

## Ozonation for the removal of bisphenol A

Michael Emmanuel Mutseyekwa, Şifa Doğan and Saltuk Pirgaloğlu

### ABSTRACT

The mechanism of byproduct formation and oxidation pathway of bisphenol A (BPA) during ozonation process have been compared under acidic, neutral and alkaline conditions at an applied ozone dose of  $5.3 \text{ mg}\cdot\text{L}^{-1} \text{ min}^{-1}$ . Alkaline conditions promoted the fastest removal and the pseudo first-order reaction rate constant was calculated as  $0.15 \text{ min}^{-1}$ . Complete removal under alkaline conditions (after 30 minutes of reaction time) was achieved with  $1.59 \text{ mg}$  ozone per  $\text{mg}$  BPA and 52% mineralization was achieved at  $6.04 \text{ mg}$  ozone application per  $\text{mg}$  total organic carbon (after 90 minutes of reaction time). Hydroxyl radical dominated degradation pathway (pH 10) resulted with opening of ring-structured products into *Heptanoic acid, methyl ester*. Sixty per cent BPA removal occurred under acidic conditions where the ozone was dominant and formation of *Cyclohexene-1-carboxylic acid, ethyl ester, Benzaldehyde, 4-hydroxy-3,5-dimethyl- and 2-Phenylbenzoquinone* were evidenced. Despite the fact that complete removal was achieved under neutral conditions, mineralization was not remarkable and both hydroxyl radical and ozone-based degradation pattern was evidenced after the treatment.

**Key words** | bisphenol A, byproduct formation, degradation kinetics, ozonation, pH effect

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### INTRODUCTION

Over 2.7 billion kilograms of bisphenol A (BPA) is produced worldwide every year (Vandenberg *et al.* 2007). Of this, 99.9% of BPA is used for the production of polycarbonate plastic, epoxy resin and other plastic products (Staples *et al.* 1998). It is consumed in a wide range of products for different purposes including optical lenses, thermal paper, protective coating, automotive lenses, electrical parts, building materials, compact disks, flame retardants and in the linings inside cans. During manufacture, handling and transportation, BPA is released into the environment as dust and other emissions, inefficiently treated industrial wastewaters and leaching through the landfill applications of the solid wastes (Staples *et al.* 1998). BPA has been detected in surface and groundwater at various magnitudes of concentrations such as  $0.05\text{--}27 \text{ }\mu\text{g}\cdot\text{L}^{-1}$  (Ning *et al.* 2007; Huang *et al.* 2012; Liang *et al.* 2015). BPA was also detected in landfill leachate  $3.61 \text{ mg}\cdot\text{L}^{-1}$  in Germany,  $740 \text{ ng}\cdot\text{L}^{-1}$  in Japan (Vandenberg *et al.* 2007) and  $17.2 \text{ mg}\cdot\text{L}^{-1}$  as reported by Escalona *et al.* (2014).

The European Union (EU) Commission set a new mechanism to monitor potentially polluting substances in aquatic environments to protect human health and the aquatic

environment. BPA has been listed in Directive 2013/39/EU in a watch list of compounds which pose risks to aqueous organisms and mammals and which have no information to model their exposure data to decide whether to prioritize the substance. The greatest concern about BPA in the environment is that it has been identified as an endocrine disrupting chemical, specifically a xenoestrogen, which is a class of chemicals that interfere with the natural operation of estradiol and other endogenous estrogens and cause disruption in hormonal system (Wozniak *et al.* 2005).

The BPA molecule is made up of two phenol moieties that are attached to an acetone molecule. BPA is solid in room temperature and has a melting point of  $155 \text{ }^\circ\text{C}$ . It has measurable vapor pressure ( $5.3 \times 10^{-6} \text{ Pa}$ ) and is not often present in its gaseous form in the environment. It is moderately hydrophobic ( $\log K_{ow} = 3.64$ ) and has water solubility  $172 \text{ mg}\cdot\text{L}^{-1}$  at  $25 \text{ }^\circ\text{C}$ . It is not ionized at environmental pH levels and has  $\text{pK}_a$  value around 9.59–11.30 (Environmental Protection Agency EPI SUITE). Treatment of BPA is difficult by conventional wastewater treatment methods because of its ring structure that poses toxicity to microorganisms, low solubility in water and low vapor

pressure which enables molecules to escape from primary and secondary treatment facilities.

In the literature, efforts were given to adapt and use microorganisms or part of living organisms such as enzymes to overcome BPA pollution from waters. These processes required long reaction times and a controlled environment which creates insufficient conditions to use in real wastewater treatment plants (Staples *et al.* 1998; Kang & Kondo 2002; Kamaraj *et al.* 2014; Peng *et al.* 2015).

Advanced oxidation processes (AOPs) have been extensively used in literature in order to remove BPA from water matrices with sufficient removal rate and reaction time. Photolysis and photocatalytic processes (Chiang *et al.* 2004; Kaneco *et al.* 2004; Zhou *et al.* 2004; Wang *et al.* 2009; Gao *et al.* 2010; Subagio *et al.* 2010; Bechambi *et al.* 2015) promoted high degradation after typical 90–120 minutes reaction time; however, longer times, such as 11–24 hours, were required for reasonable mineralization rates for BPA removal under 90–120 minutes reaction period (some cases 24 hours), various types and amounts of catalyst (TiO<sub>2</sub>, Zr-TiO<sub>2</sub>, carbon-doped ZnO), different temperatures, pH conditions and different UV-visible irradiation ( $\lambda = 355$  nm,  $\lambda = 254$  nm,  $\lambda = 465$  nm,  $\lambda = 523$  nm,  $\lambda = 589$  nm).

Ozonation process is a frequently applied technique in drinking water and wastewater treatment plants to eliminate recalcitrant compounds such as BPA. In literature, studies have been carried out to investigate the degradation mechanism of BPA by ozonation. Catalytic and non-catalytic applications resulted in fast and efficient removal of BPA from aqueous solutions (Deborde *et al.* 2008; Garoma & Matsumoto 2009; Schaar *et al.* 2010; Bertanza *et al.* 2013; Keykavoos *et al.* 2013; Kusvuran & Yildirim 2013). As much as 90% mineralization has been achieved by high dose ozone and catalyst applications (Keykavoos *et al.* 2013). Also, ozonation was combined with UV photolysis to achieve greater efficiencies, resulting in 80–100% mineralization (Oyama *et al.* 2009; Rodriguez *et al.* 2012; Sharma *et al.* 2015).

In this study, more efforts have been given to reveal the mechanism of BPA elimination, degree of mineralization and identification of byproducts under three different pH conditions: acidic, neutral and basic. Despite the fact that it is frequently used for the treatment of BPA, previous studies only monitored the degradation products under certain experimental conditions. Kusvuran & Yildirim (2013) monitored byproducts only under pH 3 conditions after the treatment of aqueous solutions containing 116.4 mg·L<sup>-1</sup> BPA by supplying 11.5 mg·min<sup>-1</sup> gaseous

ozone. Deborde *et al.* (2008) revealed the byproduct formation mechanism at pH 6.5 with 22.8 mg·L<sup>-1</sup> BPA concentration in 100 ml of aqueous solution by supplying 9.6 mg ozone gas. Also, Gültekin *et al.* (2009) monitored the byproduct formation at pH 6 by supplying high dose of ozone (4.05–10.3 mg·L<sup>-1</sup>) into 91 mg·L<sup>-1</sup> BPA containing aqueous solutions. This study focuses not only on revealing the optimum conditions to remove BPA molecules but also on the identification of byproducts under three representative pH conditions to propose the BPA elimination pathway during the ozonation process. It also identifies byproducts analyzed by EPA's database (Environmental Protection Agency EPI SUITE) to represent their potential toxicity values.

## MATERIALS AND METHODS

### Materials

BPA (97% purity, for synthesis), ortho-phosphoric acid (85%, guaranteed reagent (GR) for analysis), sodium thiosulfate (97%, anhydrous), potassium iodide (Emprove\* api, suitable for use as an active pharmaceutical ingredient), sodium chloride (99.5%, for analysis), sodium sulfate (99.0–100.5%, anhydrous suitable for use as excipient), sodium dihydrogen phosphate monohydrate (98.0–100.5%, suitable for use as an excipient), sulfuric acid (98%, reagent grade), dichloromethane (99.9%, for liquid chromatography), acetic acid (glacial, 100%, anhydrous for analysis), acetonitrile (99.9%, gradient grade for liquid chromatography), sodium carbonate (anhydrous), sodium hydrogen carbonate and potassium hydrogen phthalate were all products of Merck Millipore, Germany and were supplied by Tin Chemical and Laboratory Supplies and Devices, Turkey. Sodium hydroxide (98–100%, pellets, analytical grade) and hydrochloric acid (36.5–38%, analytical grade), potassium indigo trisulfonate (ozone scavenging reagent) and starch (reagent grade) were products of Sigma-Aldrich chemicals and purchased from Tin Chemical and Laboratory Supplies and Devices, Turkey. GL Sciences Inertsil ODS-4 5  $\mu$ m, 4.6  $\times$  250 mm C<sub>18</sub> column and a silica column coated with 5% dimethyl-95% diphenylpolysiloxane with 30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m dimensions were supplied from Teknokroma and purchased from Ant Teknik Turkey. Gaseous ozone was supplied from OPAL 400 type bench ozone generator and maintained from Tin Chemical and Laboratory Supplies and Devices, Turkey.

## Experimental setup

100 mg BPA was dissolved in 1 L under neutral pH conditions overnight to provide complete dissolution of BPA in water medium. Ozonation experiments were conducted with 100 mg·L<sup>-1</sup> aqueous BPA solutions in an Erlenmeyer flask having 2-L capacity. Gaseous ozone was supplied by a bench-type ozone generator with a rate of 5.3 mg·min<sup>-1</sup>. Gaseous ozone concentration was 25 ± 3 mg·L<sup>-1</sup> and saturated dissolved ozone concentration was found as 0.3 ± 0.1 mg·L<sup>-1</sup>. Reactor was placed on a stirrer for mixing. pH of the solution was measured and adjusted throughout the experiment by addition of 1% HCl and 1% NaOH solutions. There was no change in pH values before and after each experiment. 15 mL samples were collected during ozonation experiment at 0, 1, 3, 5, 7, 10, 25, 45, 60 and 90 minutes for concentration (high-performance liquid chromatography, HPLC) and mineralization (total organic carbon, TOC) analyses. 150 mL of the treated effluents at the end of the ozonation process were used for liquid-liquid extraction in order to identify by products in gas chromatography-mass spectrometry (GCMS).

## Analytical methods

Gaseous ozone concentration has been measured by potassium iodide method (Erol 2008) and dissolved ozone concentration was determined by indigo colorimetric methods (APHA/AWWA/WEF 2004). BPA concentration measurements were conducted by Shimadzu HPLC coupled with UV-vis detector. In HPLC method, 60:40 water:acetonitrile mobile phase was sent to a C<sub>18</sub> column (GL Sciences Inertsil ODS-4 5 μm, 4.6 × 250 mm) at 1 mL/min flow rate. Injection volume of samples was 100 μL, column oven temperature was set to 40 °C and UV detection was made at 278 nm wavelength. For pH 3 and 7 where BPA showed two prominent peaks at 15 and 17.5 minute retention time in standard solutions, first peak was found to be more reliable in calculation of BPA. Limit of Detection and Limit of Quantification for BPA concentration measurement by HPLC was calculated as 5 mg·L<sup>-1</sup>. Mineralization measurement was done by TOC Analyzer (Shimadzu, V<sub>CPN</sub> TOC-analyzer) by Non Purgeable Organic Carbon (NPOC) method (TOC-V<sub>CPN</sub> User's Manual). Limit of detection for TOC measurement was calculated as 1 mg·L<sup>-1</sup> and Limit of Quantification was 5 mg·L<sup>-1</sup>. Byproduct determination was conducted by GCMS (Shimadzu, GCMS 2010 Plus). Samples were extracted into organic phase before injection to the GCMS. The extraction of BPA molecules from water phase

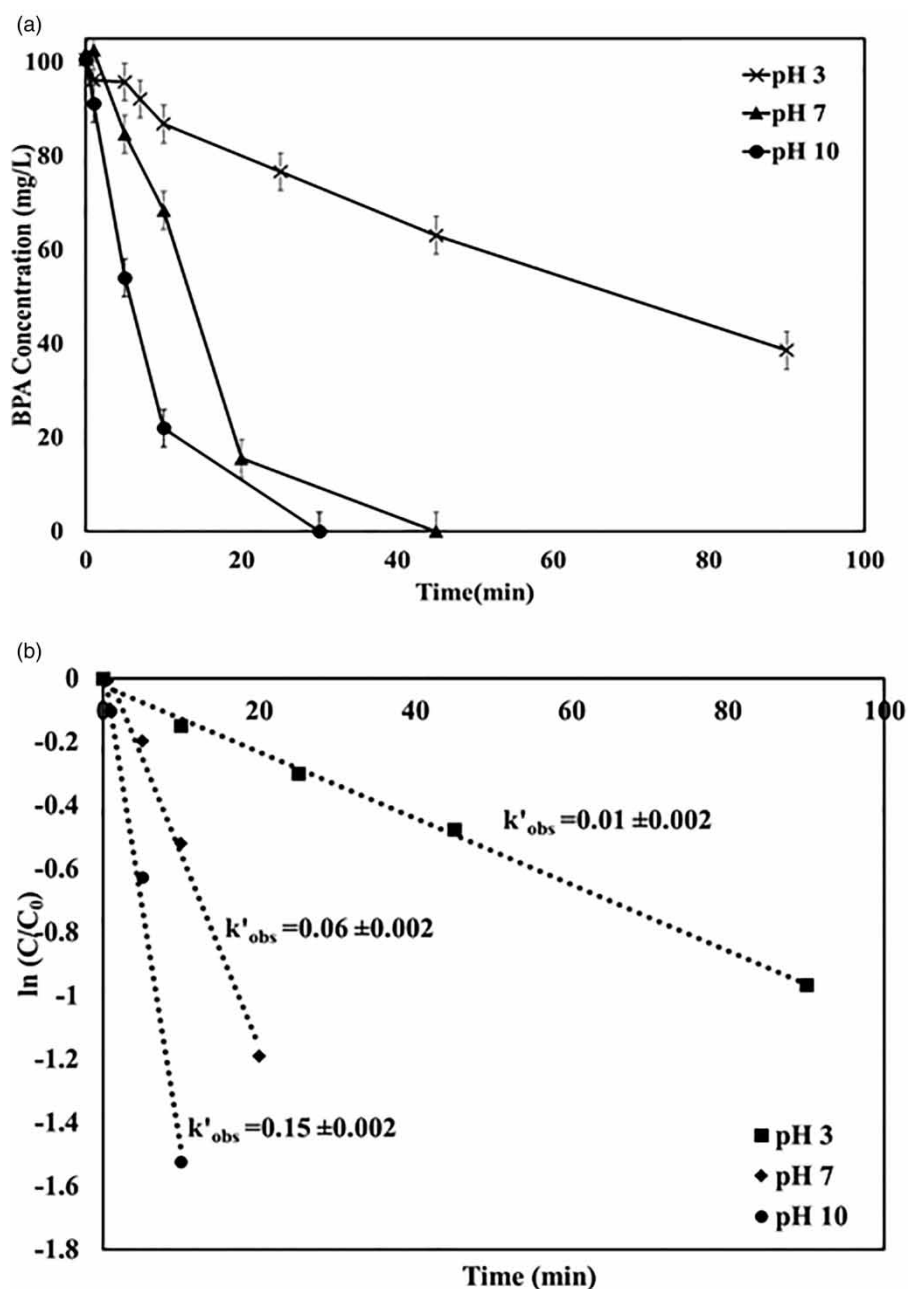
to organic phase has been followed by the methods given in literature (Kusvuran & Yildirim 2013). 50 mL of the sample was placed into an extraction flask. 3 mL of dichloromethane and 0.5 g of sodium chloride was added into the solution. The mixture was vigorously shaken for 1 minute and left for extraction for 5 minutes. Dichloromethane portion that contained BPA was been collected in a separate container. This procedure was repeated 3 times with 50 mL of treated effluents, and the dichloromethane extracts were separated. Finally, 0.4 g of sodium sulfate was added to the extracted dichloromethane and left for 20 minutes to remove any excess water in the solution. After 20 minutes the liquid part was taken by a syringe and filtered for GCMS analysis. A silica column, coated with 5% dimethyl-95% diphenylpolysiloxane having 30 m × 0.25 mm × 0.25 μm dimensions was used for chromatographic separation. Helium was used as the carrier gas at a flow rate of 1 mL·min<sup>-1</sup>. The temperature program for chromatographic separation was set as follows: initial temperature 100 °C was increased to 260 °C at a 5 °C/min rate. Injection temperature and interface temperatures were 260 °C and ion source temperature was kept at 250 °C. The detector voltage was adjusted relatively after a tuning test. Prior to GCMS analysis, a PFTBA (perfluorotriethylamine) analytical standard was used to correct the mass axis alignments.

## RESULTS AND DISCUSSION

### Effect of pH on BPA removal

In this study, three different pH values (3, 7 and 10) were used to study the BPA removal by ozonation. A relatively sharp decline in BPA concentration was observed within the first 10 minutes of ozonation at pH 10 where concentration decreased from 100 to 22 mg·L<sup>-1</sup> (Figure 1(a)). Further degradation of BPA occurred at a slower rate until 30 minutes where the concentration decreased below the detection limit. Since the reaction rate decreases with decreasing reactant concentration (less contact between BPA and radicals) this trend can be explained by the presence of fewer amounts of BPA molecules as the ozonation process proceeded. Byproducts that were formed during the oxidation process may also lower the degradation rate of BPA by competing for oxidizing species (Kusvuran & Yildirim 2013).

The complete degradation of BPA under pH 7 had a longer reaction time compared to pH 10 conditions (Figure 1(a)). This difference can be explained by the



**Figure 1** | BPA removal by ozonation under different pH conditions ( $C_{\text{BPA}} = 100 \text{ mg}\cdot\text{L}^{-1}$ ,  $C_{\text{O}_3} = 5.3 \text{ mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$ ).

relative abundance of oxidative species in solution during ozonation at different pH values. As pH increases, the production of hydroxyl radicals is favored compared to direct ozone oxidation (Pirgalioglu & Özbelge 2009). Under acidic conditions, BPA was not totally degraded even after 90 minutes of ozonation, and  $39 \text{ mg}\cdot\text{L}^{-1}$  BPA was still remaining in the solution (Figure 1(a)). Hydroxyl radicals are non-selective and have a higher oxidation

potential than molecular ozone. This can be the reason for the decrease observed in removal efficiency under acidic conditions.

Decomposition rate of molecules by oxidation are generally expressed as first order reactions in the literature (Kusvuran & Yildirim 2013; Umar *et al.* 2013). Ozonation of BPA in this study also obeyed pseudo first-order reaction kinetics model as represented in Figure 1(b). Reaction rate

equation was derived by assuming a constant ozone concentration (ozone was continuously fed to the system) throughout the oxidation process. Rate equations are given in Equations (1) and (2):

$$\frac{dC_{BPA}}{dt} = -r_{BPA} = k'_{obs} \cdot C_{BPA} \quad (1)$$

$$\frac{\ln C_{BPA}}{\ln C_{BPA0}} = -k'_{obs} t \quad (2)$$

The slope of the linear line given in Equation (2) represents the observed pseudo first-order reaction rate constants ( $k'_{obs}$ ).  $k'_{obs}$  values are given in Figure 1(b) for each pH condition and the highest rate constant was observed at pH 10 due to the presence of hydroxyl radicals. It should be noted that observed (experimental) pseudo first-order reaction rate constants do not represent real rate constants. Direct usage of these data, which were obtained from laboratory scale set-ups for design and scale up purposes, is not possible for ozonation applications. These constants depend on ozone concentration in the medium which changes by various parameters in each reaction system. It is also a useful and common practice in research articles to present these data in order to compare decomposition rate of the target pollutants which are obtained by different techniques.

## Mineralization of BPA

TOC was monitored during the ozonation of BPA in order to reveal the degree of mineralization. Figure 2 shows the percentage of TOC removal with respect to ozonation time under various pH conditions. Similar to the trend observed in degradation, the rate of TOC removal under alkaline conditions was very high within the first 30 minutes of the reaction. TOC removal was calculated as 52% after 30 minutes. The mineralization percentage did not change considerably during the rest of the process. This indicates that there is a formation of stable byproducts that resist ozonation even up to 90 minutes of reaction. Several other studies also involving non-catalytic ozonation at pH 10 have not achieved high degrees of mineralization (Umar et al. 2013). In terms of TOC removal, pH 7 recorded a significantly lower TOC removal percentage after 90 minutes compared to pH 10. Similarly, this can be explained by the phenomenon that there is a high tendency for hydroxyl radical formation during ozonation under alkaline conditions. TOC removal mainly occurred within the first 7 minutes of the reaction as shown in Figure 2. During this period 9% TOC removal was achieved and only a further 1% was removed up to 90 minutes. TOC removal was relatively low at pH 3. The maximum TOC removal percentage achieved was 10% after 90 minutes as shown in Figure 2. This was similar to the reaction at pH 7; however, unlike at pH 7, most of the mineralization occurred after

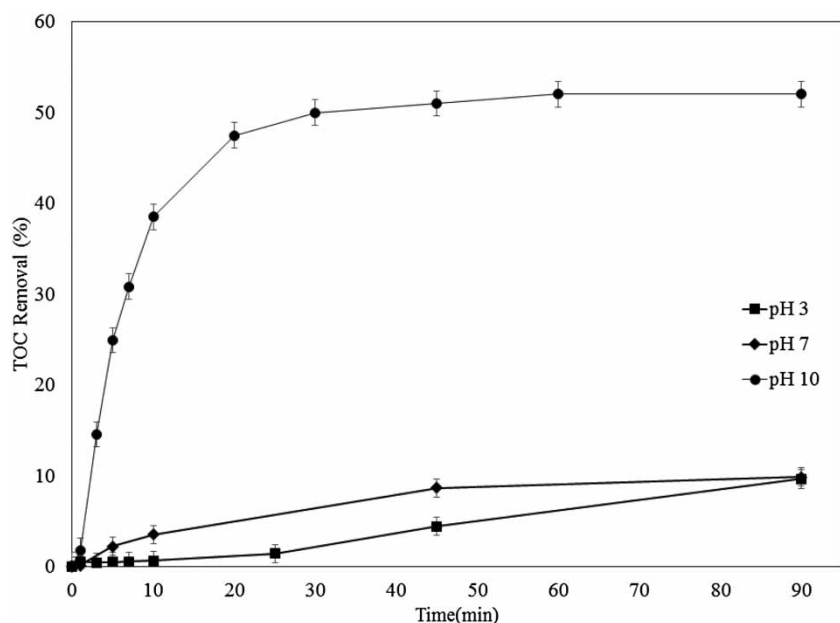
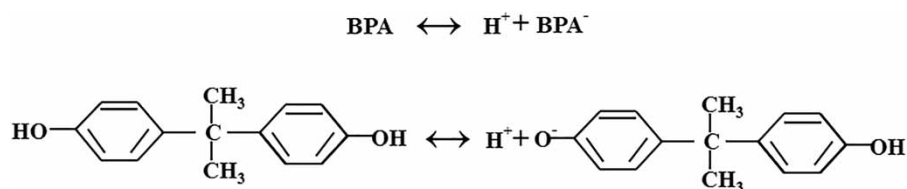


Figure 2 | TOC removal percentage under various pH conditions ( $C_{BPA} = 100 \text{ mg}\cdot\text{L}^{-1}$ ,  $C_{O_3} = 5.3 \text{ mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$ ).



**Figure 3** | Dissolution of BPA in water.

20 minutes. This trend suggests a different mineralization mechanism for BPA in each case. Proposed degradation pathways are investigated further in the next section.

### Ozonation mechanism and byproducts

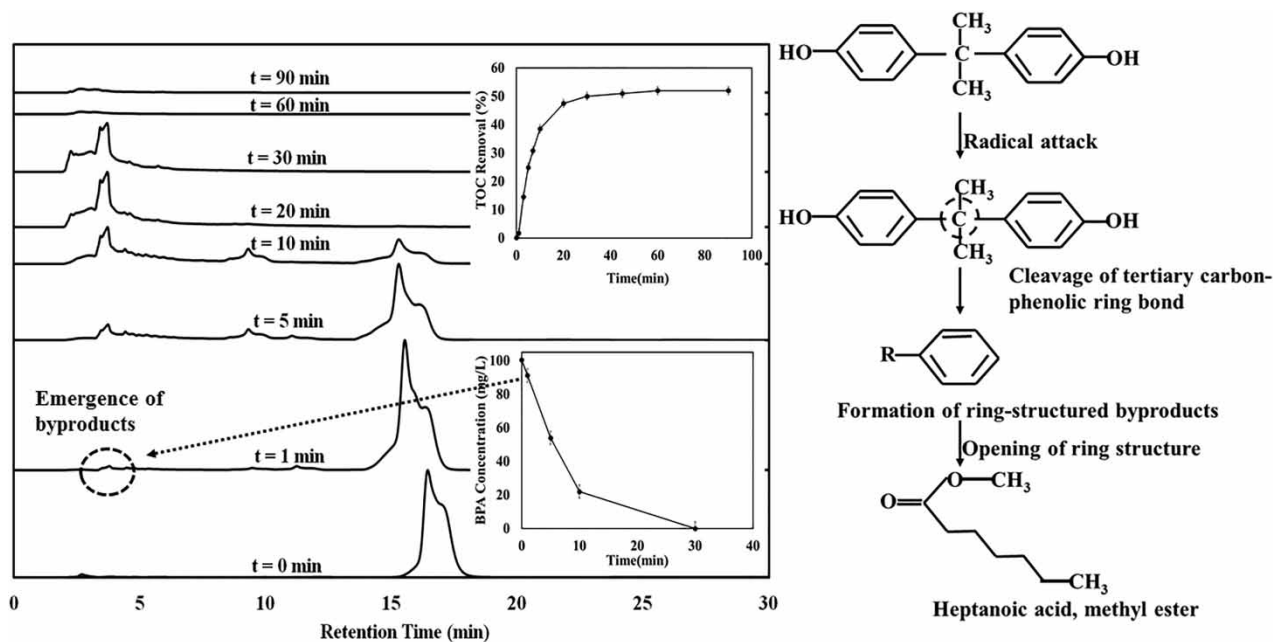
BPA is a weak acid and it gives an  $\text{H}^+$  ion to the solution when it is dissolved in water (Tay *et al.* 2012) as shown in Figure 3.

The position of the equilibrium and the dominant species under various pH conditions can be obtained from the Henderson–Hasselbalch equation and the adjusted equation for the BPA dissolution in water is given as follows (Skoog *et al.* 2014):

$$K_a = \frac{[\text{H}^+][\text{BPA}^-]}{[\text{BPA}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{BPA}^-]}{[\text{BPA}]}$$

In the literature, two  $\text{p}K_a$  values of BPA have been estimated (Tay *et al.* 2012). One, corresponds to the conditions when BPA loses one  $\text{H}^+$  which is 9.59 and the second is when BPA loses two  $\text{H}^+$  atoms which is 11.30. The comparison between the  $\text{p}K_a$  value and the pH of the reaction solution can supply useful information about the dominant species of the target during the ozonation process or more simply it will show the position of the equilibrium. Also, it helps to predict more accurate comments for the obtained chromatograms. Ozonation processes were conducted under three different pH conditions which were 3, 7 and 10. When pH of the solution is equal to  $\text{p}K_a$  value of the BPA, the molar ratio between  $[\text{BPA}]:[\text{BPA}^-]$  is 1 which means the dominant species in the solution is the ionic BPA molecule. Therefore, under pH 10 conditions it is assumed that ionic BPA molecules are dominant. However, when the solution's pH values were adjusted to 3 and 7, both ionic and nonionic species were present in the medium. In the chromatogram in Figure 4, the peak at



**Figure 4** | HPLC chromatograms and degradation pathway of BPA by ozonation under alkaline conditions.

15.5 minute retention time represents the ionized BPA molecule as previously observed in the literature (Brugnera *et al.* 2010). HPLC chromatograms during ozonation of BPA solution under pH 10 (Figure 4) showed two peaks at 3.5 and 9 minutes which can be attributed to byproducts produced during ozonation as a result of BPA decomposition. The byproducts are more polar than the BPA molecule as they appeared earlier than the BPA in a reversed phase HPLC system. In addition, they have appeared in a 278 nm wavelength scan which indicates that they might contain phenol ( $\lambda_{\max} = 270\text{--}273$  nm), benzene ( $\lambda_{\max} = 268$  nm) or benzoic acid ( $\lambda_{\max} = 275$  nm) moieties in their structures (Ziylan *et al.* 2014). They appeared as early as the first minute of ozonation, their intensities increased as the reaction progressed and they vanished after 45 minutes. However, TOC removal stayed constant after 20 minutes, which indicates that it is possible to oxidize byproducts that appeared on HPLC chromatogram. However, their oxidation might result in formation of some other more resistant molecules. In order to search these formations, GCMS chromatogram after 90 minutes of ozonation of  $100\text{ mg}\cdot\text{L}^{-1}$  BPA solution was evaluated (Figure 5). One apparent peak with a mass spectrum containing 74.05 amu (41.12), 87.05 amu (27.45), 43.05 amu (11.76), 55.05 amu (10.83), 143.10 (9.29) mass to charge ratios, which were identical for *Heptanoic acid, methyl ester* (BP4), was identified. This compound was still present at the end of the reaction and its physico-chemical details are given in

Table 1. The outcomes from both HPLC and GCMS chromatograms were evaluated and the degradation pathway for BPA removal by ozonation under pH 10 condition was proposed in Figure 4. It started with the cleavage of the tertiary carbon-phenolic ring bond (Deborde *et al.* 2008) and ended with opening of ring structure to form organic acids.

HPLC chromatogram revealed that there were 7 peaks besides main BPA peaks (two prominent peaks at 15 and 17.5 min) which can be attributed to byproduct formation during BPA degradation by ozonation under neutral conditions (Figure 6). It was previously noted that hydroxyl radical generation increases with increasing pH, therefore a decrease in BPA decomposition rate at neutral conditions with respect to alkaline conditions can be explained with lower hydroxyl radical concentration in the medium. After 5 minutes of ozonation some other peaks with retention times of 3.5, 4, 5, 5.25, 6, 9 and 10.2 minutes were observed (Figure 6) until 60 minutes when BPA peaks vanished along with most of the other peaks except those at 3.5, 4 and 5.25 minutes which were still present in chromatogram 90 minutes of ozonation. Chromatographic separation occurred at 278 nm wavelength and so those peaks might contain phenol, benzene or benzoic acid moieties in their structure (Ziylan *et al.* 2014). Previous studies have also revealed that under neutral conditions ozonation of BPA produces phenols containing acidic functional groups, alcohol product or benzoquinone, which occurs after the cleavage of tertiary carbon-phenolic ring bond (Deborde *et al.* 2008). It

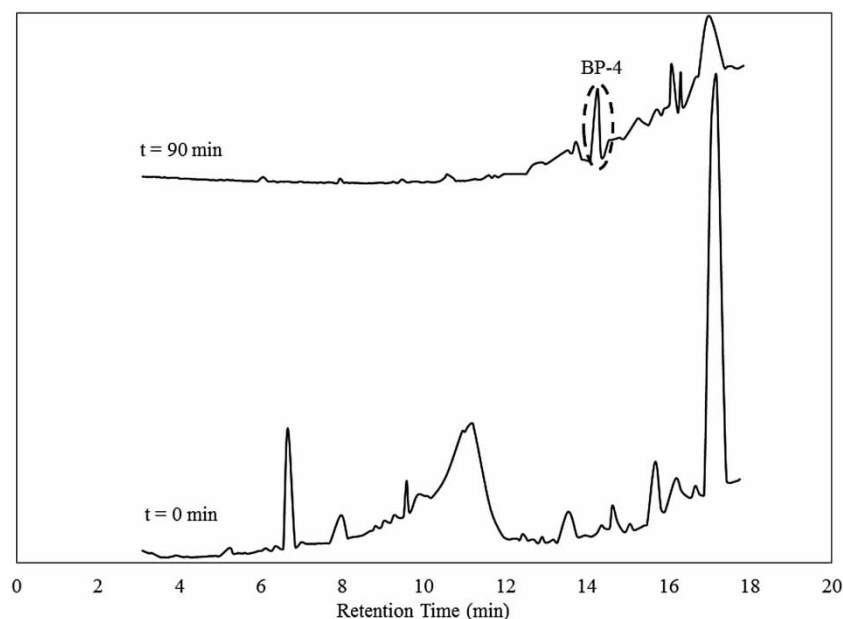


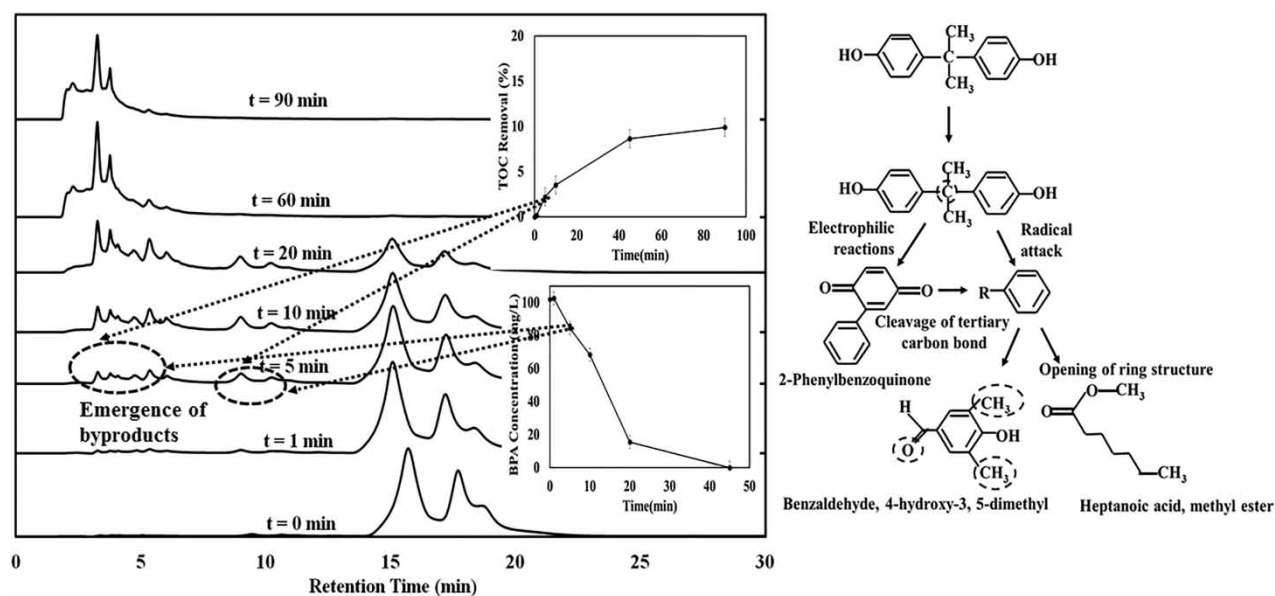
Figure 5 | GCMS chromatogram of ozonated BPA solutions at pH 10 ( $C_{\text{BPA}} = 100\text{ mg}\cdot\text{L}^{-1}$ ,  $C_{\text{O}_3} = 5.3\text{ mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$ ).

**Table 1** | Physico-chemical details of observed byproducts (Environmental Protection Agency EPI SUITE)

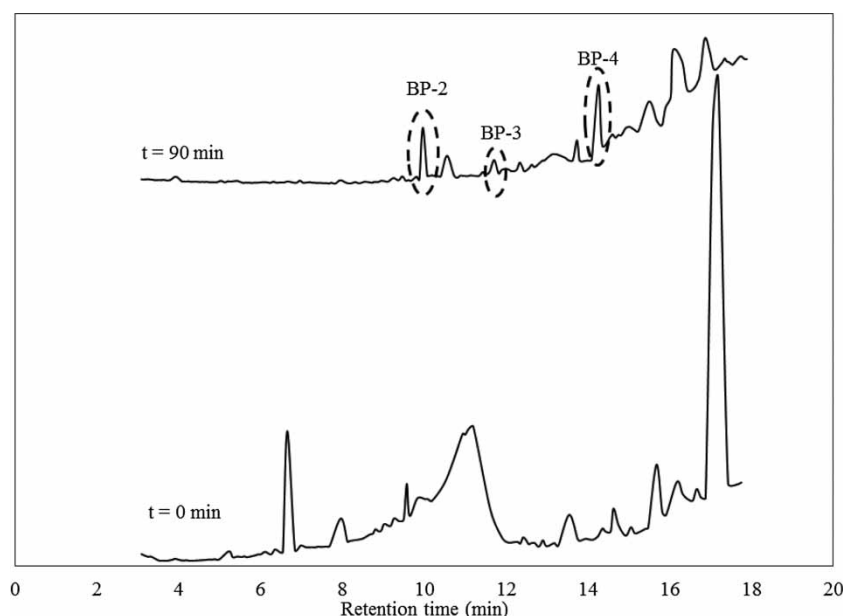
Byproduct	Name	Molecular formula	Molecular weight (g/mol)	m/z (amu)	pH	Water solubility (mg·L <sup>-1</sup> ) at 25 °C	Log K <sub>ow</sub>	EC <sub>50</sub> (ppm) Green Algae
BP1	3-Cyclohexene-1-carboxylic acid, ethyl ester	C <sub>9</sub> H <sub>14</sub> O <sub>2</sub>	154	28.00 (100)	3	233.8	2.92	4.41
				40.00 (3.60)				
				77.05 (2.03)				
				103.05 (1.38)				
				79.05 (1.27)				
BP2	Benzaldehyde, 4-hydroxy-3, 5-dimethyl-	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	150	149.05 (52.41)	3,7	9,526	0.88	120
				150.05 (6.71)				
				65.05 (4.37)				
				121.05 (4.30)				
				77.05 (1.95)				
BP3	2-Phenylbenzoquinone	C <sub>12</sub> H <sub>8</sub> O <sub>2</sub>	184	187.10 (29.22)	3,7	1,135	2.01	0.54
				119.05 (6.16)				
				55.05 (1.44)				
				157.10 (1.18)				
				81.05 (1.11)				
BP4	Heptanoic acid, methyl ester	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	144	74.05 (41.12)	7,10	309	2.83	4.7
				87.05 (27.45)				
				43.05 (11.76)				
				55.05 (10.83)				
				143.10 (9.29)				

can be observed from Figure 6 that the peaks that can be attributed to byproducts emerge at 5 minutes – the same time when TOC removal starts to increase and first considerable decrease in BPA concentration is observed (85 mg·L<sup>-1</sup>). This observation may indicate that both ozone and hydroxyl radicals attack BPA molecules and its byproducts. However, degree of mineralization was lower for pH 7 and pH 3 where only 10% TOC removal was achieved. This indicates

that hydroxyl radicals are more effective in oxidation of byproducts. Three byproducts were monitored by GCMS chromatogram after 90 minutes of ozonation (Figure 7). Byproducts can be listed as *Benzaldehyde, 4-hydroxy-3, 5-dimethyl-* (BP2), *2-Phenylbenzoquinone* (BP3), *Heptanoic acid, methyl ester* (BP4). Detailed information for the observed byproducts in GCMS is given in Table 1. The main difference of the degradation pathway of BPA under pH 7

**Figure 6** | HPLC chromatograms and degradation pathway of BPA by ozonation under neutral conditions.



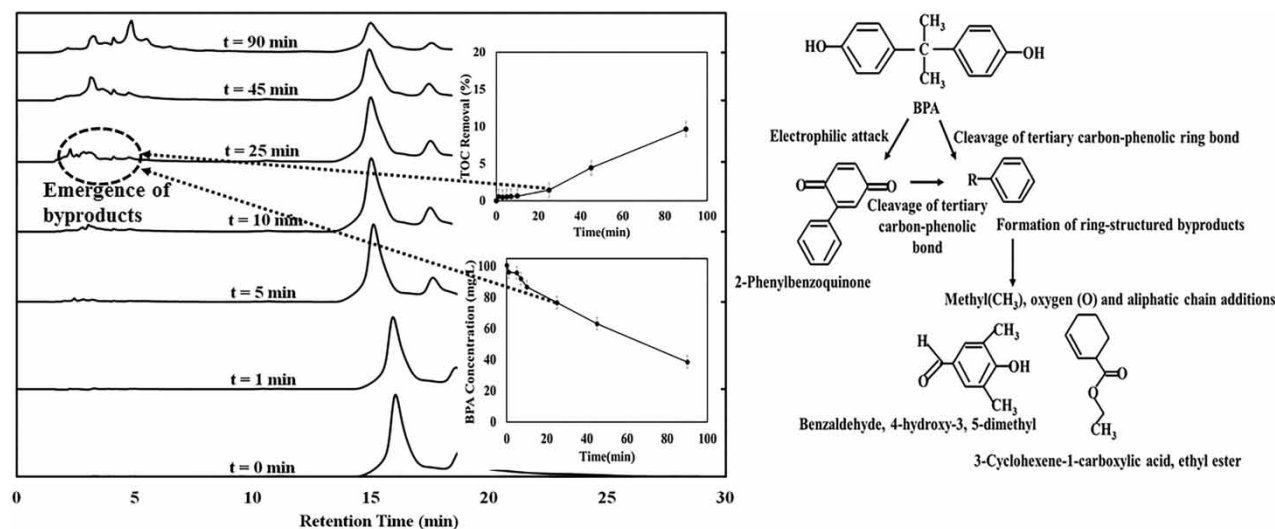


**Figure 7** | GCMS chromatogram of ozonated BPA solutions at pH 7 ( $C_{\text{BPA}} = 100 \text{ mg}\cdot\text{L}^{-1}$ ,  $O_{3(\text{g})} = 25 \text{ mg}\cdot\text{L}^{-1}$  and  $O_{3(\text{aq})} = 0.3 \text{ mg}\cdot\text{L}^{-1}$ ).

condition is the electrophilic reaction between ozone and BPA's aromatic structure containing  $-\text{OH}$  functional group (Spartan Environmental Technologies) which results with hydrogen abstraction (*2-Phenylbenzoquinone* formation). Another pathway was the cleavage of the tertiary carbon-phenolic ring bond which was also observed under alkaline pH conditions. This might initiate the formation of byproducts that contains ring products. Moreover, addition/subtraction of methyl ( $\text{CH}_3$ ), oxygen (O) and hydroxide group (OH) was also involved when *Benzaldehyde*, *4-hydroxy-3,5-dimethyl-* are formed. At neutral conditions both ozone

and radical species can be found in the medium which can explain the observed byproducts. The evidence for the cleavage of ring formation was also monitored by the presence of *Heptanoic acid, methyl ester*. The proposed degradation pathway for BPA under pH 7 conditions by ozonation is shown in Figure 6. Because of the liquid-liquid extraction done prior to GCMS analysis, BPA appeared as a small peak in pH 7 and 10 chromatograms due to the enrichment that had occurred.

Figure 8 shows the BPA removal under acidic conditions. Byproducts emerged at 25 minutes and TOC



**Figure 8** | HPLC chromatograms and degradation pathway of BPA by ozonation under acidic conditions.

removal started to increase at this point where concentration of BPA is  $77 \text{ mg}\cdot\text{L}^{-1}$ . Four peaks other than BPA can be identified from the HPLC chromatogram. Peaks having 2.25, 3, 3.9 and 4.5 minutes retention time were observed after 25 minutes of ozonation. As the reaction proceeded, the peak at 2.25 minute disappeared and the remaining ones were still present after 90 minutes of ozonation. These species which can be considered as byproducts are assumed to have same structure (containing phenol, benzene and benzoic acid moieties) as those observed under neutral pH conditions. BPA peak was present both in HPLC and GCMS chromatograms because of the incomplete degradation under acidic conditions. GCMS chromatogram of ozonated BPA under acidic conditions contains three byproducts (Figure 9): 3-Cyclohexene-1-carboxylic acid, ethyl ester (BP1), Benzaldehyde, 4-hydroxy-3,5-dimethyl- (BP2) and 2-Phenylbenzoquinone (BP3). Some physico-chemical properties of these products are given in (Table 1). Two of the byproducts (Phenylbenzoquinone and Benzaldehyde, 4-hydroxy-3,5-dimethyl-) were also observed under neutral conditions. A new byproduct was possibly formed as a result of aliphatic chain, oxygen and methyl addition to the ring-structured byproduct after the cleavage of tertiary carbon-phenolic ring which is the similar pathway for the formation of the other two byproducts. However, no evidence was observed for the opening of the ring structure. The proposed degradation pathway for BPA under acidic conditions is shown in Figure 8.

According to these results obtained at different pH values, ozone molecules are able to oxidize BPA and mineralization up to a certain extent while hydroxyl radicals have higher oxidation potential and can oxidize BPA and its byproducts more efficiently.

## CONCLUSION AND RECOMMENDATION

This study concluded that the rate of degradation and mineralization of BPA increased directly with increasing pH. BPA removal at pH 3, 7 and 10 was found 60%,  $\approx 100\%$  and  $\approx 100\%$ , respectively. Mineralization was measured as 10% for pH 3 and 7; however, it was recorded as 52% under alkaline conditions. The reaction was well fitted to pseudo first-order reaction kinetics. Several byproducts were identified for each pH condition and different degradation pathways were proposed. Basically, the lower rate of elimination of BPA under acidic conditions resulted in more ring-structured byproducts after 90 minutes; however, under alkaline conditions, byproducts included an open chain structure. The identified byproducts were found generally water-soluble however some of them poses high toxicity according to the literature (Environmental Protection Agency EPI SUITE). It should be noted that application of ozonation alone under certain dose ( $25 \text{ mg}\cdot\text{L}^{-1}$  gaseous ozone and  $0.3 \text{ mg}\cdot\text{L}^{-1}$  dissolved ozone) for real water/wastewater treatment plant could not completely mineralized BPA from aqueous solutions. In future, ozone dose should

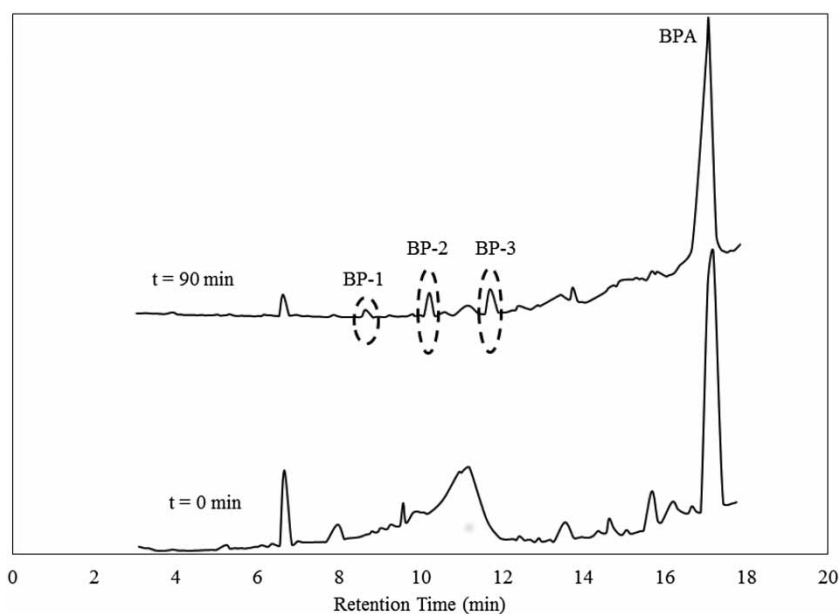


Figure 9 | GCMS chromatogram of ozonated BPA solutions at pH 3 ( $C_{\text{BPA}} = 100 \text{ mg}\cdot\text{L}^{-1}$ ,  $O_{3(\text{g})} = 25 \text{ mg}\cdot\text{L}^{-1}$  and  $O_{3(\text{aq})} = 0.3 \text{ mg}\cdot\text{L}^{-1}$ ).

be gradually increased, and after each increment, detailed mineralization and byproduct monitoring should be carried out such as in this study in order to decide optimum ozonation conditions for BPA removal. Moreover, addition of catalysts or combination with other synergistic AOPs should be applied in order to achieve BPA-free treated effluents.

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