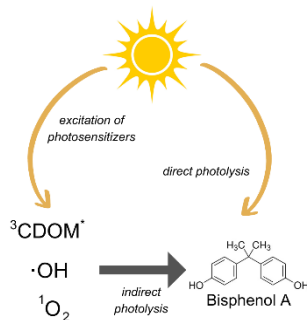


## Environmental photochemical fate of bisphenol A in surface water: A kinetic study

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Bisphenol A (BPA), a widely used industrial chemical, poses toxic risks to both aquatic organisms and humans. The persistence of pollutants in the environment can be influenced by photochemical processes triggered by sunlight, involving reactive photoproducted reactive intermediates (PPRIs), such as  $\text{HO}^\cdot$ ,  ${}^3\text{CDOM}^*$  and  ${}^1\text{O}_2$ . This study aims to explore the photochemical behavior of BPA in water. The photolytic experiments were conducted using a solar reflector, emitting  $4.34 \text{ mW cm}^{-2}$  in the 290-400 nm wavelength range. The results indicate low direct photolysis rate constants and photolysis quantum yields for BPA, suggesting its stability against direct photolysis. Furthermore, the measurement of second-order kinetic rate constants of the reactions between BPA and PPRIs using the competition kinetics approach highlights the importance of indirect photolysis as a degradation pathway in sunlit waters.

### Introduction

Bisphenol A (BPA), a common industrial compound, mimics estrogen and has been detected in surface waters. Its presence in aquatic environments is cause for concern due to its carcinogenic and teratogenic effects on humans, animals and aquatic life [1], [2].

The persistence of pollutants in the environment is influenced by various biotic and abiotic processes, including hydrolysis, photolysis, volatilization, complexation, oxidation, dilution, sorption, biodegradation and accumulation. Among these, photochemical processes, especially in sunlit waters, contribute significantly to the degradation of pollutants. Direct photolysis and indirect photolysis with reactive PPRIs, such as hydroxyl radicals ( $\text{HO}^\cdot$ ), singlet oxygen ( ${}^1\text{O}_2$ ) and triplet excited states of chromophoric dissolved organic matter ( ${}^3\text{CDOM}^*$ ) are the main pathways for pollutant degradation in aquatic environments [3].

This study aims to investigate the photochemical fate of BPA and evaluate its reaction kinetics with PPRIs ( $\text{HO}^\cdot$ ,  ${}^3\text{CDOM}^*$  and  ${}^1\text{O}_2$ ), as well as the direct photolysis quantum yield of BPA ( $\Phi_{\text{BPA}}$ ).

### Material and Methods

#### Reagents

All solutions were prepared using ultrapure water ( $18.2 \text{ M}\Omega \text{ cm}$ ) from a Milli-Q<sup>®</sup> system (Millipore). Technical grade bisphenol A (99.9%,  $\text{C}_{15}\text{H}_{16}\text{O}_2$ ) was obtained from Sigma-Aldrich. Methanol, acetonitrile (HPLC grade), glacial acetic acid (100%) and the reference compounds para-chlorobenzoic acid (pCBA), 2,4,6 trimethylphenol (TMP) and furfuryl alcohol (FFA) were purchased from Sigma-Aldrich. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30% v/v, Synth) and methylene blue (96%, Synth) served as the source

of  $\text{HO}^\cdot$  and  ${}^1\text{O}_2$  radicals, respectively, while 4-carboxybenzophenone (CBBP) acted as a proxy for CDOM.

#### Analytical methods

The HPLC analysis of BPA, pCBA, FFA and TMP used a Shimadzu LC20 system with a UV/Vis detector (SPD20A model) and a C18 column (ACE<sup>®</sup>, 100 Å, 5  $\mu\text{m}$ , 4.6 mm  $\times$  250 mm). Specific conditions were set for each compound: The mobile phase compositions were 45% aqueous acetic acid 1% (v/v) (A) + 55% acetonitrile (B) for BPA and TMP; 70% aqueous acetic acid 1% (v/v) (A) + 30% methanol (B) for FFA; and 40% aqueous acetic acid 1% (v/v) (A) + 60% methanol (B) for pCBA. The oven temperature, sample injection volume and mobile phase flow rate were maintained at 40 °C, 100  $\mu\text{L}$  and 1  $\text{mL min}^{-1}$ , respectively.

#### Spectral molar absorption coefficient

The absorption coefficient spectrum of BPA was measured with a UV-Vis spectrophotometer (Varian Cary 50), with a 1-cm path-length quartz cuvette.

#### Kinetic study

The photolytic experiments were carried out in duplicates at pH  $7.0 \pm 0.3$  and 25 °C using a parabolic reflector (Spotlux Co.) with a mercury iodide lamp (Master HPI-T Plus, Philips). The irradiance provided by the lamp was  $4.34 \text{ mW cm}^{-2}$  in the 290-400 nm wavelength range. The samples were placed in 2-mL Pyrex vials without headspace and submerged in a water bath for irradiation. The average optical path length of the samples was 6.35 mm. The second-order kinetic rate constants of BPA with PPRIs were determined using the competition kinetics method [4] (Equation 1). This method involves competition

between BPA and a reference compound for the reactive species, with kinetic constants derived from the concentration decays over time of both compounds.

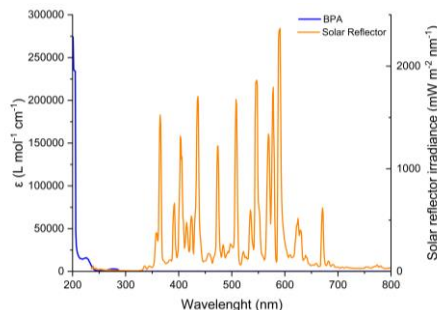
$$k_{BPA} = \frac{k_{BPA(obs)} - k_{BPA(direct\ photolysis)}}{k_{ref(obs)} - k_{ref(direct\ photolysis)}} \cdot k_{ref,RPS} \quad (1)$$

## Results and Discussion

Figure 1 shows the absorption spectra of the aqueous BPA solution and the emission spectrum of the radiation source. BPA shows limited absorption beyond 290 nm, suggesting a low molar absorption coefficient in the visible range. This indicates that BPA is expected to be predominantly degraded in surface waters through indirect photodegradation, possibly affected by natural organic matter, nitrate, and nitrite. The direct photolysis experiments revealed a slight degradation of BPA, with a pseudo-first-order photolysis rate constant (measured over 6 h) of  $k_{BPA} = 5.86 \times 10^{-6} \text{ s}^{-1}$ . The photolysis quantum yield, calculated using the method described by [5], is  $\Phi_{BPA} = 4.20 \times 10^{-3} \text{ mol Einstein}^{-1}$ , suggesting that BPA is stable against direct photolysis.

**Table 1** shows the concentrations of PPRIs sources and the second-order kinetic rate constants for BPA ( $\text{HO}^\cdot$ ,  $^1\text{O}_2$  and  $^3\text{CDOM}^*$ ). The values determined,  $k_{BPA,\text{HO}^\cdot} = (3.44 \pm 0.03) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ,  $k_{BPA,^1\text{O}_2} = (2.35 \pm 0.19) \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$  and  $k_{BPA,^3\text{CBBP}^*} =$

$(1.09 \pm 1.16) \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ , suggest that the degradation of BPA in sunlit waters is predominantly driven by the interaction between BPA molecules and  $\text{HO}^\cdot$ , as well as  $^3\text{CDOM}^*$  and  $^1\text{O}_2$ .



**Figure 1.** Molar absorption coefficient ( $\epsilon$ ) of BPA and emission spectrum of the solar reflector.

Han et al. [2] found similar second-order kinetic rate constants for BPA and  $\text{HO}^\cdot$  in pure water ( $k_{BPA,\text{HO}^\cdot} = 3.4 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ). However, the literature lacks reports on the second-order degradation rate constants of BPA with respect to  $^3\text{CDOM}^*$ ,  $^1\text{O}_2$  and its direct photolysis quantum yield ( $\Phi_{BPA}$ ) under solar radiation.

**Table 1.** Initial concentrations of the PPRIs sources, reference compounds and second-order kinetic rate constants for reactions involving BPA and PPRIs ( $\text{HO}^\cdot$ ,  $^3\text{CDOM}^*$ ).

[BPA] <sub>0</sub>	PPRI	PPRI source	Reference compound	$k_{BPA,PPRI} \text{ (L mol}^{-1} \text{ s}^{-1}\text{)}$
5 mg L <sup>-1</sup>	$\text{HO}^\cdot$	H <sub>2</sub> O <sub>2</sub> (50 mmol L <sup>-1</sup> )	pCBA	$(3.44 \pm 0.03) \times 10^9$
	$^1\text{O}_2$	Methylene blue (31,3 μmol L <sup>-1</sup> )	FFA	$(2.35 \pm 0.19) \times 10^6$
	$^3\text{CDOM}^*$	CBBP (44.3 μmol L <sup>-1</sup> )	TMP	$(1.09 \pm 1.16) \times 10^8$

## Conclusions

Direct photolysis degraded BPA minimally, while indirect photolysis driven by  $\text{HO}^\cdot$ ,  $^1\text{O}_2$ ,  $^3\text{CDOM}^*$  was significant. Future research will investigate BPA degradation in natural aqueous environments, including the contribution of carbonate radicals ( $\text{CO}_3^{\cdot-}$ ) in indirect photolysis. Mathematical modeling will be used to determine the half-life of BPA in sunlit surface waters, accounting for environmental variables.

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