Recent advances in Bisphenol A UV/H\textsubscript{2}O\textsubscript{2} degradation

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Abstract. Compounds destroying the endocrine system are a dangerous class of pollutants that are found in aquatic environments such as surface, groundwater and sewage and landfills. Bisphenol A (BPA) is a known endocrine disruptor that is acutely toxic to living organisms. BPA is still used in the manufacture of sunscreen lotions, nail polishes, body cleansers, shaving creams and lotions, in addition to its long-known other industrial applications. The paper presents the results of studies on the photolysis of BPA from water using ultraviolet radiation and an oxidizing agent.

1. Introduction

Microcontaminants more and more often fall into the focus of public discussion, especially such as endocrine drugs or other drugs that lead to various side effects for the elderly [1]. Pollution of surface and groundwater by objects of phenolic and other difficultly oxidized organic compounds occurs in the chemical, metallurgical, mining, pharmaceutical, pulp and paper, food industries and solid waste landfills.

Among synthetic xenoestrogens, bisphenol A (4,4\textsuperscript{\prime}-(propane-2,2-diyl) diphenol) is one of the most common chemically synthesized compounds with annual production of over 3.8 million tons. BPA is widely used in the synthesis of polycarbonates, epoxies and thermal paper, in the manufacture of electronic equipment, paper or toys. BPA is also used in materials in contact with food. BPA is found in the wastewater of industries associated with the thermal processing of wood, shale, peat, lignite and coal, as well as due to their high foaming properties, they are widely used in flotation, etc. BPA disrupts the normal course of embryogenesis, leading to the appearance of various types of deformities in fish.

As a result of the biochemical destruction of BPA in the water of reservoirs, all elements of the hydrochemical regime change.

One of the important tasks in modern society at the moment for the effective purification of liquid industrial effluents from phenolic compounds is the search for common patterns inherent in different schemes of transformation of substances, and the construction of models describing the effects of physico-chemical factors on the level of reduction of organic pollutants in the aquatic environment [2].

A modern and highly effective method for removing organic pollutants contained in industrial wastewater is the process based on the use of free radicals as oxidizing agents, called Advanced Oxidation Processes (AOP) [3], the advantage of which is the ease of controlling their speed in wide limits with a change in the intensity of the light flux, their rapid and complete suspension with the cessation of irradiation. It is known, •OH can be generated by irradiating water with UV light in the
presence of oxidizing agents, such as hydrogen peroxide ($\text{H}_2\text{O}_2$). UV radiation is located at the high-energy end of the light spectrum with a wavelength less than that of visible light (400 nm), but more than that of x-rays (100 nm). UV radiation can destroy organic pollutants, including BPA, by direct and indirect photolysis.

Modern mercury-free excilamps have established themselves as efficient and environmentally friendly sources of quasi-monochromatic UV radiation for the decomposition of a number of organic pollutants (phenols, dyes, and herbicides) and are considered as an alternative to traditional mercury lamps [4].

The aim of this work is to study the effect of the irradiation wavelength on the efficiency of the phototransformation of BPA in water in the presence of $\text{H}_2\text{O}_2$ when irradiated with excilamps in a stationary KrCl and XeCl photoreactor.

2. Experimental part

In this work we used Bisphenol A (BPA), of chemical purity 95% (from ALDRICH) in water. Solutions of the investigated compound were prepared by dissolving a dry weighed quantity in the amount of 45.6 mg in 500 mL of water. To achieve complete solution of BPA to a concentration $C=91.2$ mg/L we used an ultrasound mixer at 40°C for 45 min. The structural formula of the investigated molecule is shown in Fig. 1.

![Figure 1. Structural formula of the investigated compound.](image)

Spectral-luminescence characteristics of the solution of BPA were recorded before and after irradiation on a spectrophotometer “UV-Vis Spectrometry UNICAM” (Thermo Evolution 600, USA) and SOLAR CM2203 (Belarus). The prepared solutions of BPA with a concentration of 50 mg/L were irradiated in glass beakers with a diameter of 4.6 cm by KrCl and XeBr excilamps at room temperature for 120 min with constant mixing with the help of a mechanical mixer. The distance from the excilamp to the irradiated solution was 3 cm (Fig. 2). The volume of irradiated solution was $V = 50$ mL. During the irradiation time the maximum energy absorbed by the investigated solution did not exceed 10 J/cm³.

The change in the volume and the temperature during irradiation was recorded. Depletion of the investigated compound was monitored by tracking variation of the optical density in the absorption spectra at the wavelength $\lambda = 270$ nm (the measurement error did not exceed 10%).

The conversion of BPA was calculated from values of the optical density at the maximum of the long-wavelength absorption band, according to the formula taken from [5-7]:

$$X = \frac{C_0 - C}{C_0} = 1 - \frac{C}{C_0}.$$  

Designations:

$V$ = volume of the solution during the irradiation (ml); $V_0$ = volume of the solution at the initial time of the irradiation (ml); $C$ = concentration of BPA during the irradiation (mg/ml); $C_0$ = concentration of BPA at the initial time of the irradiation (mg/ml); $t$ = exposure time (min); $r$ = reaction rate (mg/ml min); $\lambda_{irr}$ = maximum wavelength of excilamps (nm).

To prepare the systems with $\text{H}_2\text{O}_2$ we determined the concentration of the oxidizer according to the equation:

$$C_{14}\text{H}_{16}\text{O}_2 + X \times \text{H}_2\text{O}_2 = 14\text{CO}_2 + n \times \text{H}_2\text{O}.$$
In order to degrade 50 mg/L of BPA to CO$_2$ and water, it is necessary to have the maximum amount of H$_2$O$_2$ equal to 4.7 mg. The solutions were prepared from 34% of aqueous solution of H$_2$O$_2$. The conversion of BPA was calculated from values of the optical density at the maximum of the long-wavelength absorption band.

The photolysis model is based on following assumptions:
1. For photodegradation of BPA the oxidant H$_2$O$_2$ is required.
2. Photochemical reaction obeys the kinetics of a pseudo first order.

Material balance of BPA in the system of a stationary KrCl or XeBr photoreactor can be represented as follows:

$$\text{Input} = \text{Output} + \text{Accumulation} – \text{Destruction}. $$

The study of BPA photolysis was carried out simultaneously both in the absence and in the presence of hydrogen peroxide (Fig. 2). The reaction between •OH and many organic pollutants occur quickly; however, this reaction on its own account does not directly lead to the mineralization of these pollutants, but rather forms oxidation by-products, which can further react with •OH. Ideally, AOP systems are designed to completely mineralize organic pollutants to CO$_2$ and H$_2$O, but this needs to be optimized, as it can require a lot of energy and large doses of chemical oxidizing agents and, ultimately, can be expensive in some applications in purification systems.

We studied the effect of the irradiation wavelength on the effectiveness of the phototransformation of BPA in water in the presence of hydrogen peroxide. Irradiation of aqueous solutions was carried out at room temperature in a stationary photoreactor, the design of which is shown in Fig. 2. Constant mixing of the solution upon irradiation was included.

![Figure 2. Scheme of a stationary photoreactor. The numbers indicate the solutions: without addition (№1) and in the presence of (№2) H$_2$O$_2$.](image)

KrCl (with a radiation wavelength of 222 nm) and XeBr (with a radiation wavelength of 283 nm) were used as sources of UV irradiation. Static lamps had a cylindrical shape and were covered by a metal case with an output UV window of 75 cm$^2$. The distance from the source (excilamp) to the irradiated solution was 3 cm. The volume of the irradiated solution was 50 ml. The average intensity of radiation supplied to the solution was 17.12 and 2.47 mW/cm$^2$ for XeBr and KrCl excimer lamps, respectively. The control exposure time was: 0, 1, 2, 5, 10, 20, 30, 40, 60 and 120 minutes. The ratio of H$_2$O$_2$: BPA in the aqueous solution was as follows: 0:1, 1:1, 2:1, 3:1, 4:1. During the irradiation, samples were taken and absorption spectra were recorded for rapid visual observation of phototransformation and fixation of the concentration of total phenol in solution.
Analysis of the decrease in BPA in solution was also carried out by fluorescence. To construct the conversion curve, a decrease in the concentration of BPA in aqueous solutions was performed using HPLC.

3. Results and discussion
Taking into account that phenol compounds of various structures are expected to form during photodegradation of BPA, we analyzed the total phenol by electron spectroscopy. For this, the wavelength $\lambda_{\text{Dmax}} = 740$ nm was chosen, at which we measured the absorbance of the BPA solutions after irradiation. The data are shown in tables 1 and 2. Spectral interpretations allow a comparative assessment of the resulting photoproducts in irradiated solutions. A high content of common phenolic components was found.

After irradiation, the optical absorption density increased in this region to a maximum value of 0.72 at a ratio of H$_2$O$_2$:BPA in an aqueous solution of 3:1 after 120 minutes of irradiation by XeBr excilamp. This indicates the active transformation of BPA and the formation of stable phenol-based photoproducts. The minimum absorbance value of 0.027 is achieved when the oxidizer to BPA ratio is 5:1 after 120 minutes of irradiation by KrCl excilamp. This suggests that with this ratio not only the destruction of BPA, but also of photoproducts occurs.

To construct the conversion curve, the decrease in the concentration of BPA in aqueous solutions was taken from the data using HPLC. An analysis of the rate constant of the decrease in BPA in water under the action of KrCl and XeBr radiation by excilamps indicates that, under the action of KrCl excilamp radiation, the efficiency of degradation of BPA without additives in water is higher than after exposure to XeBr excilamp [8]. In this case, the decrease in BPA in water after irradiation was only 60% after 120 min exposure to an excilamp (Fig. 3). The HPLC data of the final KrCl excilamp irradiated for 120 min in an aqueous solution showed that the solution also contains phototransformation products in addition to BPA.

Table 1. Absorption optical density of irradiated BPA solutions at a wavelength of 740 nm at various ratios of H$_2$O$_2$:BPA in an aqueous solution after irradiation of a KrCl excilamp using electron spectroscopy data.

| t, min | Mass ratio H$_2$O$_2$:BPA |
|--------|-------------------------|
| 0:1    | 1:1                     | 2:1 | 3:1 | 4:1 | 5:1 | 6:1 |
| 0      | 0.444                   | 0.447 | 0.474 | 0.474 | 0.457 | 0.515 | 0.521 |
| 1      | 0.393                   | 0.347 | 0.289 | 0.413 | 0.456 | 0.399 | 0.397 |
| 2      | 0.400                   | 0.364 | 0.352 | 0.543 | 0.394 | 0.398 | 0.392 |
| 3      | 0.407                   | 0.441 | 0.563 | 0.514 | 0.397 | 0.415 | 0.404 |
| 5      | 0.481                   | 0.457 | 0.477 | 0.544 | 0.499 | 0.586 | 0.554 |
| 10     | 0.473                   | 0.487 | 0.517 | 0.611 | 0.569 | 0.586 | 0.615 |
| 20     | 0.414                   | 0.508 | 0.517 | 0.504 | 0.566 | 0.508 | 0.519 |
| 30     | 0.452                   | 0.489 | 0.496 | 0.562 | 0.482 | 0.518 | 0.497 |
| 40     | 0.389                   | 0.480 | 0.489 | 0.523 | 0.466 | 0.487 | 0.448 |
| 60     | 0.353                   | 0.448 | 0.317 | 0.410 | 0.133 | 0.084 | 0.083 |
| 90     | 0.328                   | 0.432 | 0.278 | 0.135 | 0.099 | 0.036 | 0.017 |
| 120    | 0.336                   | 0.410 | 0.127 | 0.341 | 0.094 | 0.027 | 0.053 |
**Table 2.** Absorption optical density of irradiated BPA solutions at a wavelength of 740 nm at various ratios of \( \text{H}_2\text{O}_2: \text{BPA} \) in an aqueous solution after XeBr irradiation with an excilamp according to electron spectroscopy.

| t, min | Mass ratio \( \text{H}_2\text{O}_2: \text{BPA} \) | 0:1 | 1:1 | 2:1 | 3:1 | 4:1 | 5:1 | 6:1 |
|--------|---------------------------------|-----|-----|-----|-----|-----|-----|-----|
| 0      |                                 | 0.337 | 0.458 | 0.488 | 0.497 | 0.459 | 0.474 | 0.479 |
| 1      |                                 | 0.381 | 0.480 | 0.487 | 0.416 | 0.363 | 0.623 | 0.370 |
| 2      |                                 | 0.415 | 0.475 | 0.523 | 0.512 | 0.455 | 0.423 | 0.392 |
| 3      |                                 | 0.413 | 0.456 | 0.457 | 0.588 | 0.353 | 0.555 | 0.371 |
| 5      |                                 | 0.368 | 0.352 | 0.544 | 0.446 | 0.469 | 0.394 | 0.394 |
| 10     |                                 | 0.415 | 0.460 | 0.460 | 0.498 | 0.473 | 0.538 | 0.523 |
| 20     |                                 | 0.377 | 0.454 | 0.489 | 0.574 | 0.502 | 0.559 | 0.555 |
| 30     |                                 | 0.381 | 0.474 | 0.499 | 0.568 | 0.527 | 0.599 | 0.572 |
| 40     |                                 | 0.369 | 0.464 | 0.537 | 0.622 | 0.555 | 0.692 | 0.605 |
| 60     |                                 | 0.341 | 0.465 | 0.499 | 0.634 | 0.581 | 0.541 | 0.551 |
| 90     |                                 | 0.384 | 0.421 | 0.477 | 0.662 | 0.532 | 0.422 | 0.468 |
| 120    |                                 | 0.363 | 0.418 | 0.510 | 0.720 | 0.496 | 0.395 | 0.383 |

The results of the photolysis of BPA in water with the addition of hydrogen peroxide are shown in Figure 3. When using the KrCl/H\(_2\)O\(_2\) combination, the photolysis efficiency also increases in comparison with the XeBr/H\(_2\)O\(_2\) combination.

![Figure 3](image1)

**Figure 3.** The conversion of BPA in an aqueous solution in the presence of H\(_2\)O\(_2\):BPA: 1 – 0:1; 2 – 1:1; 3 – 2:1; 4 – 3:1; 5 – 4:1. The irradiation was under the action of KrCl (a) and XeBr (b) excilamps.

The obtained curves of the dependence of the decay rate on time under the action of XeBr and KrCl excilamp radiation are shown in Figure 4.
Figure 4. Decay rate of BPA in the water in relation to H$_2$O$_2$:BPA – 1:1 after the irradiation by XeBr excilamp (1) and KrCl excilamp (2).

An analysis of the nature of the obtained curves (Fig. 4) shows that the maximum rate when H$_2$O$_2$ is added to BPA solutions in water is observed upon exposure to KrCl radiation for a ratio of H$_2$O$_2$: BPA - 4:1 after 20 min of irradiation (Table 3). When exposed to XeBr radiation from the excilamp, the decrease in BPA at the same ratio with the oxidizing agent was achieved only after 120 min of irradiation (Table 4). Thus, the presence of H$_2$O$_2$ in the system contributes to an increase in the phototransformation efficiency of BPA under the influence of 222 nm irradiation.

The obtained HPLC data indicate that the irradiation wavelength changes the decay rate and the kinetics of the decomposition reaction of BPA photoproducts in the presence of an oxidizing agent.

**Table 3.** The conversion and concentration (C) of BPA in water after irradiation of KrCl excilamp according to HPLC.

| H$_2$O$_2$:BPA ratio in aqueous solution | 0:1 | 1:1 | 2:1 | 3:1 | 4:1 |
|----------------------------------------|-----|-----|-----|-----|-----|
| t, min                                 |     |     |     |     |     |
| C, mg/l                                |     |     |     |     |     |
| Conversion                             |     |     |     |     |     |
| 0                                      | 53.7| 52.4| 51.5| 50.8| 49.4|
| 1                                      | 52.4| 47.2| 44.6| 43.5| 43.3|
| 2                                      | 52  | 43  | 39.9| 37.1| 34.9|
| 3                                      | 49.4| 38.6| 36  | 34.2| 24.3|
| 5                                      | 50.9| 29.7| 23.5| 23.6| 22.4|
| 10                                     | 46.7| 19.5| 15.4| 11.9| 10.3|
| 20                                     | 44.3| 9.2 | 4.1 | 3.1 | 2   |
| 30                                     | 35.5| 11.8| 5.7 | 3.6 | 0   |
| 40                                     | 34.1| 6.2 | 3.2 | 1.9 | 0.7 |
| 60                                     | 30.7| 0.8 | 0.1 | 0   | 0   |
| 90                                     | 27.3| 0.2 | 0.1 | 0   | 0   |
| 120                                    | 10.4| 0.4 | 0.2 | 0.1 | 0   |
Table 4. The conversion and concentration (C) of BPA in water after irradiation with XeBr excilamp according to HPLC.

| H2O2:BPA ratio in aqueous solution | t, min | 0:1 | 1:1 | 2:1 | 3:1 | 4:1 |
|------------------------------------|-------|-----|-----|-----|-----|-----|
| C, mg/l                            |       |     |     |     |     |     |
| Conversion                         |       |     |     |     |     |     |
| 0                                  | 53.4  | 0.000 | 52.4 | 0.000 | 51.7 | 0.000 |
| 1                                  | 52.3  | 0.021 | 49.3 | 0.059 | 50.6 | 0.021 |
| 2                                  | 52.4  | 0.020 | 50.1 | 0.044 | 50.3 | 0.026 |
| 3                                  | 53.3  | 0.001 | 49.4 | 0.058 | 46.9 | 0.093 |
| 5                                  | 54.3  | -0.017 | 46.7 | 0.108 | 45.2 | 0.126 |
| 10                                 | 50.6  | 0.052 | 42.3 | 0.192 | 37.8 | 0.270 |
| 20                                 | 49.8  | 0.067 | 34.3 | 0.346 | 28.1 | 0.457 |
| 30                                 | 49.4  | 0.074 | 29.0 | 0.446 | 22.7 | 0.560 |
| 40                                 | 47.1  | 0.118 | 25.1 | 0.522 | 19.2 | 0.629 |
| 60                                 | 40.3  | 0.245 | 18.7 | 0.644 | 9.8  | 0.810 |
| 90                                 | 38.4  | 0.281 | 13.8 | 0.737 | 5.8  | 0.889 |
| 120                                | 37.7  | 0.294 | 7.1  | 0.864 | 4.5  | 0.912 |

Figure 5. Diagrams of the formation of photoproducts in a photoreactor under the influence of excilamp radiation (№ 1 – KrCl, № 2 – KrCl/H2O2, № 3 – XeBr, № 4 – XeBr/H2O2) according to fluorescence spectroscopy. The numbers in the figure indicate the exposure time in the photoreactor.

The UV radiation source of the KrCl excilamp with an emission wavelength of 222 nm proved to be more efficient for direct photolysis of BPA compared to the XeBr excilamp with an emission wavelength of 283 nm. However, in all cases, BPA in water is more efficiently degraded with the addition of oxidation compared to direct UV treatment. Full mineralization was achieved only in the case of a combination of UV/H2O2 when exposed to KrCl radiation excilamps. However, according to fluorescence spectroscopy, it was found (Table 5) that even after 120 minutes, fluorescent photo products remain in the BPA solution. Moreover, the diagram clearly shows (Fig. 5) that during the phototransformation of BPA under the influence of KrCl radiation, the photo-product accumulates for 1 to 10 minutes, then the product breaks up and the fluorescence of photo-product 2 increases by 120 minutes. When exposed to XeBr radiation, the excilamp increases the fluorescence intensity of the photoprodut is 1 to 120 min of irradiation, and then the photoprodut is transformed.
Table 5. The fluorescence intensities of the resulting photoproducts in the maximum bands.

| №  | Excilamp | The maximum fluorescence band of the photoproduct, nm | Exposure time, min |
|----|----------|-------------------------------------------------------|-------------------|
| 1  | KrCl     | λ = 410-420                                          | 0 1 2 5 10 30 60 120 |
| 2  | KrCl/H₂O₂| λ = 430-450                                          | 11.5 13.5 14.3 17.5 30.7 8.2 11.1 11.9 10.7 32.1 |
| 3  | XeBr     | λ = 410-420                                          | 0.2 0.4 0.5 0.6 0.7 0.5 0.4 0.5 0.4 0.3 |
| 4  | XeBr/H₂O₂| λ = 430-450                                          | 11.7 15.1 18.4 25.6 31.4 36.2 35.9 32.4 29.4 19.3 |

4. Conclusion

Prior to our studies, an assessment of human exposure to BPA was established. It has been proven that BPA can affect animals and humans when interacting with estrogens, endogenies and receptors, disrupting the function of not only the endocrine system, but also the immune or nervous system. The results of our studies showed that photodegradation of BPA in water in the presence of an oxidizing agent can be successfully used to remove the contaminant before entering into natural waters in order to reduce the risk to living organisms. We will have to further study the toxicity of BPA photolysis photoproducts and revise the kinetic model of contaminant degradation in the presence of an oxidizing agent. Perhaps the decay of the BPA will be subject to a decay curve of pseudo-second order.

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