a peristaltic pump and Teflon tubing (12); data acquisition system based on the control card USB-1024SL of Computing<sup>TM</sup> and interface designed with Labview<sup>®</sup> 8.2 software (13); temperature adjustment inside the reactor by water recirculator (Cole Parmer 7558-85 Master Flex) (14).



Figure 1. Ozone system to deionized water saturate by ozone.

## Stopped-flow setup

The kinetic experiments of BPA degradation were performed in a stopped-flow machine model SFM-300/s (Bio-Logic®) (figure 2a) equipped with a power source (1) to energize the arc lamp (2) that radiates light at a specific wavelength selected with the monochromator (3), this monochromator transmitted the light to the Stopped Flow Module (SFM) (5) using a fiber optic cable (4). Then, the injection system is permitted to provide the compounds in solution into the mixing chamber inside the main body of the SFM. Finally, the data acquisition system (7) takes the signal through the photomultiplier tube (PM-tube) (6) and shows the information through the screen. The optimal operating conditions of the stopped flow equipment were those reported in Flores Payán *et al.* 2017. The power supply signal must be at least 5 V; the equipment operated with a dead time of 1.6 ms and the valves lead is 2 ms. Data were acquired 50 ms before the mixing of compounds began. Absorbance signals were fixed at the point of maximum absorbance for measuring the concentration of BPA and O<sub>3</sub> at 275 and 258 nm, respectively. A total reaction time between BPA and O<sub>3</sub> of 3 s was chosen based on the second-order reaction kinetic profiles produced by both compounds (data not shown).



**Figure 2**. a) Stopped flow system scheme of BIO-LOGIC® SFM-300 (adapted from the user manual), b) stopped-flow equipment photograph.

# Experimental design

To identify the by-products generated by a BPA-O<sub>3</sub> reaction, the injection was programmed in two ports, one of BPA and the other of O3, into the Stopped Flow Module (SFM), obtaining different ratios that were from 1, 2, 4, 6, 8, 10 (v/v), ([BPA]>>[O<sub>3</sub>]). This experimental condition was established in the reaction to assure the total consumption of O<sub>3</sub>. On the other hand, BPA concentration in excess avoids the reaction between the ozone and the first by-products generated in the reaction (von Gunten and Laplanche, 2000; Flores-Payán *et al.*, 2017; Yong *et al.*, 2013).

The reaction was carried out at pH $\approx$ 6.5, and this was the final pH value when the BPA solution was prepared in ultrapure water. This experimental pH implied that the reactions occurred through the molecular and radical pathway (Deborde *et al.*, 2008; López-López *et al.*, 2016).

# 3. Results and discussion

The m/z ratio and retention times of the by-products of the chromatograms obtained by GC-MS were analyzed. According to the by-products reported in the literature, the identified compounds were validated to propose the BPA degradation pathway (Deborde*et al.,* 2008; Flores-Payán *et al.,* 2017).

Figure 3 shows the retention times when BPA is degraded with  $O_3$  at a relationship of BPA/ $O_3$  = 1 at pH 7, where four main by-products called  $B_1$ ,  $B_2$ ,  $B_3$ ,  $B_4$  according to the elution in chromatograms obtained by the GC-MS.



Figure 3. BPA degradation chromatogram obtained by GC-MS with  $O_3$  having a molar ratio BPA/ $O_3 = 1$ .

Figures 4a-4e show the mass spectra used to identify the by-products indicated in figure 3, according to their main ions and charge mass ratios (m/z). Specifically, figure 4a shows the pure injected BPA spectrum without undergoing degradation with ozone. The relation m/z 228 in the chromatogram represents the total molecular weight of BPA. The ion at m/z 213 was attributed to the loss of  $-CH_3$  (m/z 15) from the BPA. The ion m/z 135 was attributed to [HO-(C<sub>6</sub>H<sub>4</sub>)-C<sup>+</sup>-(CH<sub>3</sub>)<sub>2</sub>]; the ion m/z 119 to [HO-(C<sub>6</sub>H<sub>4</sub>)-C=CH<sub>2</sub>]<sup>+</sup> and the ion m/z 93 to [(C<sub>6</sub>H<sub>4</sub>)], respectively.

Figure 4b shows the by-product  $B_1$  mass spectrum with a retention time of 29.695 minutes, confirmed by the main ion at m/z 152. The spectrum shows a deprotonated molecular ion at m/z 151. Fragment ions of mass spectra were at m/z 136 ([HO-(C<sub>6</sub>H<sub>4</sub>)–C-(O<sup>-</sup>)-CH<sub>3</sub>]<sup>+</sup>) and 119 ([HO-(C<sub>6</sub>H<sub>4</sub>)–C=CH<sub>2</sub>]<sup>+</sup>), due to the loss of ion hydroxyl (HO).

Figure 4c shows the by-product  $B_2$  spectrum at minute 39.445, which shows a lower abundance than the other ions in the fragmentation; however, this ion was considered for confirmation since, according to Pavia *et al.*, (2014), it is unnecessary to have a peak high in abundance in the mass spectrum to consider it as a confirmation ion.

Aliphatic carboxylic acids show weak molecular ion peaks due to the ease with which fragmentations occur, especially in highly branched molecules or even some rearrangements. As a result, the molecule does not reach the detector. The ion m/z 173 was attributed to carboxylic group m/z 45 (COOH) loss and one oxygen atom (m/z 16). The ion m/z 111 was attributed to [+C-(CHO)-C=CH-COOH], and the m/z 99 to [(CHO)-C=CH-COOH)]<sup>+</sup>.

Figure 4d shows the by-product  $B_3$  mass spectrum at minute 42.377 and this compound was confirmed by the ion m/z 202. The ion m/z 187 was attributed to losing one methyl group of the [M]+. The ion m/z 157 was attributed to the loss of ion m/z 14 [CH<sub>2</sub>]<sup>+</sup> and monoatomic oxygen (O), in addition to the methyl group of the [M]+. The ion m/z 144 is explained by the structure [HO-(C<sub>6</sub>H<sub>4</sub>)-C-CH-CH=CH]<sup>+</sup>.

Finally, figure 4e shows the by-product  $B_4$  mass spectrum at minute 46.940, where this compound was confirmed by the ion m/z 243 which represents the main fragmentation of a compound with molecular mass of 276 that exhibits a similar behavior like  $B_2$ . The ion m/z 258 was confirmed by the loss of ion m/z 17 [OH]<sup>-</sup>; the ion m/z 243, by the loss of methyl group [CH<sub>3</sub>]+, and the ion m/z 213 by the loss of ion m/z 28 [C=O]<sup>+</sup> and the m/z [OH]<sup>-</sup>. The hypothetical fragments of  $B_4$  are shown in figure 4e.



Mass spectra and fragmentation analysis





Figure 4b. B<sub>1</sub> by-product mass spectrum, found at minute 29.695 and its hypothetical fragments.



Figure 4c.B<sub>2</sub> mass spectrum by-product, found at minute 39.445 and its hypothetical fragments.



Figure 4d.B<sub>3</sub> mass spectrum by-product, at minute 42.377 and its hypothetical fragments.



Figure 4e. B4 mass spectrum by-products, at minute 46.940 and its hypothetical fragments.

Table 1	. Shows th	he molecular	• structure	of each	by-product,	as	well d	as the	main	ions	according	to	the	mass
spectrur	n, its moled	cular structu	re and the	molar ra	itio BPA/O3.									

Compound or by-product	Retention time	More abundant	BPA/O <sub>3</sub> ratio	Molecular structure		
BPA	50.124	228, 213, 119	1/0	NO NO		
B <sub>1</sub> 4-(2-hydroxypropan-2-yl)phenol;	29.684	151, 44, 119, 136	8/1	но		
B <sub>2</sub> (2Z)-3-formyl-4-(4-hydroxyphenyl)- 4-methylpent-2-enoic acid;	39.445	112, 173, 99, 55, 44	1/1	HO		
B <sub>3</sub> (3Z)-2-[1- (4-hydroxyphenyl) ethenyl] pent-3-enal;	42.423	202, 144, 157	8/1	HO		
B <sub>4</sub> 4-[2-(4-hydroxyphenyl) propyl]-1, 3- benzenediol	46.918	243, 258, 213, 44	1/1	HO HO OH		

# By-product degradation mechanisms

 $B_1$  formation (figure 5) is explained assuming that the reaction starts inside the chain of BPA with an •OH initial attack, extracting one hydrogen and forming the radical A, later, the transposition of this radical leads to the formation of 4-isopropenylphenol which reacts with •OH forming  $B_1$ .



Figure 5. Reaction mechanisms to form by-product B<sub>1</sub>.

On the other hand,  $B_4$  formation (figure 6) can happen whether the pathway interacts directly with  $O_3$  or indirectly with •OH. This way, by-product  $B_4$  is an important intermediary for forming by-product  $B_3$ .



Figure 6. H formation mechanisms.

B<sub>2</sub> formations (figures 7) were carried out by •OH on the BPA generating intermediaries E, F, and G to later form B<sub>4</sub> and by hydrogen evolution form I. Finally, from intermediary B<sub>4</sub> through attacks of •OH, B<sub>2</sub> is generated.



Figure 7. B<sub>2</sub> formation mechanisms.

Similarly, the formation starts by •OH attacking H, forming the intermediates (L-X) shown in figure 8.



Figure 8. B<sub>3</sub> formation reaction mechanism adapted from Tay in 2012.

Finally, starting from these compounds found in the chromatograms and specifically in each of its mass spectra, this research paper proposes the following global pathway of BPA degradation to different by-products during ozone and radical's reaction (figure 9).



Figure 9. BPA reaction with O<sub>3</sub>, proposed pathway.

This research identified four by-products from the BPA oxidation (B<sub>1</sub>, B<sub>2</sub>, B<sub>3</sub> and B<sub>4</sub>), which look like dominant transformation products under established experimental conditions.

# 4. Conclusions

The methodology kinetic evaluation of rapid reaction between BPA and O<sub>3</sub>, designed for this research, allowed to identify four main analytes degradation experimentally. Which were generated in the reaction between BPA and O<sub>3</sub>, using the analytic method proposed in this research to identify the degradation products: solid phase extraction, gas chromatography, and mass spectrometry. The by-products chemical structures were observed by the instrumental analysis of GC-ME, based on their m/z ratios and retention times.

The identification of reaction by-products between BPA and  $O_3$  is a valuable contribution of this research, establishing a reaction mechanism of its own. Knowing this by-product degradation mechanism can help design and build treatments processes more efficient; so, this knowledge will allow the generation of lower-risk compounds in the process treatment that have less impact on living beings in ecosystems and humans and ensure the supply of reliable drinking water to the population.

## 5. Acknowledgements

Funding: This research work was funded by National Council of Science and Technology (CONACYT) for supported this research through the grant project 287242.

## **Authors Information**

Ramiro Vallejo Rodríguez <sup>1</sup> - orcid.org/0000-0003-3684-3870 Roberto E. San Juan Farfán <sup>2</sup> - orcid.org/0000-0002-4662-0366 Elizabeth León Becerril <sup>1</sup> - orcid.org/0000-0002-7220-5254 Valeria Ojeda Castillo <sup>3</sup> - orcid.org/0000-0002-1397-0589 Daryl Osuna Laveaga <sup>4</sup> - orcid.org/0000-0001-9735-3627 Valentín Flores Payán <sup>1,5</sup> - https://orcid.org/0000-0003-3849-7107

## **Contribution of the authors**

The authors declare that they contributed equally to the development of the study.

## Interest conflict

The authors declare no conflict of interest.

## References

- Benotti, M.J.; Trenholm, R.A.; Vanderford, B.J.; Holady, J.C.; Stanford, B.D.; Snyder, S.A. Pharmaceuticals and Endocrine Disrupting Compounds in U.S. Drinking Water. 2009, 43, 597–603, doi:10.1021/es801845a. CDHFINECHEMICAL MATERIAL SAFETY DATA SHEET SDS/MSDS Available online: https://www.cdhfinechemical.com/images/product/msds/37\_2113175157\_BisphenolA-CASNO-80-05-7-MSDS.pdf (accessed on Jun 1, 2020).
- Deborde, M.; Rabouan, S.; Mazellier, P.; Duguet, J.P.; Legube, B. Oxidation of bisphenol A by ozone in aqueous solution. Water Res.2008, 42, 4299–4308, doi:10.1016/j.watres.2008.07.015.
- Eaton, A. 4500-O3 B. Indigo colorimetric method. In: Standard methods for the examination of water and wastewater,; APHA, AWWA, W., Ed.; 21 stedn.; Washington, DC, 2005;
- Flores-Payán, V.; León-Becerril, E.; López-López, A.; Vallejo-Rodríguez, R. Novel real-time method using the stopped-flow for evaluating bisphenol A degradation kinetics by molecular ozone and radical mechanisms. Chem. Eng. Commun.2017, doi:10.1080/00986445.2017.1344652.
- Garoma, T.; Matsumoto, S.A.; Wu, Y.; Klinger, R. Removal of Bisphenol A and its Reaction-Intermediates from Aqueous Solution by Ozonation. Ozone Sci. Eng.2010, 32, 338–343, doi:10.1080/01919512.2010.508484.
- Handbook of Environmental Fate and Exposure Data: For Organic Chemicals ... PhilipH. Howard Google Libros Available online:
- Hoigné, J.; Bader, H. Rate constants of reactions of ozone with organic and inorganic compounds in water-II. Dissociating Organic Compounds. Water Res. 1983, 17, 185–194.
- https://books.google.es/books?hl=es&lr=&id=GGlQDwAAQBAJ&oi=fnd&pg=PP1&dq=Howard+(1990).+Hand book+of+environmental+fate+and+exposure+data+for+organic+chemicals,+Lewis+publishers,+Michig an+USA.&ots=UBqKjqRjWZ&sig=aULBzxRCG1xbI4avY577ELTZlOo#v=onepage&q&f=false (accessed on Jun 1, 2020).
- Huber, M.M.; Canonica, S.; Park, G.-Y.; Von Gunten, U. Oxidation of Pharmaceuticals During Ozonation and Advanced Oxidation Processes Oxidation of Pharmaceuticals during Ozonation and Advanced Oxidation Processes. Environ. Sci. Technol.2003, 37, 1016–1024, doi:10.1021/es025896h.

- Jabesa, A., & Ghosh, P. (2022). Oxidation of bisphenol-A by ozone microbubbles: effects of operational parameters and kinetics study. Environmental Technology & Innovation, 26, 102271.
- Kosky, P.G.; Silva, J.M.; Guggenheim, E.A. The Aqueous Phase in the Interfacial Synthesis of Polycarbonates. 1. Ionic Equilibria and Experimental Solubilities in the BPA-NaOH-H2O System. Ind. Eng. Chem. Res.1991, 30, 462–467, doi:10.1021/ie00051a005.
- Lee, J.; Park, H.; Yoon, J. Ozonation characteristics of bisphenol a in water. Environ. Technol.2002, 24, 241–248, doi:10.1080/09593330309385555.
- López-López, A.; Flores-Payán, V.; León-Becerril, E.; Hernández-Mena, L.; Vallejo-Rodr?guez, R. Competitive kinetics versus stopped flow method for determining the degradation rate constants of steroids by ozonation. Springerplus2016, 5, doi:10.1186/s40064-016-2782-4.
- López-López, A.; Pic, J.S.; Debellefontaine, H. Ozonation of azo dye in a semi-batch reactor: A determination of the molecular and radical contributions. Chemosphere2007, 66, 2120–2126, doi:10.1016/j.chemosphere.2006.09.025.
- Pavia, D. L., Lampman, G. M., Kriz, G. S., & Vyvyan, J. A. (2014). Introduction to spectroscopy. Cengage learning.
- Staples, C. a; Dom, P.B.; Klecka, G.M.; Sandra, T.O.; Harris, L.R. A review of the environmental fate, effects, and exposures of Bisphenol A. Chemosphere1998, 36, 2149–2173, doi:10.1016/S0045-6535(97)10133-3.
- Takeuchi, T.; Tsutsumi, O. Serum Bisphenol A Concentrations Showed Gender Differences, Possibly Linked to Androgen Levels. Biochem. Biophys. Res. Commun.2002, 291, 76–78, doi:10.1006/bbrc.2002.6407.
- Tay, K.S.; Rahman, N.A.; Abas, MR Bin Degradation of bisphenol A by ozonation: Rate constants, influence of inorganic anions, and by-products. Maejo Int. J. Sci. Technol.2012, 6, 77–94.
- Umar, M.; Roddick, F.; Fan, L.; Aziz, H.A. Application of ozone for the removal of bisphenol A from water and wastewater A review. Chemosphere2013, 90, 2197–2207, doi:10.1016/j.chemosphere.2012.09.090.
- USEPA Environmental Endocrine Disruption: An effects assessment and analysis; 1997; Vol. 106;.
- Vallejo-Rodríguez, R.; Murillo-Tovar, M.; Navarro-Laboulais, J.; León-Becerril, E.; López-López, A. Assessment of the kinetics of oxidation of some steroids and pharmaceutical compounds in water using ozone. J. Environ. Chem. Eng.2014, 2, 316–323, doi:10.1016/j.jece.2013.12.024.
- Vandenberg, L.N.; Maffini, M. V.; Sonnenschein, C.; Rubin, B.S.; Soto, A.M. Bisphenol-a and the great divide: A review of controversies in the field of endocrine disruption. Endocr. Rev.2009, 30, 75–95, doi:10.1210/er.2008-0021.
- von Gunten, U.; Laplanche, A. Oxidation and Desinfection with Ozone, an overview. Proceeding Fundam. Eng. Concepts Ozone React. Des.2000, 39–45.
- Yong, E.L.; Lin, Y.P. Kinetics of Natural Organic Matter as the Initiator, Promoter, and Inhibitor, and Their Influences on the Removal of Ibuprofen in Ozonation. Ozone Sci. Eng.2013, 35, 472–481, doi:10.1080/01919512.2013.820641.
- Zhang, H., He, Y., Lai, L., Yao, G., & Lai, B. (2020). Catalytic ozonation of Bisphenol A in aqueous solution by Fe3O4–MnO2 magnetic composites: Performance, transformation pathways and mechanism. Separation and Purification Technology, 245, 116449.