

PHOTOTRANSFORMATION OF BISPHENOL A IN WATER IN THE PRESENCE OF MATERIALS BASED ON ULTRAFINE POLYPROPYLENE FIBERS

O. N. Tchaikovskaya, E. N. Bocharnikova, N. P. Bezlepkina,
I. A. Lysak, T. D. Malinovskaya, and G. V. Lysak

UDC 539, 538.958

The effect of UV radiation on the efficiency of bisphenol A (BPA) phototransformation in water in the presence of polypropylene nonwoven material based on ultrafine fibers has been studied. The absorption and fluorescence spectra of the investigated substance with fibers of different properties have been obtained. After excitation with an excilamp, the main photoproduct – BPA – fluoresces in the region of ~408 nm. With an increase in the irradiation time from 0 to 10 min, the fluorescence intensity of this photoproduct increases. The absorption and fluorescence spectra of cyclohexane containing compounds desorbed from the fiber surface indicate the adsorption of the photoproduct on its surface during UV irradiation.

Keywords: bisphenol A (BPA), phototransformation, spectral and luminescent properties, photoreactor, ultrafine polypropylene fibers.

INTRODUCTION

Bisphenol A (BPA) is widely used as an inexpensive hardener for obtaining and recycling plastics. Practically 95 % of packing materials (especially plastic bottles and ware) contain BPA [1]. The main ways of BPA penetration and accumulation in the human body are foodstuff incorrectly stored in packing [2]. The danger to humans is that BPA disrupts the endocrine system and causes infringements of metabolism and brain activity [3, 4]. Due to large turnover of the BPA industry, its huge amount is thrown out in drains of chemical enterprises, and pollution spreads by waters of rivers and lakes. Investigations [6] showed that conventional sumps do not eliminate dissolved BPA from wastewater [5] and do not prevent its migration in the environment. In the modern world, the problem of water purification is relevant; therefore, it is very important to develop technologies of natural and waste water purification from this pollutant. Studies [7, 8] showed that BPA can degrade through aerobic microbial processes [9] with half-life period from several days to several ten weeks that can explain relatively low efficiency of BPA removal from the habitat. In addition to the technologies based on the use of complex biological methods, technologies using physical and chemical methods are also being actively developed; most of them include pretreatment by UV radiation [10, 11]. One more no less significant method of water treatment is the use of different filtering materials possessing sorption properties [12–14]. Many researches showed that fibrous materials based on polypropylene can be used effectively as filtering materials to remove disperse pollutants from gas and liquid environments; they also possess high sorption capacity to oil products in water [15]. According to the results obtained by Tret'yakova *et al.* [16], filtering materials based on polypropylene can be used effectively for wastewater treatment from water-soluble dyes. Subsequent research showed that a combination of a fibrous polypropylene material with UV irradiation provides sufficiently efficient method of

National Research Tomsk State University, Tomsk, Russia, e-mail: tchon@phys.tsu.ru; bocharnikova.2010@mail.ru; nadezhda.bezlepkina174833@mail.ru; lysak_ia@mail.ru; malino@sibmail.com; h-0-h@yandex.ru. Translated from *Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika*, No. 11, pp. 78–83, November, 2021. Original article submitted August 23, 2021.

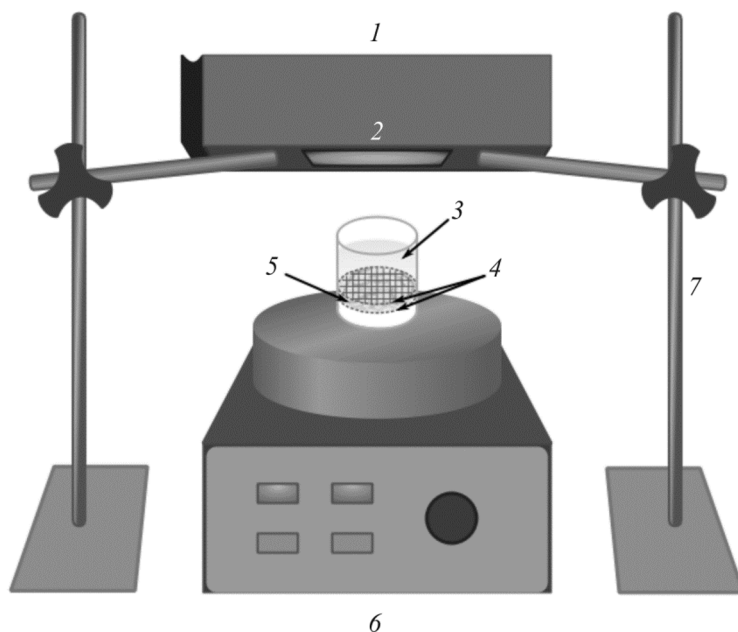


Fig. 1. Schematic of the stationary photoreactor comprising KrCl excilamp 1, output radiation window 2, irradiated solution 3, metal grids 4, fiber 5, magnetic mixer 6, and support 7.

removal of the organic impurity containing phenol and its photoproducts. The materials containing ultrafine fibers with sizes from several micrometers to several tenths of a micrometer are best suited for treatment of liquid media. Fibrous structures based on polypropylene formed by pneumatic atomization of the melt represent polydisperse ultrafine nonwoven materials containing fibers with diameters from several hundred nanometers to several micrometers. In this case, large fibers form a supporting frame providing mechanical strength and thin fibers form the specific surface area characterizing the capacity of the material to interact with a medium. The development and improvement of such technologies will help the researchers to solve the problem of polluted water purification from an organic impurity. Early studies [17] of BPA photolysis under the action of sunlight by the methods of computer modeling showed that in this case, the phototransformation efficiency is low. Therefore, an attempt to increase the efficiency of BPA phototransformation under UV irradiation was undertaken. This research is aimed at studying the efficiency of BPA photodegradation in water in the presence of polypropylene materials (PPM) based on ultrafine fibers during UV irradiation.

EXPERIMENTAL PART

Distilled water was used as a solvent. To prepare the water solution with the initial concentration $C = 10^{-3}$ mol/L, 45 mg of BPA dry sample were used. To improve the BPA solubility, the solution was poured into an ultrasonic mixer and heated to 40°C. The solution for photodegradation was prepared from the matrix solution by diluting to the concentration $C = 2.2 \cdot 10^{-4}$ mol/L. The prepared BPA solutions with a volume of 50 ml were poured into glasses with diameters of 4.6 cm in the presence of PPM weighing 0.05 g. The solution was irradiated in a photoreactor at room temperature (Fig. 1).

The KrCl excilamp with the wavelength $\lambda = 222$ nm was used as the UV radiation source. A ring was placed at the bottom of the glass on which metal grids lay with PPM between them. The distance from the excilamp to the irradiated solution was 4 cm, and the total irradiation time was 60 min. During irradiation, the maximum energy absorbed by the investigated solution did not exceed 10 J/cm³. Data were sampled at fixed times (0, 1, 5, 10, 20, 30, 40, and 60 min), and the absorption and fluorescence spectra were registered with an SM2203 fluorimeter (SOLAR,

TABLE 1. Statistical Characteristics of the Polypropylene Fiber Size Distribution

No.	410	425	325	240	440	225	310	340	210
D_{av} , μm	1.4	1.82	2.02	2.05	2.4	2.54	2.66	2.68	3.88
K_v , %	84	88	76	67	76	51	67	40	110

Note: Here No. is the sample code, d_{av} is the average diameter of the normal fiber diameter distribution, and K_v is the coefficient of variation.

Belarus). Polypropylene PP H270 GP/1 (Sibur, Russia) was used as initial material for aerodynamic formation of ultrafine fibers. The characteristics of the PPM samples used to study their sorption properties are presented in Table 1.

To analyze the sorption properties of the PPM samples, they were extracted from irradiated solutions, were dried during 40 min in an oven at 70°C, and then were placed into 5 ml cyclohexane. Then the absorption and fluorescence spectra were registered.

RESULTS AND DISCUSSION

Previously, the BPA phototransformation in water was studied during irradiation with KrCl- and XeBr-excilamps [18, 19]. From the conversion curves obtained by the method of high-performance liquid chromatography (HPLC), it was found that the rate constant of BPA loss in water irradiated with the KrCl-excilamp was higher than with the XeBr-excilamp. Moreover, the BPA loss in water was only 60 % after 120 min irradiation with the KrCl-excilamp. The HPLC data for water solution irradiated with KrCl-excilamp during 120 min showed that in addition to BPA, it also contained phototransformation products. According to the data of fluorescent spectroscopy, it was established that fluorescing photoproducts remained in the BPA solution even after 120 min irradiation. The photoproduct fluorescing in the region with a maximum in the range of 410–420 nm first accumulated during irradiation with the KrCl-excilamp, decomposed during the time period from 1 to 30 min, and then the second photoproduct was formed. The maximum of the fluorescence intensity of BPA transformation products was observed after 2 and 40 min irradiation with the KrCl-excilamp.

The absorption intensities of BPA in the presence of PPM samples depending on the irradiation time are presented in Table 2. An analysis of the absorption spectra of the investigated solutions without irradiation showed that in the presence of the PPM sample No. 310, active BPA removal from the solution was observed (row 1 of Table 2). This indicated that a certain amount of BPA is adsorbed from the water solution. The most active accumulation of BPA photoproducts was observed in the presence of PPM samples Nos. 210 and 410 (row 8 of Table 2). During irradiation, the least amount of photoproducts was formed in the presence of PPM sample No. 310 (row 8 of Table 2).

In the regions of 240–260 nm and >300 nm, an increase in the intensity of the BPA absorption was observed after irradiation as evidenced by the formation of BPA photoproducts. During irradiation of the investigated solution in the presence of the PPM samples with the KrCl-excilamp, BPA degraded with the formation of the photoproduct fluorescing in the region with a maximum at ~408 nm (Fig. 2a).

During irradiation of solutions of BPA with PPM, the effective photodegradation of the initial toxicant and the formation of different photoproducts were observed. This is evidenced by the increase of the fluorescence intensity in the BPA spectra when the irradiation time increased from 0 to 10 min (Fig. 2). The maximum fluorescence intensity of the BPA photoproduct in the presence of sample No. 440 was observed after 10 min irradiation (Fig. 2a). It should be noted that the photoproduct accumulation time in the solution changed. Whereas the maximum fluorescence intensity without PPM was observed after 2 min irradiation (Fig. 2b), the BPA photoproduct in the presence of PPM was accumulated during 10 min, and then the photoproduct started to decompose actively (Fig. 2a). However, in our experiment we did not reach the fluorescence intensity of the photoproduct in the presence of PPM compared to the experiment without fiber (Fig. 2). One of the reasons could be the active adsorption of BPA and its photoproduct on the PPM surface and hence, approximately two times lower fluorescence intensity than without PPM.

When the irradiation time of BPA in water in the presence of all PPM samples increased from 10 to 60 min, a decrease in the emission band intensity was observed in the fluorescence spectra. This suggests that the

TABLE 2. Intensity of the BPA Absorption Band in the Region of 270 nm in the Presence of PPM

No.	UV irradiation time, min	Without PPM	PPM No.								
			210	225	240	310	325	340	410	425	440
			D _{max} , rel. units								
1	0	0.63	0.63	0.61	0.63	0.57	0.62	0.61	0.63	0.62	0.63
2	1	0.63	0.63	0.63	0.63	0.58	0.65	0.62	0.69	0.60	0.65
3	5	0.64	0.67	0.64	0.64	0.59	0.69	0.60	0.70	0.64	0.68
4	10	0.65	0.70	0.67	0.65	0.63	0.69	0.63	0.73	0.70	0.69
5	20	0.66	0.73	0.67	0.67	0.62	0.72	0.70	0.74	0.67	0.69
6	30	0.67	0.74	0.70	0.69	0.64	0.75	0.67	0.75	0.69	0.73
7	40	0.68	0.75	0.71	0.70	0.68	0.76	0.66	0.78	0.71	0.75
8	60	0.69	0.83	0.73	0.75	0.65	0.79	0.71	0.83	0.76	0.78

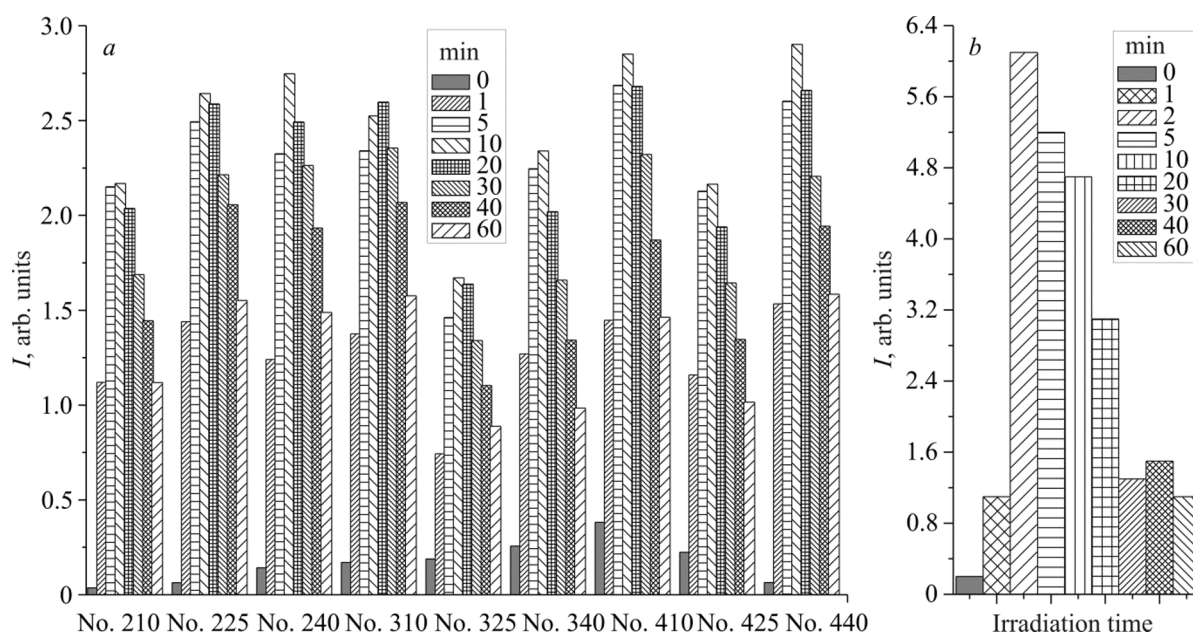


Fig. 2. Diagram illustrating the change of the fluorescence intensity of BPA with (a) and without PPM samples (b) in the stationary photoreactor in the region of 408 nm depending on the KrCl-excimer lamp irradiation time.

photodegradation of the BPA product occurs during irradiation. It was obtained that the BPA fluorescence intensity after irradiation in the presence of PPM sample No. 325 is lower than for other samples (Fig. 2a). This can be due to the BPA and photoproduct adsorption on the PPM surface during UV irradiation. To compare the sorption properties of the PPM samples, the absorption and fluorescence spectra of flushes from fiber surfaces were registered. Figure 3 shows the absorption spectra of desorbed compounds in cyclohexane.

An analysis of the obtained data showed that the maximum optical densities in the absorption spectra (Fig. 3) were registered for samples No. 210 and 225. This suggests that these samples possess higher sorption capacity than other samples. In the absorption spectrum of BPA in cyclohexane, two bands in regions of 230 and 280 nm were observed. In the fluorescence spectra (Fig. 4), the form of the spectrum characteristic for polyaromatic compounds can be seen for sample No. 425 in the region of 450–500 nm. In the region of 325 nm (Fig. 4), sample No. 210 had the maximum luminescence intensity. In this region, BPA and photoproducts adsorbed on the surface of this fiber may fluoresce.

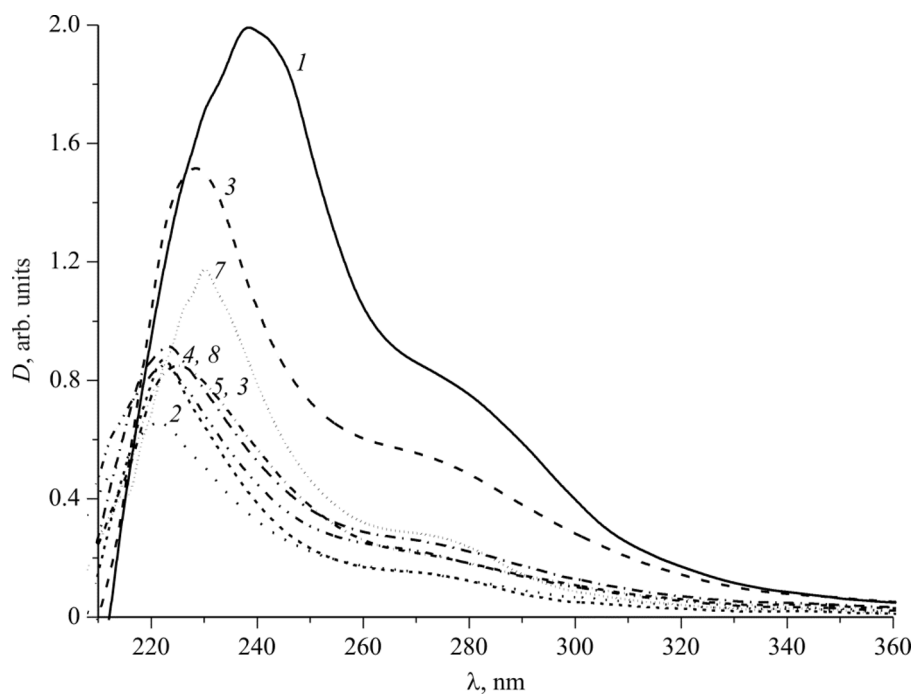


Fig. 3. Absorption spectra of the compounds desorbed from the surface of the PPM samples in cyclohexane after irradiation with the KrCl excilamp of water solution of BPA with PPM Nos. 210 (curve 1), 410 (curve 2), 225 (curve 3), 325 (curve 4), 425 (curve 5), 240 (curve 6), 340 (curve 7), and 440 (curve 8).

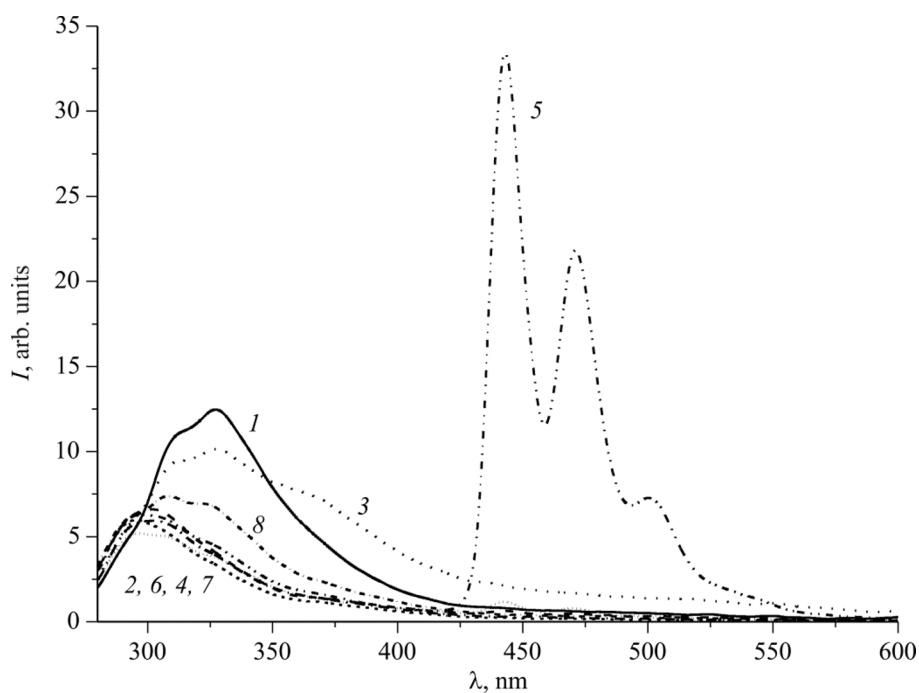


Fig. 4. Fluorescence spectra of the compounds desorbed from the surface of PPM samples in cyclohexane after irradiation with the KrCl excilamp of water solution of BPA with PPM Nos. 210 (curve 1), 410 (curve 2), 225 (curve 3), 325 (curve 4), 425 (curve 5), 240 (curve 6), 340 (curve 7), and 440 (curve 8); the fluorescence excitation wavelength was $\lambda = 270$ nm.

CONCLUSIONS

As a result of our study, the fluorescence and absorption spectra of BPA in water in the presence of the PPM samples have been registered before and after irradiation with the excilamps. The absorption and fluorescence spectra of cyclohexane containing flushes of organic compounds from the PPM surface were obtained. A comparative analysis of the sorption capacities of the PPM samples was performed. Based on the obtained experimental data, we can conclude that the accumulation time of the BPA photoproduct in the presence of the PPM samples 5-fold increased compared to the experiment without PPM [20]. PPM sample No. 425 caused additional contamination of the investigated solutions. Samples Nos. 210 and 225 with average fiber diameters of 3.88 and 2.54 μm , respectively, had the best sorption capacity to BPA and its photoproducts.

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. E. Yamazaki, N. Yamashita, S. Taniyasu, *et al.*, *Ecotoxicol. Environ. Saf.*, **122**, 565–572 (2015).
2. A. Ballesteros-Gómez, S. Rubio, and D. Pérez-Bendito, *J. Chromatogr. A*, **1216**, No. 3, 449–469 (2009).
3. M. Mezcuca, I. Ferrer, M. D. Hernando, and A. R. Fernandez-Alba, *Food Addit. Contam.*, **23**, No. 11, 1242–1251 (2011).
4. F. J. Rivas, A. Encinas, B. Acedo, and F. J. Beltrán, *J. Chem. Technol. Biotechnol.*, **84**, No. 4, 589–594 (2008).
5. P. J. Chen, K. G. Linden, D. E. Hinton, *et al.*, *Chemosphere*, **65**, No. 7, 1094–1102 (2006).
6. R. A. Torres, F. Abdelmalek, E. Combet, *et al.*, *J. Hazard. Mater.*, **146**, No. 3, 546–551 (2007).
7. M. Ike, C. S. Jin, and M. Fujita, *Water Sci. Technol.*, **42**, Nos. 7–8, 31–38 (2000).
8. G. M. Klecka, S. J. Gonsior, R. J. West, *et al.*, *Environ. Toxicol. Chem.*, **20**, No. 12, 2725–2735 (2001).
9. J. H. Kang and F. Kondo, *Chemosphere*, **49**, No. 5, 493–498 (2001).
10. J. C. C. da Silva, J. A. Reis Teodoro, C. F. de Afonso, *et al.*, *Rapid Commun. Mass Spectrom.*, **28**, No. 9, 987–994 (2014).
11. Y. Ohko, I. Ando, C. Niwa, *et al.*, *Environ. Sci. Technol.*, **35**, No. 11, 2365–2368 (2001).
12. A. A. Nekrasova, D. M. Privalov, M. V. Dvadnenko and N. M. Privalova, *Sci. J. KubSAU*, No. 125 (01), 1–10 (2017).
13. N. M. Privalova, M. N. Dvadnenko, A. A. Nekrasov, *et al.*, *Sci. J. KubSAU*, No. 113 (09), 1–10 (2015).
14. M. V. Bazunova, E. S. Hlobystova, R. K. Fakhretdinov, *et al.*, *Vestnik of Kazan National Research Technological University*, **20**, No. 18, 5–8 (2017).
15. V. V. Bordunov, S. V. Bordunov, and V. V. Leonenko, *Ecol. Ind. Russ.*, No. 8, 8–11 (2005).
16. A. E. Tret'yakova, E. A. Montenegrins, and V. V. Safanov, *Proc. Higher Educ. Inst. Textile Technol.*, No. 2, 127–132 (2016).
17. E. N. Bocharnikova, O. N. Tchaikovskaya, O. K. Bazyl, *et al.*, *Adv. Quantum Chem.*, **81**, 191–217 (2019).
18. G. V. Lysak, I. A. Lysak, T. D. Malinovskaya, and G. G. Volokitin, *Inorg. Mater.*, **46**, 183–186 (2010).
19. E. N. Bocharnikova, O. N. Tchaikovskaya, V. S. Chaidonova, *et al.*, *IOP Conf. Ser. Mater. Sci. Eng.*, **696**, 012006-1–012006-9 (2019).
20. O. N. Tchaikovskaya, E. N. Bocharnikova, I. A. Lysak, *et al.*, *Micro and Nanosyst.*, **12**, No. 3, 345–357 (2020).