Advanced Oxidative Degradation of Bisphenol A and Bisphenol S

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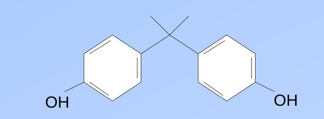
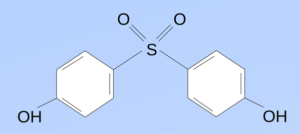
Background

Emerging contaminants studied in municipal wastewater:

	Bisphenol A (BPA)	Bisphenol S (BPS)
Molecular Structure		
Applications	- Polycarbonate production - Can coatings - Powder paints - Dental fillings - Food and drink packaging	- Glues - Additive in pesticides - Dyes - Colorfast agents - Leather tanning agent
Adverse Effects	- Breast cancer - Infertility - Impair brain development in fetuses and children	- Lymphocyte proliferation - Endocrine disruptor

Regulations:

- Health Canada (October 2008): Total allowable concentration of BPA in drinking water = 0.1 mg/L
- USEPA and the European Food Safety Authority: Oral reference dose (RfD) = 50 µg/kg body weight (bw)/day

BPA has been banned in baby bottles in Canada, US and Europe, leading to manufacturers replacing BPA with BPS.

One of the major sources of BPA and BPS in the environment: wastewater treatment plant effluents.

Most wastewater treatment plant processes are not able to treat these highly stable compounds to adequate levels.

A high percentage of these compounds pass through secondary biological treatment, entering the aquatic environment.

BPA concentrations at wastewater treatment plant influents: 0.08 to 4.98 µg/L, and effluents: 0.01 to 1.08 µg/L

Advanced Oxidation Processes (AOPs):

- Uses UV, oxidants such as O_3, H_2O_2, photocatalysts such as TiO_2 or their combinations
- Generates highly reactive oxidation species such as hydroxyl radicals and/or positive holes in semiconductors

e.g. in UV/H_2O_2: $H_2O_2 \xrightarrow{h\upsilon} 2\ {}^{\bullet}OH$

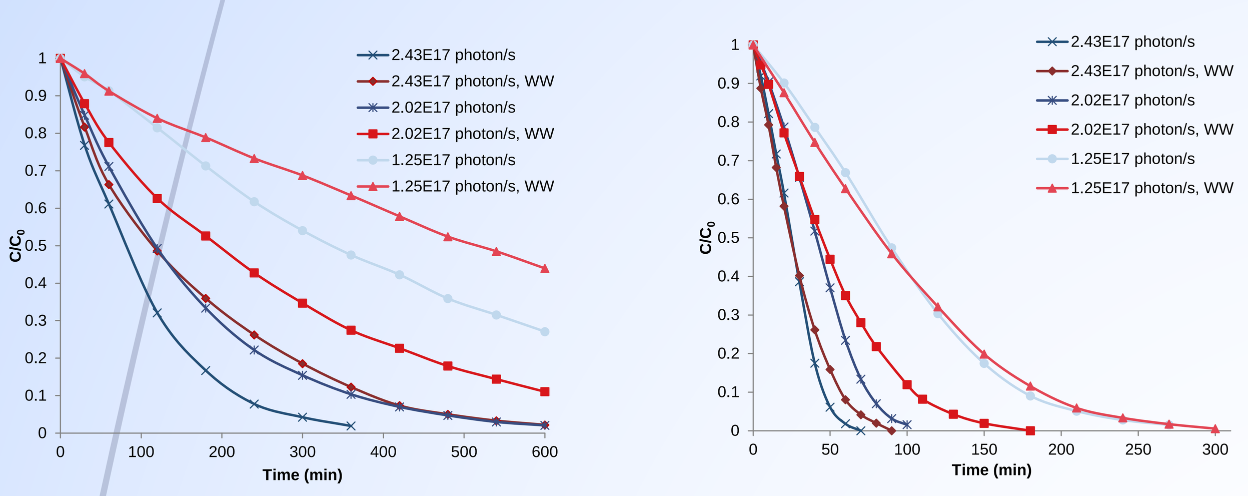
- Can degrade contaminants to convert them to CO_2, H_2O and inorganic ions

Objectives

Application of advanced oxidation processes (AOPs) to degrade BPA and BPS in municipal wastewater effluents

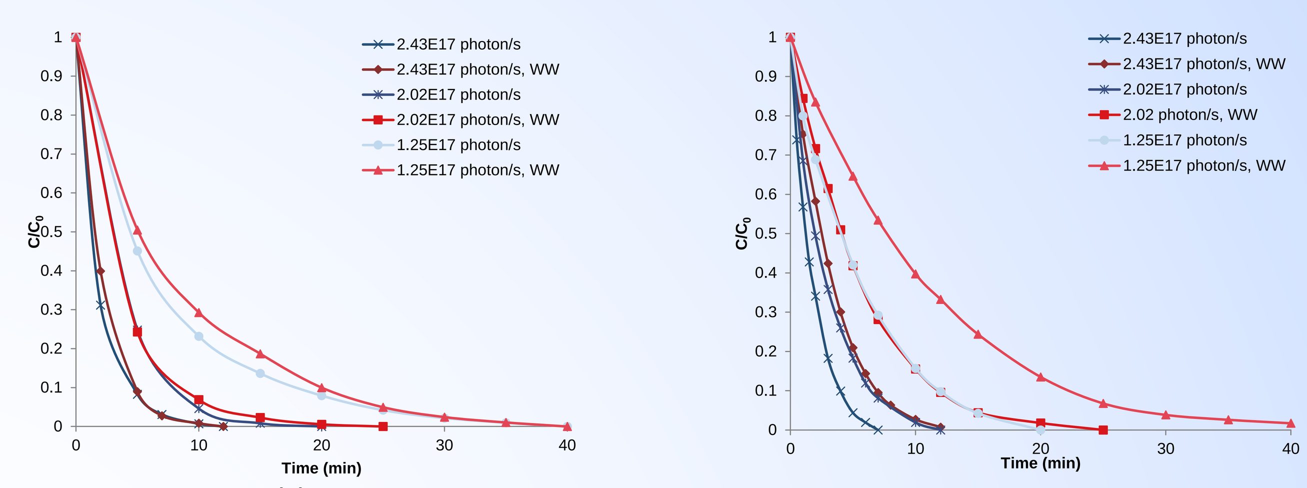
- Degradation by different AOPs in a batch photo-reactor in
  - spiked water
  - post-secondary treated wastewater
- Effect of inorganic ions and remaining organics present in post-secondary treated wastewater
- Identify the intermediates and by-products produced during chemical oxidation and their degradation pathways
- Fate in a UV disinfection unit of a wastewater treatment plant
- Extent of mineralization of BPS in a flow-through photo-reactor

Results – Different AOPs



(a) BPA (b) BPS

Fig. 1. Effect of light intensity on the UVC only process in water and wastewater (WW)

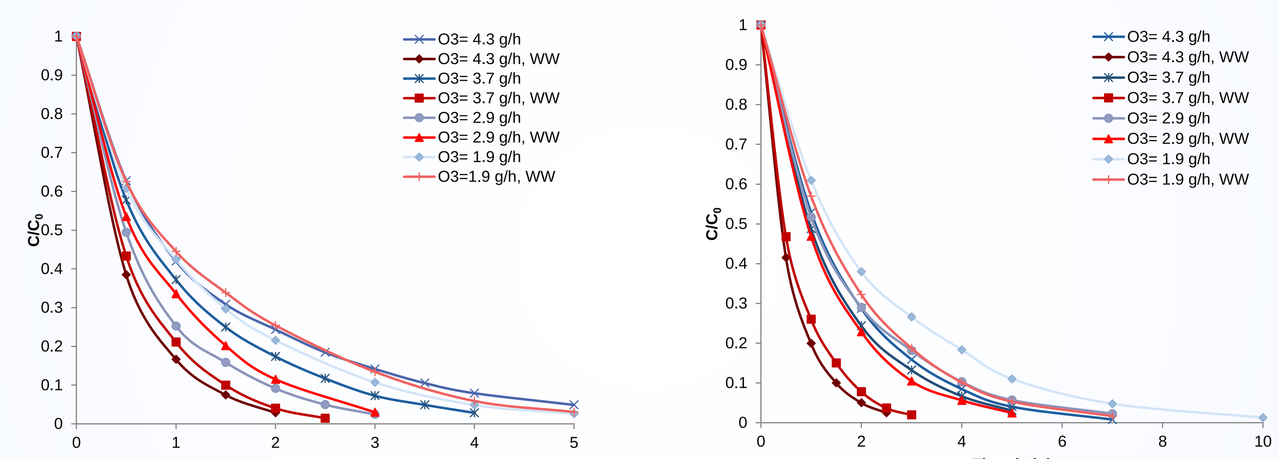


(a) BPA (b) BPS

Fig. 2. Effect of light intensity on the UVC/H_2O_2 process in water and wastewater, [H_2O_2]= 0.042 M

Table 1. Effect of H_2O_2 concentration in the UVC/H_2O_2 process in water and wastewater, Light intensity = 1.25E17 photon/s

[H_2O_2] (ppm)	BPA, $t_{1/2}$ (min)		BPS, $t_{1/2}$ (min)	
	Water	Wastewater	Water	Wastewater
500	5.3	4.1	3.6	7.7
1000	4.3	4.1	3.5	6.3
5000	4.9	4.3	2.9	6.9



(a) BPA (b) BPS

Fig. 3. Effect of O_3 flow rate on the O_3 process in water and wastewater (WW)

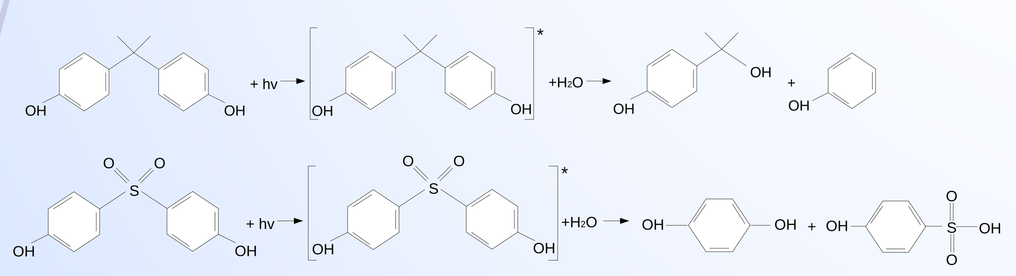
Table 2. Effect of O_3 flow rate in the UVA/O_3 process in water and wastewater, Light intensity = 0.587E17 photon/s

O_3 (g/h)	BPA, $t_{1/2}$ (min)		BPS, $t_{1/2}$ (min)	
	Water	Wastewater	Water	Wastewater
4.3	0.38	0.31	0.74	0.36
3.7	0.49	0.38	0.76	0.53
2.9	0.53	0.46	0.84	0.49
1.9	0.75	0.58	1.0	0.90

Intermediates and Degradation Pathway

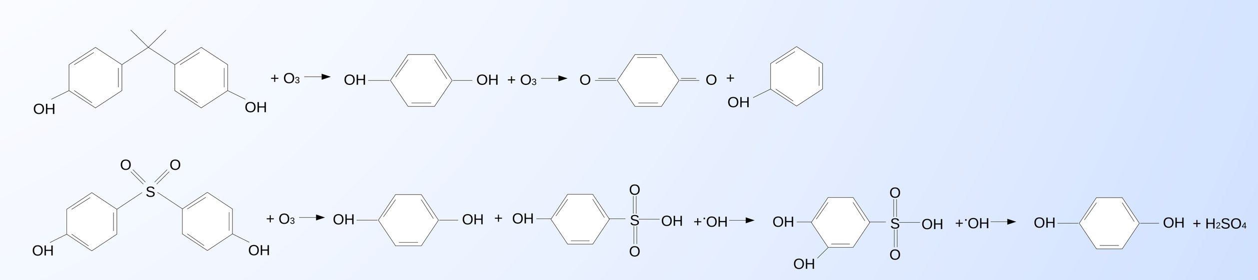
UVC only

BPA / BPS



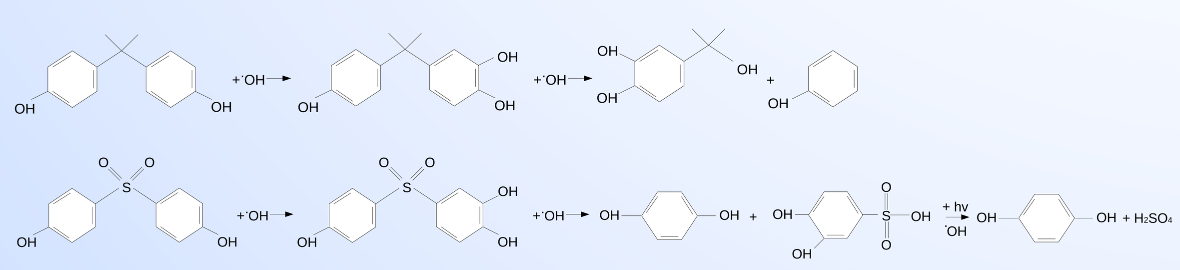
O_3

BPA / BPS



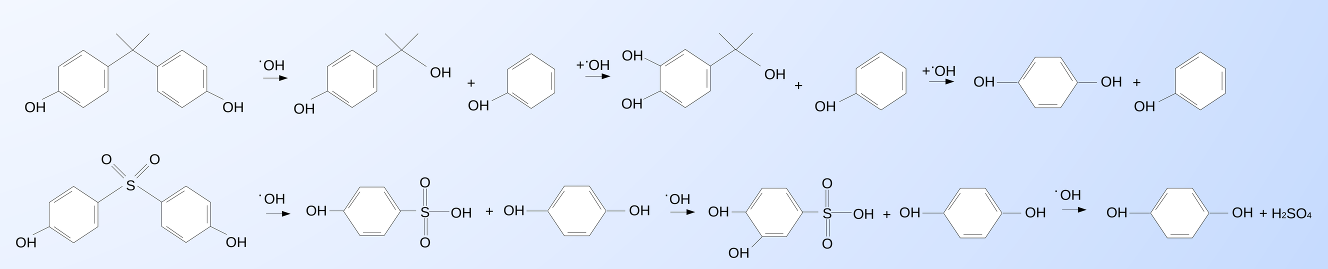
UVC/H_2O_2

BPA / BPS



UVA/O_3

BPA / BPS



Mineralization of BPS in a Flow-through Photo-reactor

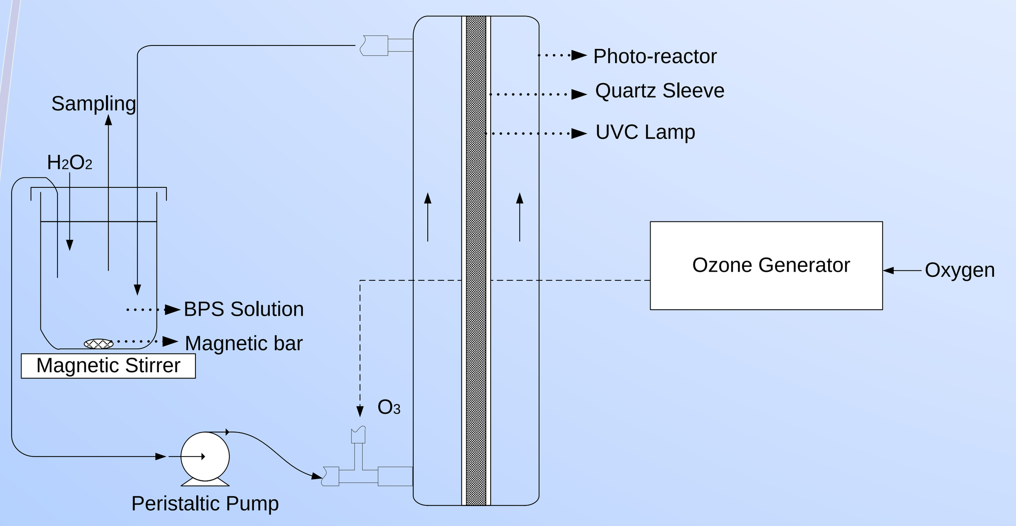


Fig. 4. Schematic of experimental setup

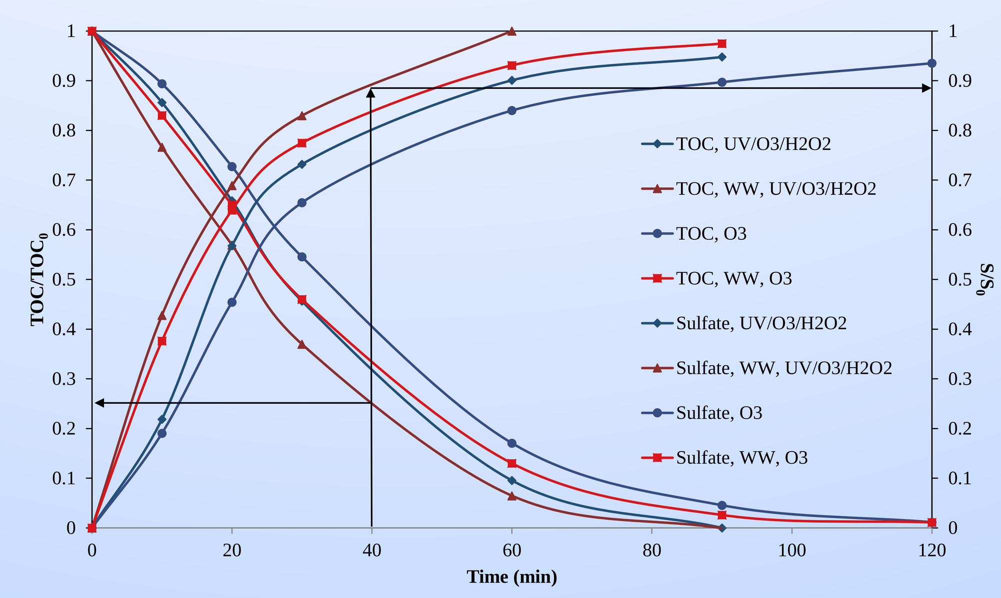


Fig. 5. TOC reduction and sulfate production in the UVC/O_3/H_2O_2 process (WW: wastewater samples, [H_2O_2] = 2.94 mM, O_3= 3.7 g/h)

- Sulfate was measured as it's presence indicates mineralization of organically bound sulfur.
- Release of the sulfur atom from BPS indicates the cleavage of BPS into two phenols or their oxidation products.
- S is released prior to completion of ring oxidations.

S_0 : theoretical calculated value of element S in BPS

S : amount of sulfur converted to sulfate and released

Mineralization in wastewater is higher compared to water, due to photosensitization of organic and inorganic ions in post-secondary treated wastewater.

Comparison to Wastewater Treatment Plant

UV dose in a typical UV disinfection unit of a municipal wastewater treatment plant = 4140.6 W/m^3

Influent flow rate = 500,000 m^3/d

Residence time in the disinfection unit = 5 – 8 sec

Total degradation of BPA = 1% and BPS = 6%

However, by addition of 1000 ppm H_2O_2 to the influent wastewater, turning the UVC only to UVC/H_2O_2,
Total degradation of BPA = 56% and BPS = 47%

Conclusions

- Degradation of BPA and BPS with UVC only: very low, due to low absorbance in the UVC range
- Addition of H_2O_2 enhanced degradation rates by an order of magnitude
- BPA and BPS degradation: UVA/O_3 > O_3 > UVC/H_2O_2 > UVC
- Effect of organics and inorganic ions in wastewater,
  - Presence of CO_3^{2-}, $H_2PO_4^-$ with O_3: $k_{BPS,WW} = 2 \times k_{BPS,W}$
  - Increased degradation of BPA and BPS by 30 and 40%, respectively, due to photosensitization of organics
- BPS in flow-through photo-reactor,
  - Best process for mineralization: UVC/O_3/H_2O_2
- Production of sulfate = Good indicator of BPS mineralization rate

Acknowledgements

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