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Degradation of 17β-estradiol and bisphenol A in aqueous medium by using ozone and ozone/UV techniques

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Abstract

Decomposition and complete degradation of two endocrine disrupters, namely 17β-estradiol (E_2) and bisphenol A (BPA) in aqueous medium by using ozone (O_3) only and O_3/UV advanced oxidation techniques (AOT) has been studied. The efficiency of the O_3 systems used were determined based on the initial conversion and complete degradation of the substrates. Within the limits of the O_3 dosages used, coupling of UV decreased the O_3 consumption by 22.5% in converting the same amount of E_2. Also the time to convert the same amount of E_2 was considerably decreased. It was observed that there is no significant difference in O_3 amount consumed for complete conversion of BPA by O_3 and O_3/UV systems. However, when O_3 dosage decreased the amount of BPA conversion exhibits significant differences between two processes. The intermediate products formed during the oxidation of E_2 were determined to be formed by oxidation of aromatic side of E_2 with O_3/$^{\bullet}$OH radical.

Keywords: 17β-Estradiol; Bisphenol A; Ozone; UV; Degradation; Endocrine disrupters

1. Introduction

An endocrine disrupter (or in other terms endocrine modulator) is defined as an exogeneous agent that interferes with the synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development and/or behavior [1]. Chemicals which vary widely in their structures and which have numerous different uses have been identified as endocrine disrupters. They include certain types of pesticides (e.g. dicofol, DDE, methoxychlor, toxaphene), plastics and other industry related materials (bisphenol A (BPA), alkylphenols, butyl and dibutylphthalates, hydroxy-polychlorinated biphenyls, etc.) and natural compounds that include human hormones and their breakdown products such as estrogen and the estrogen sterols, 17β-estradiol (E_2) and the synthetic hormone 17α-ethinyl estradiol.

It has been argued that endocrine disrupters may be responsible for decline in sperm counts, abnormalities in the male reproductive tract, slow development in infants and increases in the rate of testicular and breast cancer. Possible links to earlier puberty in females, a shift in the ratio of male to female births, prostate cancer and enlargement, non-Hodgkins lymphoma have also been discussed [2]. The anomalies in reproductive and other systems of juvenile alligators [3], fish intersexuality [4] and synergistic activation of estrogen receptor via the combination of some environmental chemicals [5] are some of the reported observations which had increased the concerns on these type of environmental chemicals. Halling-Sørensen et al. [6] and Daughton and Ternes [7] reviewed the relevant literature in detail explaining the potential risks due to the presence of pharmaceuticals in various environmental matrixes. On the other hand, a group of scientists reported that the extremely low concentrations of these chemicals in environmental matrices do not pose a

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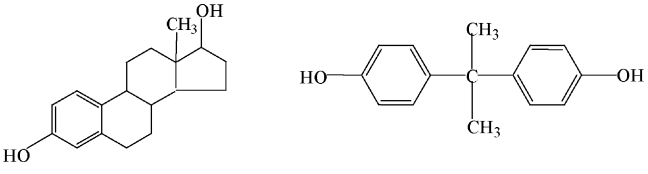


Fig. 1. Structural formulas of E_2 and BPA.

threat on both wildlife and on human health ([8] and the relevant references therein). Because the situation is not clear yet these chemicals in the environmental matrixes are being monitored intensively [9–11].

Besides the works on removal or mineralization of these chemicals have been carried out using various advanced oxidation techniques (AOT) are effective in decomposing refractory organic chemicals [12–14]. In this study, O_3 oxidation was chosen as the main chemical treatment to decompose 17β-estradiol (E_2) and bisphenol A in aqueous medium (Fig. 1). E_2 is the principal intracellular human estrogen and is substantially more active than its metabolites, estrone and estriol. E_2 may enter the aquatic environment from contraceptive pill residues, hormone replacement therapy residues and human excretion [9]. E_2 resists degradation in the course of typical sewage treatment operation [9] and be released into surface waters [15–17]. When the sludges from wastewater treatment plants, which contain these chemicals, are used in agricultural fields they can be transported into surface and/or ground waters [18].

BPA is a monomer of various polymeric materials. In addition to being used as monomers for the production of polycarbonates, epoxide phenol resins, etc., it is also being utilized as an antioxidant in numerous types of plastics [19]. Recent studies have shown that BPA can leach out of the plastic lining of cans used for foods, polycarbonate baby bottles, tableware, white dental fillings and sealents [20]. Epoxy resins used for the renovation of water pipes are based on BPA diglycidyl ether or a mixture of BPA and diglycidyl ether. Residues of this compound in water appear to be due to incomplete polymerization [21]. BPA was also frequently encountered in waters [22]. When BPA was subjected to metabolic activity it bounded to DNA [23].

O_3 reacts with organic compounds through a direct pathway by molecular ozone and a radical pathway by means of hydroxyl radicals. Under acidic conditions and in presence of radical scavengers which inhibit the chain reaction which accelerates the decomposition of O_3, the direct ozonation pathway dominates but under basic conditions or in presence of solutes which promote the radical-type chain reaction which accelerates the transformation of ozone into $^{\bullet}OH$ radicals the latter, i.e. hydroxyl radical reactions dominate [24,25]. When the medium is basic, O_3 decomposes to generate hydroxyl radical, which is non-selective and highly reactive oxidant for destruction of toxic organic compounds in wastewater.

Ozone decomposition proceeds with chain reactions including initiation, propagation and termination steps [25,26]:

- Initiation step:
  Decomposition reaction of ozone is initiated by OH^- ions in the solution yielding $^{\bullet}OH$ radicals.

$$O_3 + OH^- \rightarrow O_2^{\bullet -} + HO_2^{\bullet} \quad k_1 = 70\,M^{-1}\,s^{-1} \tag{1}$$

- $HO_2^{\bullet}$ radical is in acid–base equilibrium:

$$HO_2^{\bullet} = O_2^{\bullet -} + H^+ \quad pK_a = 4.8 \tag{2}$$

- Propagation step:

$$O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet -} + O_2 \quad k_2 = 1.6 \times 10^9\,M^{-1}\,s^{-1} \tag{3}$$

$$HO_3^{\bullet} = O_3^{\bullet -} + H^+ \quad pK_a = 6.2 \tag{4}$$

$$HO_3^{\bullet} \rightarrow {}^{\bullet}OH + O_2 \quad k_3 = 1.4 \times 10^5\,s^{-1} \tag{5}$$

$$O_3 + {}^{\bullet}OH \rightarrow HO_4^{\bullet} \quad k_5 = 2.0 \times 10^9\,M^{-1}\,s^{-1} \tag{6}$$

$$HO_4^{\bullet} \rightarrow HO_2^{\bullet} + O_2 \quad k_6 = 2.8 \times 10^4\,s^{-1} \tag{7}$$

- Termination step:
  This step includes any recombination of $^{\bullet}OH$, $HO_2^{\bullet}$ and O_2

The combination of ultraviolet (UV) radiation with O_3 may be a more effective advanced oxidation technique than using O_3 alone for certain target materials due to the formation of additional H_2O_2 and $^{\bullet}OH$ radical generation via photolysis [27].

$$O_3 + H_2O \xrightarrow{h\nu} H_2O_2 + O_2 \tag{8}$$

$$H_2O_2 \xrightarrow{h\nu} 2{}^{\bullet}OH \tag{9}$$

However, the photolysis of H_2O_2 to produce two $^{\bullet}OH$ radicals is rather slow because molar extinction coefficient of hydrogen peroxide is much lower ($19.6\,M^{-1}\,cm^{-1}$) than that of ozone ($3300\,M^{-1}\,cm^{-1}$) at 254 nm [28]. A fraction of hydrogen peroxide is dissociated into HO_2^- ($pK_a = 11.8$) by following reaction [29]:

$$H_2O_2 \rightarrow HO_2^- + H^+ \tag{10}$$

This reacts with further ozone by producing $O_3^{\bullet -}$ radicals,

$$HO_2^- + O_3 \rightarrow HO_2^{\bullet} + O_3^{\bullet -} \tag{11}$$

and it therefore acts as a further chain carrier [25].

The decomposition of endocrine disruptors E_2 and BPA in aqueous medium by O_3 and O_3/UV oxidation has not been investigated previously. Therefore, in this study E_2 and BPA were treated with both O_3 and O_3/UV in aqueous medium at 0.40 mM initial concentration. The depletion of the initial substrates throughout the treatments were monitored and the efficiency of conversions and complete degradations in two different systems were compared.

2. Experimental

2.1. Chemicals

17β-Estradiol (>98%; Sigma, 272.4 g/mol) and Bisphenol A (99%; Aldrich, 228.29 g/mol) were used without further purification. All the solvents used were HPLC grade. E_2 solution was prepared by dissolving it in acetonitrile followed by the addition water due to its low aqueous solubility. Final composition of the solution with respect to solvents was 30% CH_3CN, 70% H_2O (v/v). Acetonitrile was chosen as the co-solvent because it was miscible with water and has a low reactivity with ozone ($k \leq 6 \times 10^{-5}\,M^{-1}\,s^{-1}$, [30]). It's rate of scavenging •OH radicals was about two to three orders of magnitude less than the rate of scavenging of •OH radicals via the competing target materials in the same medium [31]. Standard solutions of E_2 were prepared by diluting the 0.40 mM stock solution and standard working curve based on mean HPLC peak areas was constructed for a concentration range of 0.40–0.020 mM.

BPA is directly dissolved in water with a concentration of 0.40 mM. Standard solutions of bisphenol A were prepared by diluting the 0.40 mM stock solution and standard working curve based on mean HPLC peak areas was constructed for a concentration range of 0.40–0.025 mM.

2.2. Ozonization and UV irradiation

Experimental set up for ozonization is shown in Fig. 2. A cylindrical glass reactor of 250 mL volume was used. O_3 was produced by the ozone generator OL100 model (from Ozone Services, Burton, BC, Canada). Production of ozone was controlled by changing the power input of ozone generator and adjusting of oxygen gas flow. The gas flow rate was adjustable by a valve. Ozone generator was tested by different flow rates of oxygen to produce different ozone dosages. During the O_3 application, aliquots of 1 mL were withdrawn from the reactor at specified time intervals and quenched immediately in glass vials with excess sodium thiosulfate–sodium sulphite mixture to decompose any residual O_3 and •OH radicals.

The UV radiation was produced by a 15 W, low-pressure mercury UV lamp (UVP Inc., Upland, CA, USA). In the UV-induced oxidation experiments, the Pen-Ray UV lamp was immersed vertically in the solution in the center of the reactor.

In all ozonization experiments, the initial E_2 and BPA concentrations were 0.40 mM. pH values of E_2 and BPA were 6.25 ± 0.05 and pH 5.25 ± 0.03, respectively, and ozonization was performed at original pH values for each solution.

2.3. Analysis

Residual E_2 and BPA concentrations in the aliquot of samples withdrawn from the reactor were determined by using high performance liquid chromatograph equipped with a multiple UV wavelength detector (Dionex HPLC system, Sunnyvale, CA, USA). UV detector was set at 280 nm for all analysis. Sphereclone 5 μm, ODS (2), 150 mm × 4.6 mm Phenomenex Column and Zorbax Chromatography Column (ODS 4.6 mm × 25 cm) were used for the analysis of E_2 and BPA concentrations in ozonated samples. The eluent for the former case was acetonitrile:water (38:62, v/v) solution and the same components with 43:57 (v/v) for

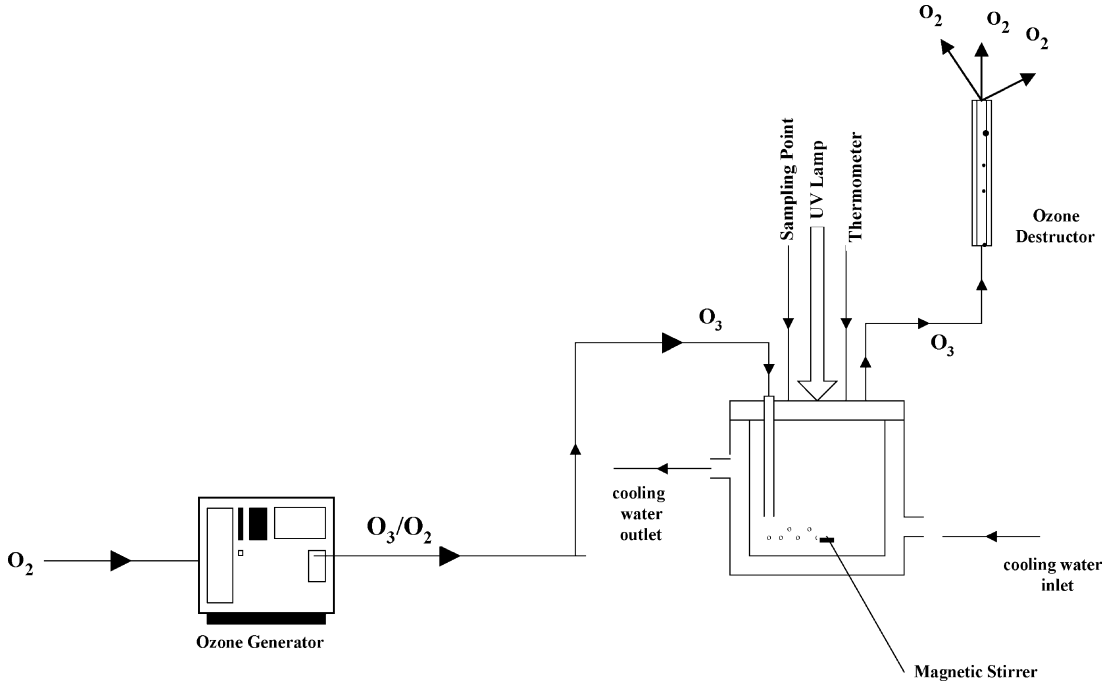


Fig. 2. Experimental set up for ozonization.

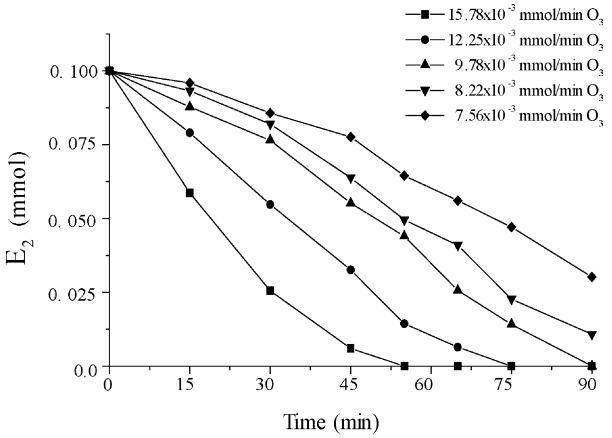


Fig. 3. Decrease of 0.1 mmol E_2 during application of O_3 at different dosages.

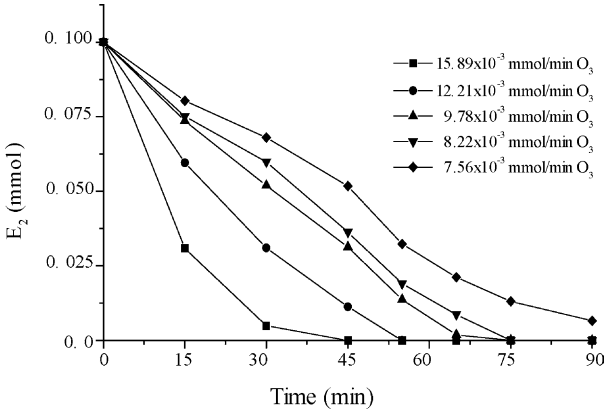


Fig. 4. Decrease of 0.1 mmol E_2 during application of O_3/UV at different O_3 dosages.

the latter case was used with 0.5 mL/min flow rate for all cases. The products formed during the oxidation of E_2 were determined by Finnigan Mat-Spectrasystem liquid chromatograph/mass spectrometer instrument with APCI interface and triple quadrupole mass analyzer (Finnigan TSQ 700 system, Hemel Hempstead, UK).

3. Results and discussion

3.1. Processing of E_2 by O_3 and O_3/UV

The oxidation of E_2 was carried out by using various O_3 dosage and results were given in Fig. 3 and Table 1. The flow rate of ozone ranged between 15.78×10^{-3} and 7.56×10^{-3} mmol min^{-1}. The time needed for complete conversion of E_2 (0.1 mmol) were 55, 75 and 90 min for the applied O_3 dosages of 15.78×10^{-3}, 12.25×10^{-3} and 9.78×10^{-3} mmol/min, respectively. At 8.22×10^{-3} and 7.56×10^{-3} O_3 dosages, 0.013 and 0.030 mmol concentrations of E_2 remained without oxidation at the end of 90 min. Thus, 0.868, 0.919 and 0.880 mmol of O_3 were consumed for complete conversion of 0.1 mmol E_2. This shows that roughly equal amounts of O_3 (0.889 ± 0.027 mmol) are consumed for the conversion of 0.1 mmol of E_2. Therefore, O_3/E_2 ratio for complete oxidation of E_2 by this process is 8.89.

Fig. 4 shows the degradation of E_2 throughout O_3/UV. Although O_3 needed for complete conversion of E_2 (0.1 mmol) by O_3/UV applications was lower than O_3 alone oxidation rate was observed to be higher (Fig. 3 and Table 1). 7.56×10^{-3} mmol min^{-1} O_3 dosage for 90 min was not enough for complete oxidation of E_2 by this process. During O_3/UV applications, the time needed for complete conversion of E_2 were 45, 55, 67 and 75 min for the applied O_3 dosages of 15.89×10^{-3}, 12.21×10^{-3}, 9.78×10^{-3} and 8.22×10^{-3} mmol/min, respectively (Table 1). Thus, for complete conversion of 0.1 mmol E_2, 0.715, 0.672, 0.655 and 0.616 mmol of O_3 were consumed. This shows that roughly equal amounts of O_3 (0.664 ± 0.041 mmol) are consumed to transform 0.1 mmol of E_2. O_3/E_2 ratio for complete oxidation of E_2 by O_3/UV process is 6.64, in other words, coupling of UV decreased the O_3 consumption by 22.5% in converting the same amount of E_2. Also the time to convert the same amount of E_2 was considerably decreased.

3.2. Intermediate products formed during oxidation of E_2

HPLC chromatogram and mass total ion chromatogram of an ozonated sample of E_2 are seen in Figs. 5 and 6,

Table 1
O_3 dosages used in the oxidation experiments and the fractions of O_3 reacted with E_2

Oxidation system	O_3 dosage × 10^{-3} mmol/min	Total O_3, reacted with E_2 and by-products (mmol)	E_2 oxidation time (min)	Unreacted E_2 (mmol)
O_3	15.78	0.868	55	0.000
O_3	12.25	0.919	75	0.000
O_3	9.78	0.880	90	0.000
O_3	8.22	0.740	90	0.013
O_3	7.56	0.680	90	0.030
O_3/UV	15.89	0.715	45	0.000
O_3/UV	12.21	0.672	55	0.000
O_3/UV	9.78	0.655	67	0.000
O_3/UV	8.22	0.616	75	0.000
O_3/UV	7.56	0.680	90	0.008

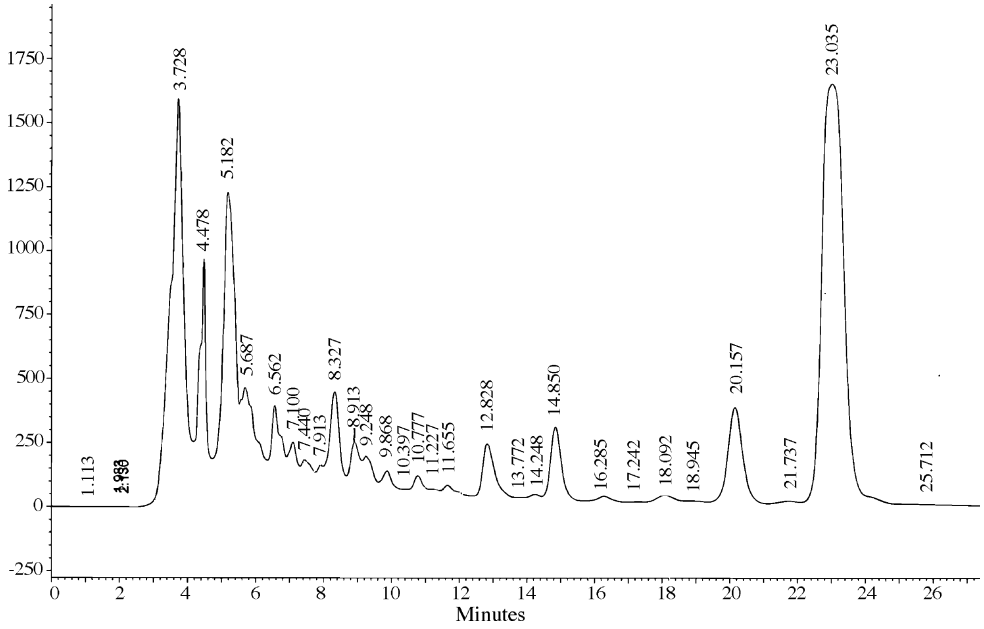


Fig. 5. HPLC chromatogram of an ozonation sample of E_2 (0.1 mmol of E_2 and 0.34 mmol of O_3).

respectively. Some peaks observed in HPLC were not seen in MS. Because of lower sensitivity of MS detection for these compounds some peaks were not detected or detected in low intensity in MS. Fig. 5 shows the intermediate products formed during oxidation of 0.1 mmol of E_2. In this chromatogram, the peak corresponding to E_2 (22.88 min) is seen after the intermediate products peaks.

Addition of O_3/$^{\bullet}$OH radical to the different positions of aromatic ring leads to formation of various intermediates with different polarity. The peaks of more polar products have earlier retention times in polar eluent (acetonitrile/water) in HPLC. The intermediate products identified from MS spectra are given in Table 2. The most probable attack of O_3 molecules was to one of the ortho positions (with respect to phenolic hydroxyl group) of the aromatic ring of E_2. One of the intermediate products identified is the product with 5.06 minutes retention time in mass total ion chromatogram. However, this product formed at very low yield in O_3/UV oxidation and did not persist because of further oxidation. This product was suggested to be one of the most polar intermediate products that was unretained by the HPLC column in the polar mobile phase and was also similar to the product seen at 7.21 min because of same *m*/*z* base peak (261.5). Therefore, these intermediate products are supposed to be dicarboxylic acids that are formed by attack of O_3 molecules to two of the ortho positions of E_2. The intermediate seen at 8.15 min was formed during the early stages of the O_3 application. However, it was not observed in O_3/UV process. This product is second most polar product and supposed to be monohydroxylated E_2. The mass spectra of intermediate product in 19.99 min indicated that this product should be diketone formed by oxidation of aromatic ring. Formation

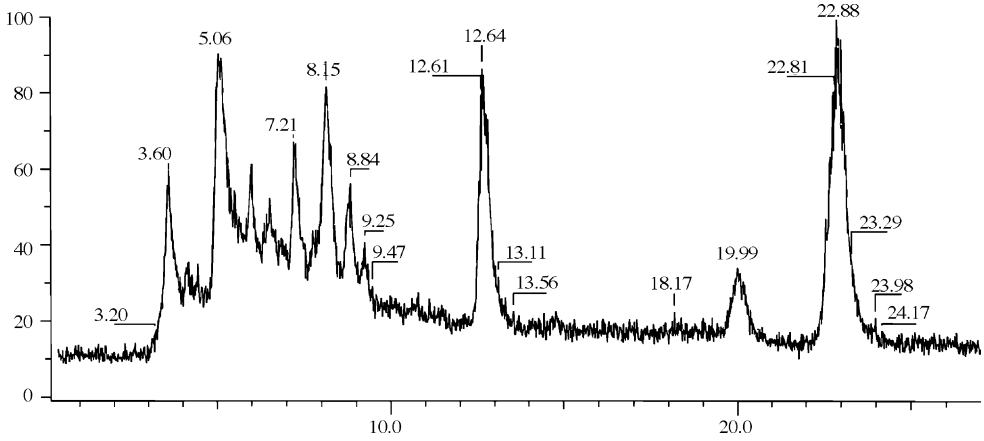
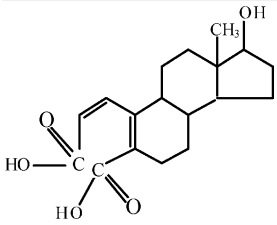
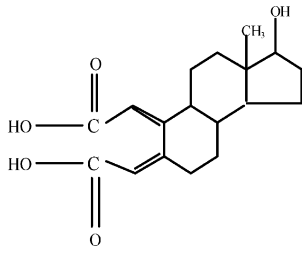
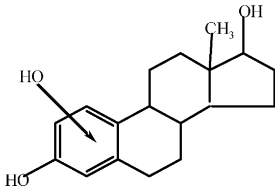
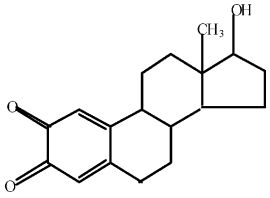
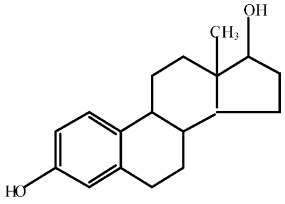


Fig. 6. Mass total ion chromatogram of an ozonation sample of E_2 (0.1 mmol of E_2 and 0.34 mmol of O_3).

Table 2
Intermediate products formed during ozonization of E_2

By-product	Retention time	Mass/relative abundance of predominant ions
	5.06	261/100; 114/90; 147/68; 247/65
and/or		
	7.21	261/100; 114/20; 163/15; 279/10
	8.15	123/100; 287/30; 163/25; 259/15
	19.99	271/100; 133/70; 122/65; 253/58; 114/38; 159/36
	22.88	159/100; 133/30; 255/28; 109/14; 271/08

of this intermediate was very low when compared to other intermediates. It was observed in lower yield in O_3 process than O_3/UV oxidation process. The suggested oxidation of monohyroxylated of E_2 to diketone intermediate probably is only minor reaction since monohyroxylated E_2 undergoes a high conversion to dicarboxylic acids.

Fig. 7 shows two pathways for the formation of these intermediate products for direct ozonation of E_2 regarding the intermediate products formed and mechanisms proposed for the O_3 oxidation of phenol [32–35]. Meanwhile, indirect reaction of O_3 with the organic substrate, i.e. via $^{\bullet}OH$ radicals can lead to production of the same dicarboxylic acids. All these different dicarboxylic acids are further decomposed in various competing oxidation reactions and smaller products are formed.

3.3. Processing of BPA by O_3 and O_3/UV

Three different O_3 dosages, which were lower and upper level used for complete oxidation of E_2 (10.33×10^{-3} and 18.67×10^{-3} mmol/min) used for oxidation of BPA. Fig. 8 and Table 3 show the results throughout applications for bisphenol A. As seen in Fig. 8, O_3 dosage used for complete oxidation of 0.1 mmol of E_2 (15.78×10^{-3} mmol/min) was not enough for complete oxidation of 0.1 mmol of BPA during 90 min of oxidation. However, the complete conversion of BPA was achieved by 18.67×10^{-3} mmol/min O_3 dosage for 80 min at which 1.494 mmol O_3 was consumed. O_3/BPA ratio for complete oxidation of BPA is 14.94, which is 1.68 times higher than that of obtained for E_2.

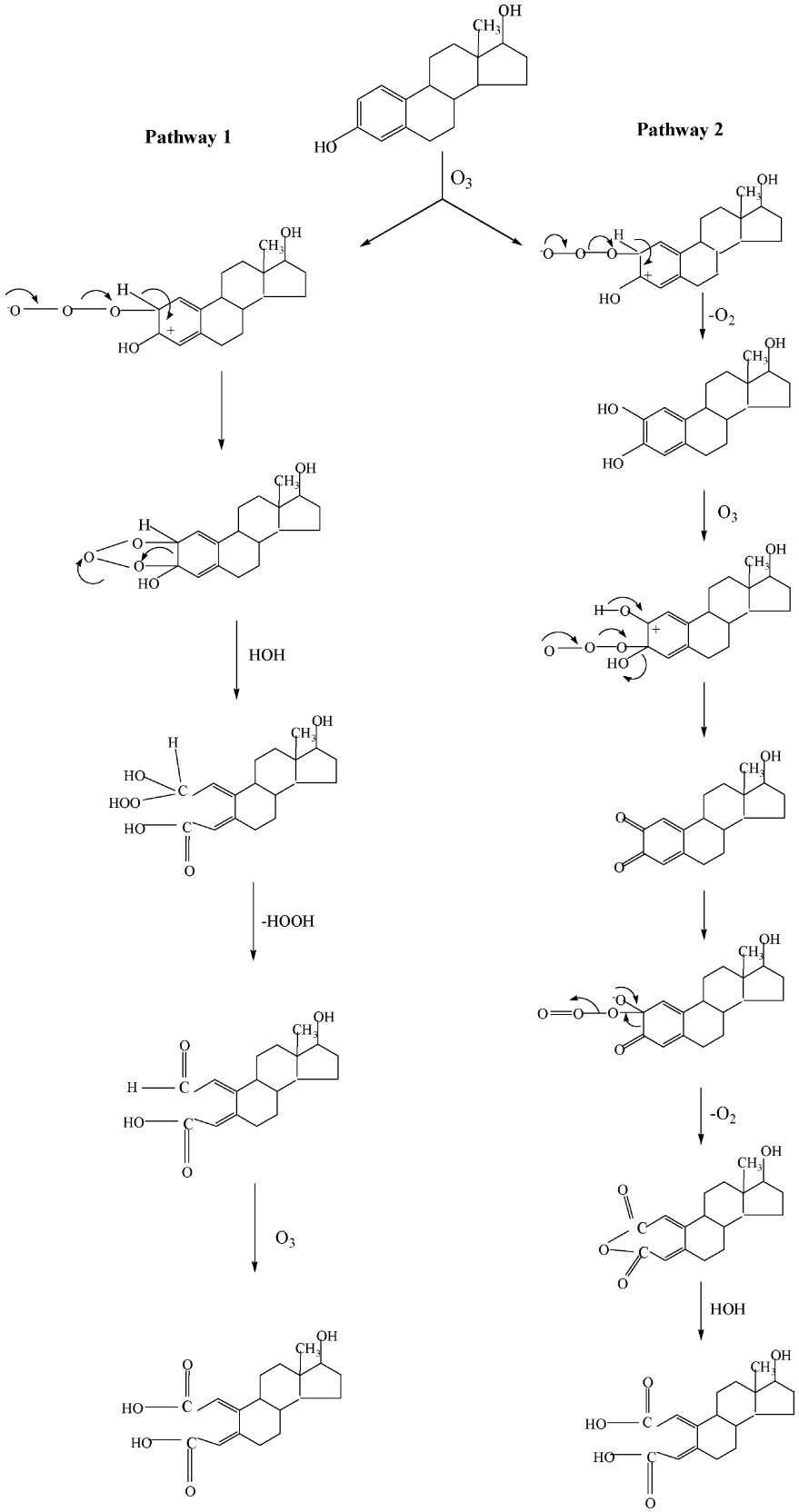


Fig. 7. Mechanism for direct reaction of O_3 with the aromatic ring of E_2.

Table 3
O_3 dosages used in the oxidation experiments and the fractions of O_3 reacted with BPA

Oxidation system	O_3 dosage $\times 10^{-3}$ (mmol/min)	Total O_3, reacted with BPA and by-products (mmol)	BPA oxidation time (min)	Unreacted BPA (mmol)
O_3	18.67	1.494	80	0.000
O_3	15.78	1.420	90	0.023
O_3	10.33	0.930	90	0.080
O_3/UV	18.67	1.400	75	0.000
O_3/UV	15.78	1.420	90	0.008
O_3/UV	10.33	0.930	90	0.028

Fig. 9 shows that the conversion rates of BPA become faster in all dosages when UV is coupled with O_3 treatment. However, the complete conversion was still achieved by 18.67×10^{-3} mmol/min O_3 dosage for 75 min. Thus, 1.4 mmol of O_3 was consumed for complete conversion of BPA by O_3/UV process. Although there was no significant differences between two treatment techniques in terms of O_3/BPA ratio at high O_3 dosage, 0.023 mmol BPA was remained without oxidation using 15.78×10^{-3} mmol/min O_3 dosage in O_3 only application while in O_3 coupled with UV application, 0.008 mmol BPA remained using the same O_3 dosage.

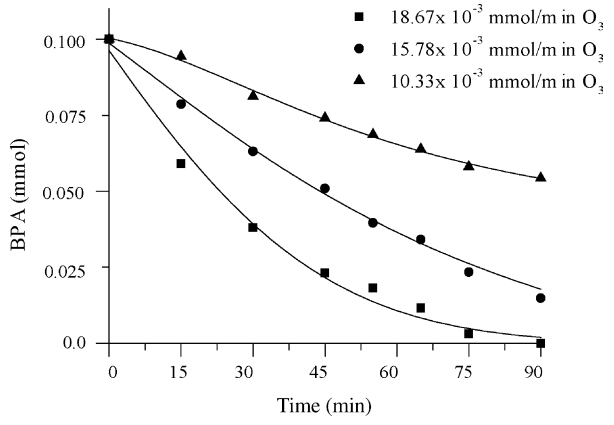


Fig. 8. Decrease of BPA during application of O_3 at different O_3 dosages.

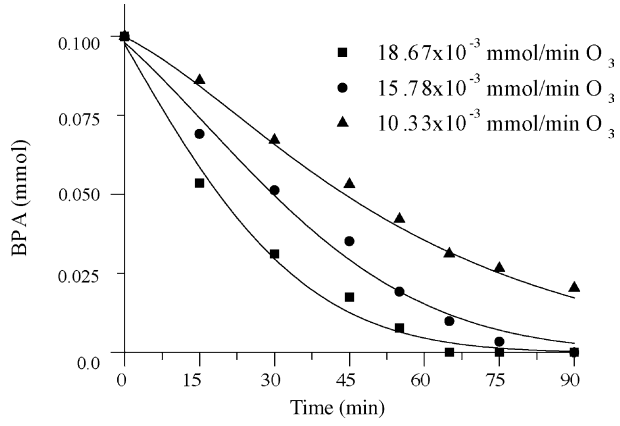


Fig. 9. Decrease of BPA during application of O_3/UV at different O_3 dosages.

3.4. Complete degradation of E_2 and BPA during O_3/UV application

Experiments for the ozonation of E_2 and BPA with UV coupling were also carried out until complete degradations were achieved. It should be mentioned that since the solution of E_2 contains acetonitrile as solvent in addition to water it was not possible to follow mineralization by measuring "total organic carbon" contents or by measuring the chemical oxygen demands of the solutions. HPLC analysis of the samples were carried out until all the products disappeared in the chromatogram and this point was accepted as the marker of complete degradation of the organic substrate. Although BPA solutions did not contain acetonitrile, their complete degradations were also followed by HPLC analysis to compare with the results obtained for E_2 solutions.

When 9.70×10^{-3} mmol/min O_3 dosage is used, complete degradation of 250 mL of 0.40 mM E_2 solution is achieved following 195 min of treatment. The corresponding figure for the complete degradation of 250 mL of 0.40 mM BPA was 218 min. Calculations based on O_3 dosages and the times needed for complete degradation showed that for 1 mole of E_2, 18.9 moles of O_3 had to be consumed while the corresponding figure for 1 mole of BPA was 21.1 moles of O_3.

Some important considerations can be highlighted under the results of this study. O_3 and O_3/UV advanced oxidation techniques are successfully applied to degradation of E_2 and BPA using certain amount of O_3 dosage. Considering the economical aspects, the use of these techniques as advanced oxidation techniques are not cheap technologies. These techniques must be optimized by adjusting process conditions and/or coupled with another economically feasible method. The operating conditions for attaining maximum efficiency can be investigated using various metal catalyst in various pH solutions. The toxicity and the refractory nature of the pollutants can be reduced up to a certain level, and then biological treatment may follow-up.

4. Conclusion

17β-Estradiol (E_2) and bisphenol A (BPA) have been oxidized by O_3 and O_3/UV radiation by varying O_3 dosages. The initial concentration of subject materials was 0.1 mmol in 250 mL solution and kept constant in all treatments. Coupling of UV with O_3 decreased the O_3 consumption compared

to O_3 only. The results indicated that the reaction between BPA and O_3 is slower than the reaction between E_2 and O_3. In complete degradation experiments, 1 mole of E_2 reacted with 18.9 moles of O_3 while for 1 mole of BPA, 21.1 moles of O_3 was consumed. Intermediate products formed during oxidation of E_2 were analyzed by LC–MS. They were determined to be oxidation products of E_2 via addition of O_3/•OH radical to the different positions of aromatic ring of E_2.

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