



## DEGRADATION OF BISPHENOL A USING ADVANCED OXIDATION PROCESSES

Mitra Mehrabani-Zeinabad<sup>1</sup>, Gopal Achari<sup>1</sup>, Cooper H. Langford<sup>2</sup>

<sup>1</sup> Department of Civil Engineering, University of Calgary, Calgary, Alberta, Canada

<sup>2</sup> Department of Chemistry, University of Calgary, Calgary, Alberta, Canada

### Abstract:

The aim of this study is to investigate the effectiveness of different oxidation methods including UVC, UVC/H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> in degrading Bisphenol A (BPA) in water and treated wastewater samples. The effective parameters for each process were identified and further investigated along with the effect of inorganic and organic matter present in secondary treated wastewater. The reaction kinetics of each process was obtained in both spiked water and secondary treated wastewater samples. The results showed the degradation is slow when only UV is used but it improved significantly upon addition of hydrogen peroxide to the solution. The highest degradation rates were measured with ozone (O<sub>3</sub>) bubbling in the solution. By applying an ozone flow rate of 1 L/min, the first order rate constant was found to be 1.2 min<sup>-1</sup> and 1.1 min<sup>-1</sup> in water and treated wastewater, respectively. After 3 minutes of reaction, no BPA was detected in solution. The degradation mechanism of each of the three processes has also been proposed.

**Keywords:** BPA, AOPs, UVC, ozone

### 1 Introduction

Emerging contaminants (EC) are a loose group of contaminants comprising of pharmaceuticals, personal care products (PPCPs), surfactants, pesticides and others. Waste Water Treatment Plant (WWTP) effluents are one of the major sources of release of ECs to the environment. Due to the high stability of these compounds, most WWTP operations are not able to treat them causing them to pass through secondary biological treatment processes and enter the aquatic environment (Petrovic, et al. 2003). Some of these are endocrine disrupting compounds (EDCs) which act as hormones in aquatic species. One of these EDCs of concern often detected in water bodies is Bisphenol A [BPA: 2,2-bis(4-hydroxyphenyl) propane] (Kolpin, et al. 2002) which is used in the production of polycarbonate and epoxy resins, unsaturated polyester-styrene resins and flame retardants. Their final products are used as can coatings, powder paints, dental fillings and antioxidants in plastics (Staples, et al. 2000) which are used in food and drink packaging (Rivas, et al. 2009). BPA has been detected at wastewater treatment plant influents ranging from 0.08 to 4.98 µg/L and in effluents from 0.01 to 1.08 µg/L (Hing-Biu and Peart 2000). The molecular structure of BPA is shown in Figure 1.

Research has shown the lowest adverse effects observed in aquatic ecosystems could be below 1 µg/L (Oehlmann, et al. 2000). The hydrophobicity of BPA leads to its bioaccumulation in the tissues of living organisms. The guideline for the maximum allowable concentration (MAC) of Bisphenol A in drinking water is set to 0.1 mg/L (Environment Canada, 2008). It has been banned from application in baby bottles in Canada, US and Europe.

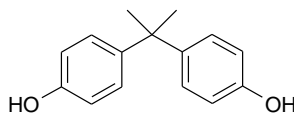


Figure 1. Molecular structure of BPA (adapted from Umar, et al. 2013)

While several studies have investigated the degradation of BPA in water including use of Fenton's reagent (Gozmen, et al. 2003), photocatalytic degradation (Watanabe, et al. 2003), photo-Fenton reactions (Katsumata, et al. 2004) and aerobic microbial processes (Mezcua, et al. 2006), this paper advances the current state of the art by including UV, UV/H<sub>2</sub>O<sub>2</sub> and ozone (O<sub>3</sub>) to the degradation of BPA in water and treated wastewater. The effective parameters for each process were identified and investigated. The effect of organic and inorganic ions present in the wastewater on the degradation rate was also studied.

## 2 Materials and Methods

### 2.1 Chemicals

BPA with 99% purity was purchased from Sigma Aldrich Co. (Canada). High-performance liquid chromatography (HPLC)-grade acetonitrile and Milli-Q water were obtained from VWR (Canada). All reagents were of analytical grade.

### 2.2 Photoreactor

A standard Rayonet photoreactor (Southern New England Ultraviolet Co.) equipped with a varying number of 254 nm mercury discharge lamps was used. The irradiation experiments were performed in this photoreactor in a batch mode. The UV dosage in the photoreactor, was changed by varying the number of lamps (7, 4 and 2 UV lamps) used. The light intensity inside the reaction vessel was measured by ferrioxalate actinometry (Calvert and Pitts 1996) and was found to be 2.43E17, 2.02E17 and 1.25E17 photon/s for 7, 4 and 2 UV lamps, respectively. Domestic wastewater after secondary treatment was obtained from the Bonnybrook WWTP in Calgary, Canada.

### 2.3 Ozonator

For ozonation purposes, an A2ZS-3Glab ozone generator (A2Z Ozone System Inc.) along with an x-coarse diffuser was used. The solution was mixed well with a magnetic stirrer.

### 2.4 Experimental Procedure

In order to study the reaction kinetics of BPA degradation by different methods, stock solutions of 50 mg/L BPA were prepared by ultra-sonication. Experiments were conducted on spiked Milli-Q water as well as spiked treated (post-secondary) wastewater. The experimental conditions are described as:

- (1) UVC only and UVC/H<sub>2</sub>O<sub>2</sub>: A cylindrical (D=2.0 cm, L=11.0cm) quartz reaction vessel containing 20.0 mL of solution was used in the Rayonet photoreactor.
- (2) O<sub>3</sub>: A glass cylinder (D = 7.0 cm, L = 13.0 cm) containing 400 mL of solution was used as the reaction vessel. 0.5 mL samples were collected at pre-specified time intervals and quenched with 2.5 mM sodium thiosulphate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) solution.



## 2.5 Sample Analysis with High-Pressure Liquid Chromatography (HPLC)

All samples were quantified using a Varian Prostar 210 HPLC instrument equipped with a 325 nm liquid chromatography (LC) UV-visible detector. A Zorbax SB C-18 (4.6 × 150mm, 5µm) column was used to separate the target compound from its by-products. An isocratic elution with a 0.5 mL/min flow rate was used in analysis; the eluent comprised of 35% water (phase A) and 65% acetonitrile (phase B). The UV-visible detector wavelength was set at 280 nm and the temperature was kept constant at 25°C. A calibration curve was prepared by using six different concentrations of standard solutions. Identification and quantification of each compound was achieved by comparing their retention time and peak area, respectively, with known standards. The detection limit was 1 mg/L.

## 2.6 Sample Analysis with Liquid Chromatography – Mass Spectrometry (LC/MS)

An Agilent 1200 series HPLC connected to an Agilent 6520 Accurate-Mass Q-TOF LC/MS was used for analyzing the intermediates produced during the photodegradation process. A flow rate of 0.5 mL/min (35% water and 65% acetonitrile) was applied. The electron spray ionization source was set at 325°C, with a drying gas flow rate of 11 L/min and a nebulizer pressure of 60 psi. The fragmentor voltage was set at 140V.

## 3 Results and Discussion

UV light (254 nm) photolysis was employed in order to degrade BPA in solution. These experiments were performed at three different levels of light intensity by using 7, 4 and 2 UV lamps. The variation of normalized concentration ( $C/C_0$ ) of BPA in pure water and in treated wastewater with reaction time is presented in Figure 2.

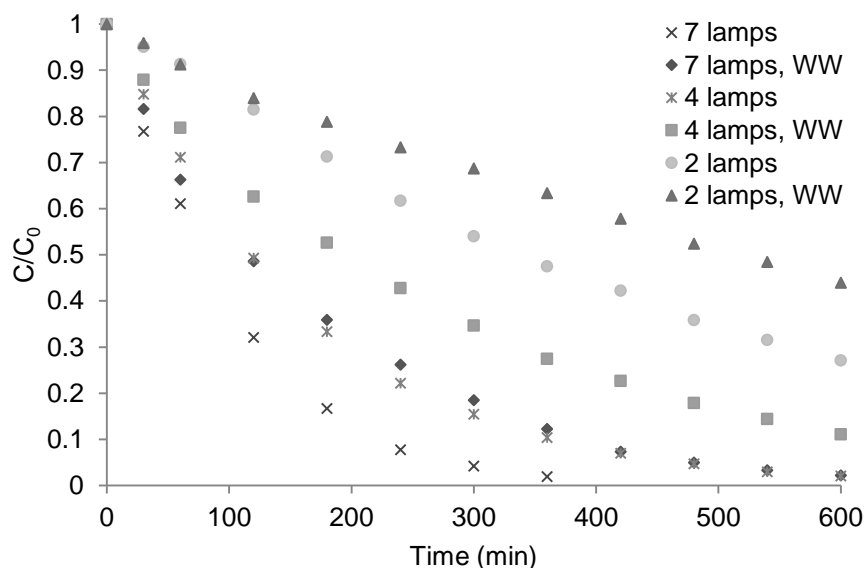


Figure 2. Effect of light intensity on UV only degradation process of BPA in water and treated wastewater

As it can be seen in Figure 2, the degradation rate using only UV is quite slow. In water samples no BPA was detected after 6.5 hours of irradiation with 7 lamps or after 10 hours of irradiation with 4 or 2 lamps, respectively. In case of wastewater samples, 90%, 70% and 50% degradation was achieved after 10 hours of irradiation. This very low degradation rate can be explained by the absorbance spectrum of BPA presented in Figure 3. It can be observed that this compound has very low absorbance at 254 nm.

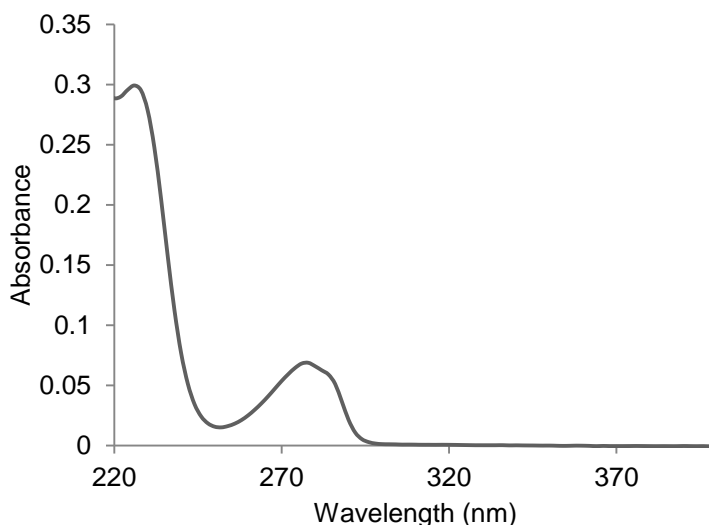


Figure 3. Absorption spectrum of BPA (25 mg/L)

In both cases of water and treated wastewater as the solution medium, the degradation rate increased as the light intensity increased. This was expected as there is a higher availability of photons at higher light intensities causing more BPA molecule to absorb these photons and go through oxidation. It was also noted that the degradation rates are lower in treated wastewater than in spiked waters. As the treated wastewater samples contain other organic and inorganic matter, these extraneous materials also compete with BPA molecules to absorb photons decreasing the chance for BPA molecules to be exposed to these photons and absorb them. In other words, light shielding by inorganic and organic matter present in the treated wastewater led to this higher photon demand for the same degradation.

The data seems to fit a first order kinetic model ( $R^2 > 0.99$ ), which agrees with the findings of Jing and Yongqiang (2010) and Felis, et al. (2011). Table 1 presents the rate constants for BPA degradation.

Table 1. Rate constants of BPA degradation with UV only in water and wastewater

No. of lamps	Water		Wastewater	
	k (min <sup>-1</sup> )	R <sup>2</sup>	k (min <sup>-1</sup> )	R <sup>2</sup>
7	0.011	0.997	0.006	0.995
4	0.006	0.999	0.004	0.999
2	0.002	0.998	0.001	0.997

In order to improve the degradation rates from the UV only values, investigations on use of UV/H<sub>2</sub>O<sub>2</sub> were conducted. In the UV/H<sub>2</sub>O<sub>2</sub> process, UV absorption (254 nm) leads to splitting of H<sub>2</sub>O<sub>2</sub> producing two hydroxyl radicals per molecule ( $H_2O_2 + h\nu \rightarrow 2 HO\cdot$ ). Hydroxyl radicals can react non-selectively with the organic molecules present in the medium. The impact of UV light intensity and H<sub>2</sub>O<sub>2</sub> concentration on the degradation rate of BPA was studied. The effect of light intensity, similarly to UV only, was investigated at 3 levels of UV irradiation with constant hydrogen peroxide concentration of 0.042 M and presented in Figure 4.

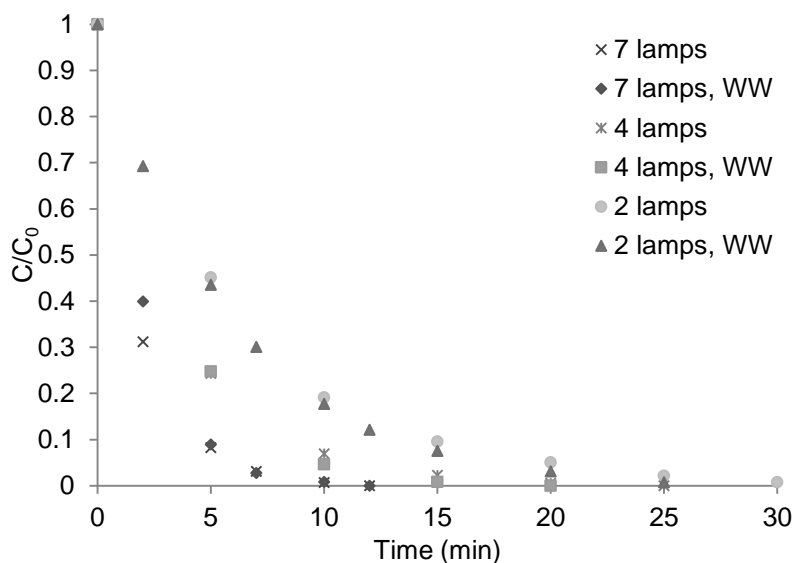


Figure 4. Effect of light intensity on UV/H<sub>2</sub>O<sub>2</sub> process (0.042 M H<sub>2</sub>O<sub>2</sub>) in water and treated wastewater

It can be observed from Fig. 4 that upon addition of hydrogen peroxide the degradation rate has improved significantly compared to the UV only process. Increasing the light intensity increased the degradation rate due to production of more hydroxyl radicals from the cleavage of H<sub>2</sub>O<sub>2</sub> excited state. This suggests that the reaction is light intensity limited under our conditions. The first order rate constants in water with 7, 4 and 2 lamps were 0.49, 0.32 and 0.16 min<sup>-1</sup>, respectively. Comparing water and treated wastewater, it can be seen that the degradation rate hasn't significantly changed giving first order rate constants of 0.49, 0.26 and 0.17 min<sup>-1</sup> with 7, 4 and 2 lamps, respectively.

In order to study the effect of hydrogen peroxide concentration on the UV/H<sub>2</sub>O<sub>2</sub> process, three levels of 0.021, 0.042 and 0.21 M H<sub>2</sub>O<sub>2</sub> were used with constant light intensity of 2 lamps (see Figure 5).

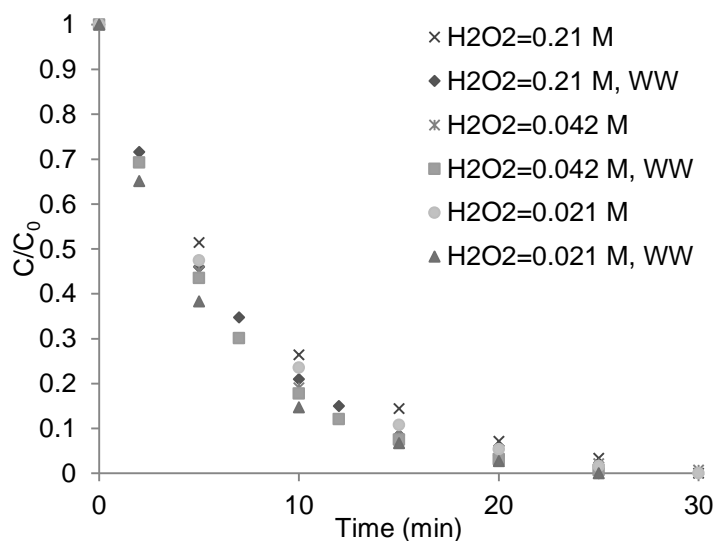
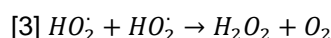
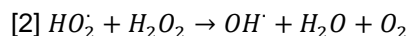
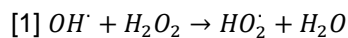


Figure 5. Effect of H<sub>2</sub>O<sub>2</sub> concentration on UV/H<sub>2</sub>O<sub>2</sub> process (2 UV lamps) in water and treated wastewater



Figure 5, shows that as the H<sub>2</sub>O<sub>2</sub> concentration is increased up to 0.042 M, the degradation rate constant has increased only marginally from 0.13 min<sup>-1</sup> to 0.16 min<sup>-1</sup>. This supports the idea that light intensity is the key variable, with only a slight increase from increasing the solution absorptivity, but further increase of the H<sub>2</sub>O<sub>2</sub> concentration causes the degradation rate to decrease to 0.14 min<sup>-1</sup>. Jing and Yongqiang (2010) and Yue and Legrini (1992) have also shown there is an optimum H<sub>2</sub>O<sub>2</sub> concentration. As the concentration of H<sub>2</sub>O<sub>2</sub> increases beyond this optimum, they act as hydroxyl radical scavengers and reduce the oxidation rate which is shown in the reactions below. In addition, there is a potential increase of recombination as radical concentrations increase. The following equations illustrate this:



However, in case of wastewater, the degradation rate constant appeared to be almost unchanged from 0.17 min<sup>-1</sup> to 0.16 min<sup>-1</sup> with increasing the H<sub>2</sub>O<sub>2</sub> concentration from 0.021 M to 0.21 M, a one order increase. Water quality can have a significant effect on the fate of ·OH radicals. Inorganic ions such as alkalinity (carbonates), chloride, sulfate and nitrate in wastewater compete for ·OH radicals (Jing and Yongqiang 2010).

Figure 6 presents the results of O<sub>3</sub> sparging in solution containing BPA. The sparging was conducted at four flow rates of 0.5, 1, 2, 4 L/min. From Figure 6, it is observed that O<sub>3</sub> is faster in degrading BPA than either UV or UV/H<sub>2</sub>O<sub>2</sub>.

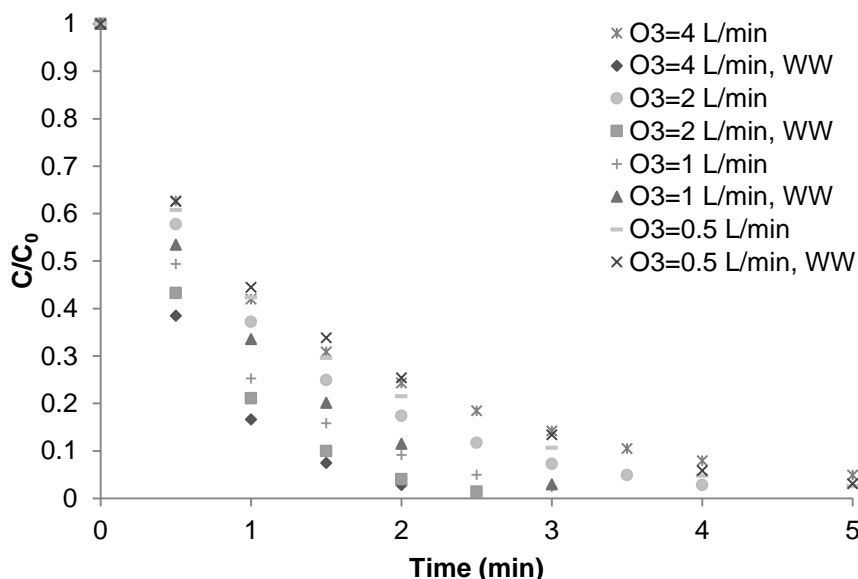


Figure 6. Effect of O<sub>3</sub> flow rate on degradation process of BPA in water and treated wastewater

An ozone molecule can either react directly with organic compounds and reactions are known to be selective and slow, or it can dissociate to produce hydroxyl radicals and then react with organic compounds where reaction rates are fast and non-selective (Lee, et al. 2007). In Figure 6, as the O<sub>3</sub> flow rate increases in water samples from 0.5 to 1 L/min (presumably increases ozone concentration) the degradation rate constant increases from 0.72 to 1.2 min<sup>-1</sup>. However, by further increase of the flow rate

the degradation rate decreases. This is probably caused by merging of ozone bubbles at higher flow rates causing less surface area for dissolution of ozone (Alvares, et al. 2001).

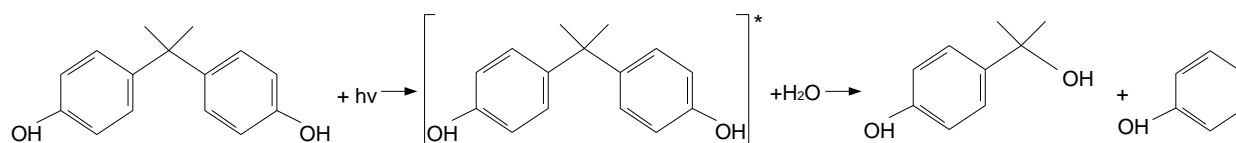
Several studies have shown that BPA degradation follows pseudo first order kinetics (Umar, et al. 2013). Since ozone is continuously sparged into the solution, the concentration of  $\cdot\text{OH}$  and  $\text{O}_3$  can be assumed to be in excess over trace BPA.

Table 2. Rate constants of BPA for ozone degradation process in water and wastewater

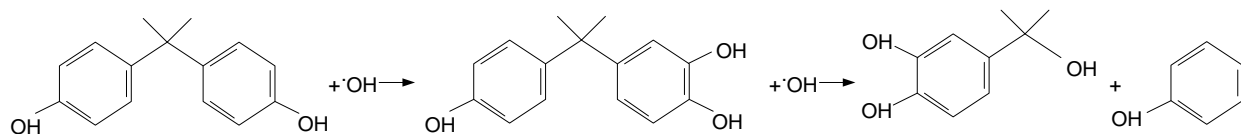
O <sub>3</sub> flow rate (L/min)	Water		Wastewater	
	k (min <sup>-1</sup> )	R <sup>2</sup>	k (min <sup>-1</sup> )	R <sup>2</sup>
4	0.58	0.991	1.8	0.998
2	0.86	0.997	1.7	0.995
1	1.2	0.997	1.1	0.995
0.5	0.72	0.998	0.68	0.997

In wastewater samples, it is observed that the degradation of BPA has increased as the O<sub>3</sub> flow rate has increased. If ozone decomposition is rapid, oxidation will be by  $\cdot\text{OH}$  radicals rather than ozone molecules.  $\cdot\text{OH}$  radicals are reactive and non-selective (Gehr, et al. 2003; Umar, et al. 2013). Since the wastewater has a high organic content, it can be concluded that the ozone decomposition is fast and in to hydroxyl radicals, resulting in higher degradation rates compared to pure water.

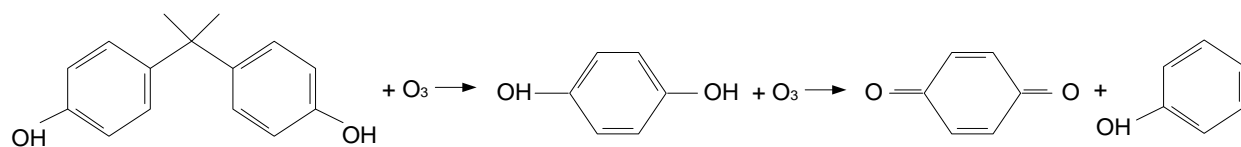
In order to study the degradation mechanism in water samples, LC/MS analysis was performed and the intermediates were identified. The degradation mechanisms for each method are proposed. In the UV only process, the following degradation mechanism is proposed which is in agreement with the findings of Mezcua, et al. (2006).



In the UV/H<sub>2</sub>O<sub>2</sub> process, based on the LC/MS results on water samples and the well-known reactivity of hydroxyl radicals towards organic molecules, the following route is proposed for BPA degradation. The first stage involves hydroxylation of the benzene ring which is followed by the dissociation of C-C bond to release phenol.



As mentioned above, in water samples bubbled with O<sub>3</sub>, BPA molecule is oxidized through direct reaction with molecular ozone. Molecular ozone attacks structures with high electron density such as the benzene ring in BPA by electrophilic substitution (Umar, et al. 2013). The proposed degradation pathway with direct ozone attack is as follow:



#### 4 Conclusions

In this study, several oxidation processes including UV, UV/H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> were applied to study the degradation of BPA. The key conclusions based on this study are:

- Bisphenol A degradation rates achieved with simple UV irradiation is low. The addition of hydrogen peroxide caused a significant increase in degradation rates.
- There is an optimum H<sub>2</sub>O<sub>2</sub> concentration in spiked water samples. However, in wastewater samples the degradation rate marginally decreased with increasing H<sub>2</sub>O<sub>2</sub> concentration due to the scavenging effects, probably of inorganic ions, present in solution.
- By bubbling ozone into the solution, the highest degradation rates were achieved. In case of water, the highest degradation was achieved at 1 L/min flow rate. For treated wastewater, no specific optimum was determined and the reaction rate constant increased steadily with ozone dose.





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