

PROCEEDINGS OF SPIE

SPIDigitalLibrary.org/conference-proceedings-of-spie

Photodegradation of bisphenol A in the presence of superfine microfiber polypropylene

Tchaikovskaya, O., Bocharnikova, E., Bezlepkina, N., Lysak, I., Malinovskaya, T., et al.

O. N. Tchaikovskaya, E. N. Bocharnikova, N. P. Bezlepkina, I. A. Lysak, T. D. Malinovskaya, G. V. Lysak, "Photodegradation of bisphenol A in the presence of superfine microfiber polypropylene," Proc. SPIE 12086, XV International Conference on Pulsed Lasers and Laser Applications, 1208602 (2 December 2021); doi: 10.1117/12.2593831

SPIE.

Event: XV International Conference on Pulsed Lasers and Laser Applications, 2021, Tomsk, Russian Federation

Photodegradation of bisphenol A in the presence of superfine microfiber polypropylene

O.N. Tchaikovskaya¹, E.N. Bocharnikova¹, N.P. Bezlepina^{1*}, I.A. Lysak²,
T.D. Malinovskaya², G.V. Lysak²

¹ National Research Tomsk State University, Tomsk, Russia

² Innovation and technology center, Siberian Physical Technical Institute, Tomsk, Russia

ABSTRACT

The effect of UV radiation on the efficiency phototransformation BPA in water in the presence of polypropylene superfine microfibers. The absorption and fluorescence spectra of the investigated substance with three types of PPM of various properties were obtained. After excitation with an excilamp, the main photoproduct BPA fluoresces in the region of 405 ÷ 410 nm. With an increase in the irradiation time from 0 to 10 minutes, an increase in the fluorescence intensity of this BPA photoproduct was recorded. This indicates that in the course of irradiation, effective photodegradation of the initial toxicant occurs and a photoproduct is formed. In the course of irradiation, the degradation of the resulting photoproducts occurs, which is associated with their adsorption on the surface of the PPM.

Keywords: bisphenol A; BPA; degradation; photolysis; spectral and luminescent properties; photoreactor.

1. INTRODUCTION

Bisphenol A (BPA) is a toxic persistent pollutant that is endocrine disrupting at low concentrations and causes metabolic and brain damage [1, 2]. BPA is widely used as an inexpensive hardener in the preparation and processing of plastics, and a large amount of wastewater is discharged in chemical plants. Almost 95% of packaging materials, plastic bottles and tableware contain BPA [3]. Improper storage and use of products from these packages are guaranteed to lead to the ingestion and accumulation of BPA in a person. BPA has been found in natural waters [4]. There is still an urgent need to study the question of the fate of BPA in nature and living organisms.

For effective removal of BPA several new technologies have been developed from contaminated water, most of which are based on photodegradation [5, 6]. Studies have shown that conventional sedimentation tanks do not remove dissolved BPA from wastewater [7]. For efficient removal of BPA from natural and wastewater scientists developed technologies based on the use of the complex physicochemical and biological methods, most of which include preprocessing the ultraviolet ray. Many studies done to date [8, 9] showed that BPA can be degraded through aerobic microbial processes [10] to the reported half-life of several days to dozens of weeks, which may explain the relatively low efficiency of removal of the BPA in the natural environment.

In this paper a study effectiveness phototransformation BPA in water in the presence of superfine microfibers of polypropylene under the influence of UV radiation.

2. EXPERIMENTAL PART

In this work, bisphenol A (BPA) of chemical purity 95% from Sigma Aldrich was used, dissolved in distilled water to a concentration of $C = 2.2 \times 10^{-4}$ mol/L using an ultrasonic stirrer and heating to 40 degrees. The structural formula of the compound under study is shown in Fig. 1. The irradiation of aqueous solutions in the presence of superfine microfiber polypropylene (PPM) is conducted at room temperature under conditions of stationary irradiation photoreactor whose diagram is represented in Fig. 2.

* nadezhda.bezlepina174833@mail.ru; phone +79234152983

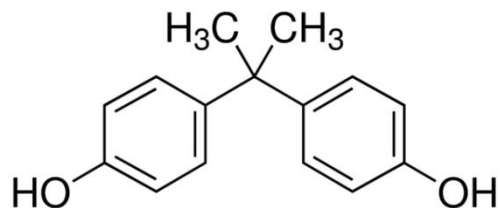


Figure 1. The structural formula of BPA

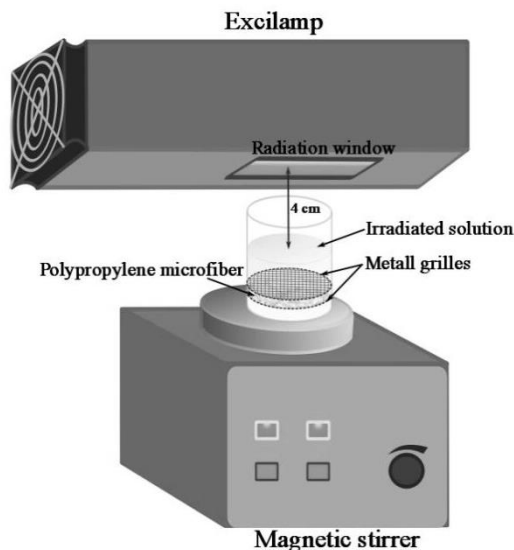


Figure 2. The scheme of a stationary photoreactor

The prepared BPA solutions with a concentration of $C = 2.2 \times 10^{-4}$ mol / L were irradiated in glass beakers 4.6 cm in diameter (Fig. 2). As an irradiation source used KrCl excilamp with wavelength 222 nm. The lamp radiation populates highly excited electronic states of the BPA, from which active phototransformations are expected. Our early studies of BPA photolysis under the action of sunlight using computer simulation methods [11] showed that the efficiency of phototransformations is low. Therefore, an attempt was made to increase the efficiency of BPA phototransformation under the action of radiation from a KrCl excilamp. The weighed portion of PPM (Fig. 3) was 0.05 g. The volume of the irradiated solution is $V = 50$ ml. The control of irradiation: 0, 1, 5, 10, 20, 30, 40 and 60 minutes. The distance from the excilamp to the irradiated solution is 4 cm (Fig. 2). During the irradiation, the maximum energy absorbed by the test solution did not exceed 10 J/cm^3 . The spectral-luminescent characteristics of the BPA solution were recorded before and after irradiation on a CM2203 spectrofluorimeter (*SOLAR*, Belarus) [12].

PPMs were synthesized by a group of researchers from the Siberian Institute of Physics and Technology. The raw material for the synthesis of nanoparticles was obtained by the sol-gel method [13]. As starting materials for the formation of superfine fibers polypropylene grades PP H080 GP, PP H270 GP/1 were used. The study of the gas dynamics of the flow of gas jets formed by an annular ejector for various variants of the critical cross-sectional area of an annular convergent nozzle and the differential pressure of gas in a nozzle was accomplished using theoretical numerical simulation. The calculations were performed using Solid Works + ANSYS integrated software. The preparation of the geometric 3D model of the ejector was carried out in the Solid Works program, then the model was imported into the ANSYS Fluent computational module, where a gas-dynamic calculation was performed. The experimental formation of PPM was carried out using the laboratory setup by pneumatic spraying of a freely flowing melt jet. A key element of the setup is a coaxial ejector atomizer with an annular convergent nozzle [13].



Figure 3. The external view of PPM

This method was used to prepare three samples of materials based on PPM to study their sorption properties. The samples were formed with various combinations of the critical area of the tunnel nozzle, the gas pressure drop in the nozzle, and the melt flow rate (Table 1).

Table 1. Dependence of the statistical characteristics of the size distribution of PPM (MFI 25 g/10 min) on the production modes

№	$\mu F, \text{mm}^2$	N_{pr}	Q_{r-n}	$d_{cp}, \mu\text{m}$	$K_n, \%$
210	8.2	2	3.9	3.88	110
225	16.5	2	7.7	2.54	51
240	22.0	2	10.3	2.05	67

Table 1 shows that the gas pressure drop in the nozzle, the effective critical cross-sectional area of the annular converging nozzle and the melt flow rate in mixed solvents affect the morphology and diameter of the formed fibers. Fiber diameter tends to decrease with a decrease in the critical area of the nozzle.

3. RESULTS AND DISCUSSION

As a result of the experiment, the absorption and fluorescence spectra of the compound under study were obtained in the presence of three PPM samples (Table 1). The maximum of the long-wavelength absorption band of BPA in water in the presence of PPM lies in the region of 276 nm, and the maximum of the short-wavelength band is at 220 nm. The maximum of the fluorescence spectrum of the test compound is located in the region of 310 nm when excited in the long-wavelength absorption band (270 nm).

Table 2. The maximum of the band of absorption and fluorescence spectra of the BPA in the presence of MRP

№	Time of exposure, min	№ PPM					
		210		225		240	
		$D_{\max}, \text{rel.un.}$	$I_{\max}, \text{rel.un.}$	$D_{\max}, \text{rel.un.}$	$I_{\max}, \text{rel.un.}$	$D_{\max}, \text{rel.un.}$	$I_{\max}, \text{rel.un.}$
1	0	2.344	0.025	0.608	0.061	0.638	0.059
2	1	0.626	1.117	0.625	1.44	0.65	1.533
3	5	0.666	1.443	0.637	2.494	0.675	2.602
4	10	0.699	2.154	0.671	2.642	0.691	2.901
5	20	0.726	2.037	0.668	2.588	0.691	2.66
6	30	0.74	2.145	0.695	2.215	0.73	2.204
7	40	0.745	1.443	0.7	2.056	0.751	1.943
8	60	0.83	1.081	0.726	1.552	0.779	1.585

Radiation from a KrCl excilamp is effective for direct degradation of BPA; it also changes the composition of photoproducts in quantity with excited sunlight. When considering a BPA solution, both with PPM sample № 210 and № 225 and № 240 in the regions of 250 nm and 325-450 nm, an active increase in the optical absorption density of BPA occurs, which indicates the formation of a BPA product. After irradiation of BPA solutions with PPM, an emission band appears in the fluorescence spectra in the region with a maximum of about 405÷410 nm. With an increase in the irradiation time from 0 to 10 minutes, an increase in the fluorescence intensity of this BPA photoproduct was recorded (Table 2). This indicates that in the course of irradiation, effective photodegradation of the initial toxicant occurs and a photoproduct is formed.

Degradation of the resulting photoproducts occurs during irradiation. After 10 min of irradiation with BPA in water in the presence of all PPM samples with different properties, photodegradation of BPA products formed earlier occurs. This is indicated by a decrease in the intensity of the band in the fluorescence spectra (Figs. 4a, 4b, 4c). The intensity of BPA fluorescence after irradiation in the presence of PPM sample № 210 is lower than for samples № 225 and № 240 (Fig. 4). This may be due to the fact that BPA and photoproducts are adsorbed on the surface of the PPM.

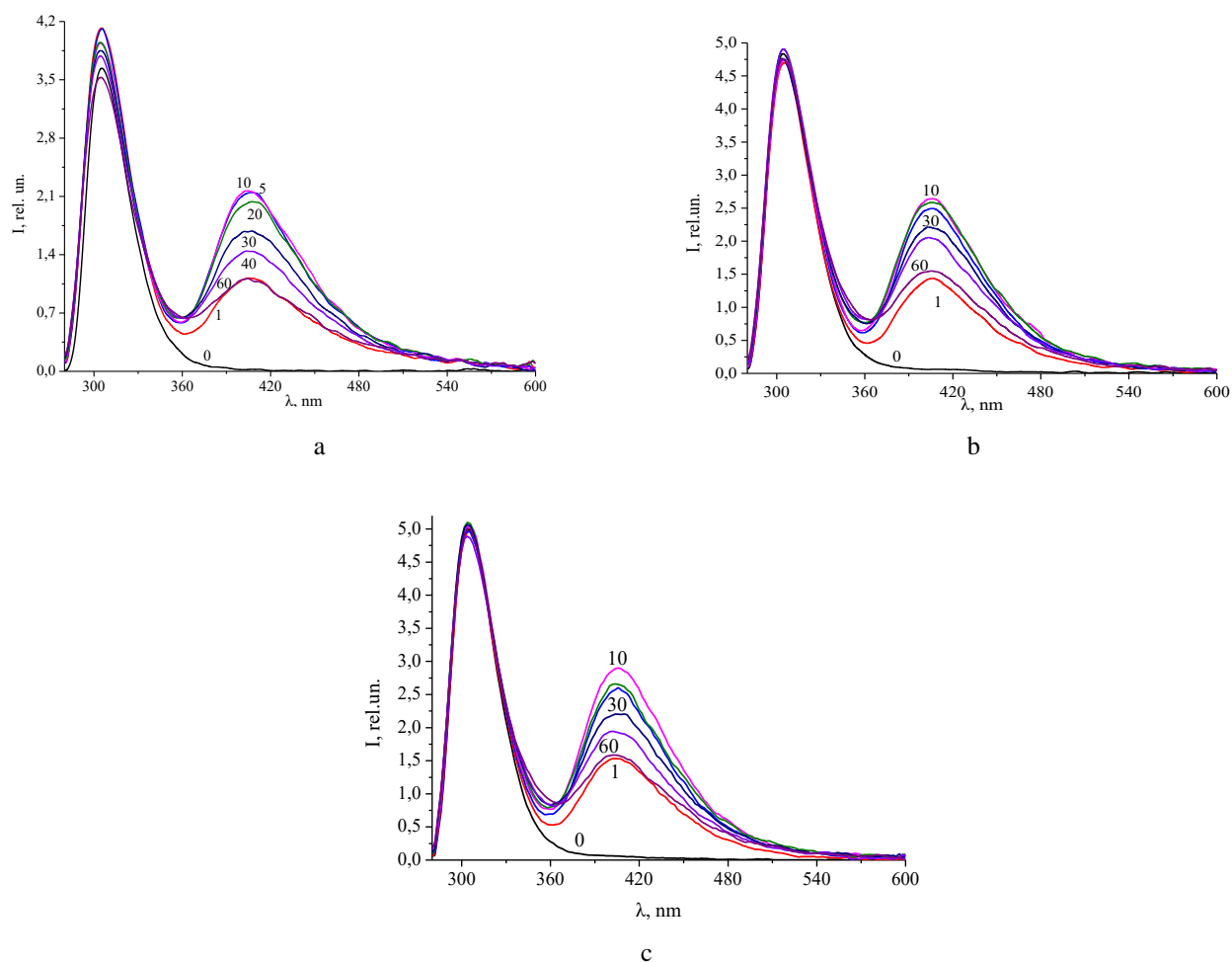


Figure 4. Fluorescence Spectra of BPA in water under the influence KrCl excilamp radiation in the presence of MRP: 210 (a) 225 (b) 240 (c). Excitation wavelength 270 nm. The numbers in the figure indicate the exposure time

After irradiation from aqueous solutions, PPM samples were sequentially squeezed out, dried, and then placed in cyclohexane. The obtained absorption and fluorescence spectra of cyclohexane containing the washings from the surface PPM recorded phototransformation BPA formation of products which are adsorbed on the surface of PPM during irradiation. The obtained absorption and fluorescence spectra of the studied samples No. 210 (Fig. 5 and 6, curve 1), 225 (Fig. 5 and 6, curve 2) and 240 (Fig. 5 and 6, curve 3) in cyclohexane are shown in Fig. 5 and 6. It was found that the best sorption capacity for BPA is possessed by PPM sample no. 210 with the largest diameter of $3.88 \mu\text{m}$ (Fig. 6, curve 1).

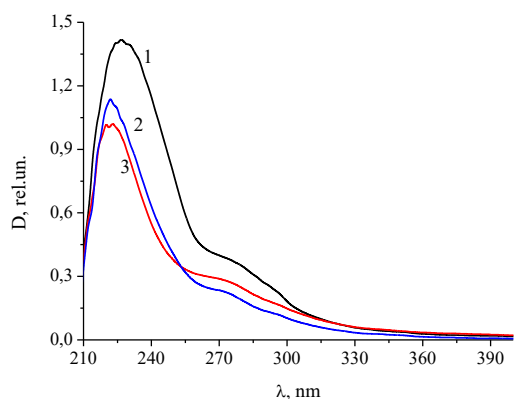


Figure 5. The absorption spectra of BPA in cyclohexane after irradiation with a KrCl excilamp

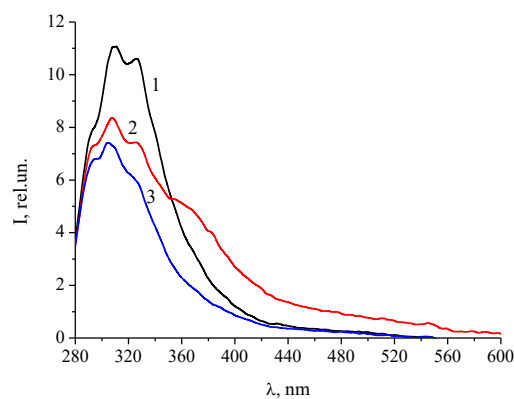


Figure 6. The fluorescence spectra of BPA in cyclohexane after irradiation with a KrCl excilamp. Excitation wavelength $\lambda = 270$ nm

4. CONCLUSION

Based on the experimental data obtained on the formation of BPA photoproducts in the presence of PPM, it can be concluded that the formation time of photoproducts is longer than in the experiment without PPM [14]. The identification of BPA photolysis products using nanoparticle-modified PPMs is the goal of our further research.

ACKNOWLEDGMENTS

This work was performed within the framework of the State Assignment of the Ministry of Education and Science of the Russian Federation (Project No. 0721-2020-0033).

REFERENCES

- [1] Mezcua M., Ferrer I., Hernando M.D., Fernandez-Alba A.R. "Photolysis and photocatalysis of bisphenol A: identification of degradation products by liquid chromatography with electrospray ionization/time-of-flight/mass spectrometry (LC/ESI/ToF/MS)", *Food Additives and Contaminants. Papers* 23 (11), 1242-1251 (2011).
- [2] Rivas F.J., Encinas A., Acedo B., Beltrán F.J. "Mineralization of bisphenol A by advanced oxidation processes", *J Chem Technol Biotechnol. Papers* 84(4), 589-594 (2008).
- [3] Yamazaki E., Yamashita N., Taniyasu S., Lam J., Lam K.S., Moon H.B., Jeong Y., Kannan P., Achyuthan H., Munuswamy N., Kannan K "Bisphenol A and other bisphenol analogues including BPS and BPF in surface water samples from Japan, China, Korea and India", *Ecotoxicology and Environmental Safety. Papers* 122, 565-572 (2015).
- [4] Torres R.A., Abdelmalek F., Combet E., Petrier C., Pulgarind C. "A comparative study of ultrasonic cavitation and Fenton's reagent for bisphenol A degradation in deionised and natural waters", *Journal of Hazardous Materials. Papers* 146(3), 546-551 (2007).
- [5] da Silva J.C.C., Reis Teodoro J.A., Afonso R.J. de C. F., Aquino S.F., Augusti, R. "Photodegradation of bisphenol A in aqueous medium: Monitoring and identification of by-products by liquid chromatography coupled to high-resolution mass spectrometry", *Rapid Communications in Mass Spectrometry. Papers* 28(9), 987-994 (2014).
- [6] Ohko Y., Ando I., Niwa C., Tatsuma T., Yamamura T., Nakashima T., Kubota Y., Fujishima A. "Degradation of Bisphenol A in Water by TiO₂ Photocatalyst", *Environ. Sci. Technol. Papers* 35(11), 2365-2368 (2001).

- [7] Chen P.-J., Linden K.G., Hinton D.E., Kashiwada S., Rosenfeldt E.J., Kullman S.W. "Biological assessment of bisphenol A degradation in water following direct photolysis and UV advanced oxidation", *Chemosphere. Papers* 65(7), 1094-1102 (2006).
- [8] Ike M., Jin C.S., Fujita M. "Biodegradation of bisphenol A in the aquatic environment", *Water Science and Technology. Papers* 42(7-8), 31-38 (2000).
- [9] Klecka G.M., Gonsior S.J., West R.J., Goodwin P.A., Markham D.A. "Biodegradation of bisphenol A in aquatic environments: River die-away", *Environmental Toxicology and Chemistry. Papers* 20(12), 2725-2735 (2001).
- [10] Kang J.-H., Kondo F. "Effects of bacterial counts and temperature on the biodegradation of bisphenol A in river water", *Chemosphere. Papers* 49(5), 493-498 (2002).
- [11] Bocharnikova E.N., Tchaikovskaya O.N., Bazyl O.K., Artyukhov V.Ya., Mayer G.V. "Theoretical study of bisphenol A photolysis", *Advances in Quantum Chemistry. Papers* 81, 191-217 (2019).
- [12] GOST 12997-84 "GSP products. General technical conditions ". Specifications TU BY 100424659.013-2006 "Spectrofluorimeter CM 2203".
- [13] Lysak G.V., Lysak I.A., Malinovskaya T.D., Volokitin G.G. "Microwave synthesis of SnO₂ nanocrystals on the surface of fine polymer fibers", *Inorganic Materials. Papers* 46, 183-186 (2010).
- [14] Bocharnikova E.N., Tchaikovskaya O.N., Chaidonova V.S., Gómez M., Murcia M., Gómez J. "Recent advances in Bisphenol A UV/H₂O₂ degradation", *IOP Conf. Series: Materials Science and Engineering. Papers* 696, 1-9 (2019).