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RADIATION-CHEMICAL DEGRADATION OF POLYCHLOROBIPHENYL IN AN AQUEOUS MEDIUM

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Abstract: It has been studied the regularities of the change of pH indicator, chemical oxygen demand (COD) and the formation of hydrogen peroxide and carbon dioxide, as well as UV absorption spectra during the radiolysis of two-phase system of transformer oil, containing 5-40 ppm polychlorobiphenyls with water under the influence of γ -radiation.

It has been established that, the increase in the initial concentration of PCB leads to an increase in the radiation-chemical yield of hydrogen peroxide up to 4.7 molecule/100 eV. The increase of the PCB concentration in the oil leads to an increase in the yield of CO₂ from 0.18 to 0.24 molecule/100 eV in the range of PCB concentration 5-40 ppm in the oil.

It has been shown that, the values of Abs increase from 3 up to ~10 with the increase of absorption dose during the radiolysis of a system, containing 5 ppm PCB. A further increase in the dose leads to a decrease in Abs up to ~ 3.6 at 68.4 kGy.

Keywords: polychlorobiphenyls, γ -radiation, degradation, UV absorption spectra, radiation-chemical yield

1. Introduction

One of the chemically stable and toxic organic substances is polychlorobiphenyls. They get into the environment due to leaks from electrical equipment. Their entry into the aqueous medium - into the water of rivers and seas, which poisons the living part of nature, is especially dangerous. Therefore, the study of their degradation in aqueous media is an urgent scientific issue. Although there are various chemical processes of degradation, they can be divided into two groups: oxidative and reduction processes. Simulation of oxidative degradation processes can be carried out by initiating active particles, such as OH radicals, hydrated electrons, peroxide radicals and others by the influence of ionizing radiation on aqueous media contaminated with chloroaromatic compounds.

In this aspect, it is of interest to study the processes of radiolytic decomposition of polychlorobiphenyls in an aqueous medium. PCBs are a part of technical transformer oil "Sovtol-10" used in the energy sector and they get into the environment, including in the aqueous medium with long-term use of transformers [1, 2].

In this paper, we studied the regularities of the change of pH indicator, chemical oxygen demand (COD) and formation of hydrogen peroxide and carbon dioxide, as well as UV absorption spectra during the radiolysis of two-phase system of transformer oil, containing 5-40 ppm polychlorobiphenyls with water under the influence of γ -radiation.

1. Methods

It has been used transformer oil under the trademark "Sovtol-10", which contained 10 wt. % - trichlorobenzene for reducing the viscosity of oil. PCB has 209 isomers, but "Sovtol-10" contains basically three, tetra-pentachlorobiphenyls.

Fresh transformer oil T-1500, which is a production of refinery named after. H. Aliyev in Azerbaijan.

Irradiation of two-phase system of oil + water was carried out under the influence of γ -radiation from ⁶⁰Co isotope under static condition in glass ampoules at room temperature. Two-phase systems are prepared adding 5 ml PCB, containing oil in water (10 ml). The dose rate was determined by the method of ferrosulfate dosimetry, which was 0.21 Gy/s.

UV absorption spectra were recorded on a Varian-Cary-50 spectrophotometer in the wavelength range of 200-400 nm.

The measurement of pH indicator was conducted by pH-meter, chemical oxygen demand (COD) by the method of permanganate oxidation of hydrocarbons, the CO₂ analysis was carried out on an AgilentTechnologies-7890 Gas chromatograph with detectors: TCD-carbon oxides, H₂O₂-titration.

2. Results

It has been studied the regularities of change of pH-indicator and COD depending on the absorption dose in the radiolysis of two-phase system of PCB, containing transformer oil and water. The results have been shown in Table 1.

Table 1. Dependence of pH-indicator and COD on the absorption dose in the radiolysis of two-phase system of transformer oil, containing 5-40 ppm polychlorobiphenyl + water. The volume of transformer oil and water is 5 ml and 10 ml, respectively.

D, kGy	pH			COD, mg O/l		
	5 ppm PCB	15 ppm PCB	40 ppm PCB	5 ppm PCB	15 ppm PCB	40 ppm PCB
0	6.7	6.5	6	267	433	683
4.1	6.3	6	5.8	350	600	766
27.4	6.1	5.9	5.7	433	766	933
68.4	5.8	5.6	5.4	600	933	1183
136.8	5.5	5.3	5	766	1266	1516

As it is seen from table 1, the values of pH-indicator decrease with the increase of absorption dose, that is associated with the radiolytic decomposition of polychlorobiphenyl molecules with the formation of hydrochloric acid. An increase in the dose leads to a growth in the values of COD that indicates an increase in the content of hydrocarbon in the irradiated mixture. The obtained results indicate the additional dissolution (diffusion) of radiolysis products of oil in water and the leakage of chemical reactions of active particles of water radiolysis.

The formation of H₂O₂ and CO₂ also occurs in the radiolysis of considered system. The dependence of concentration H₂O₂ on absorption dose in the radiolysis of system of PCB – transformer oil – water has been shown in the figure 1.

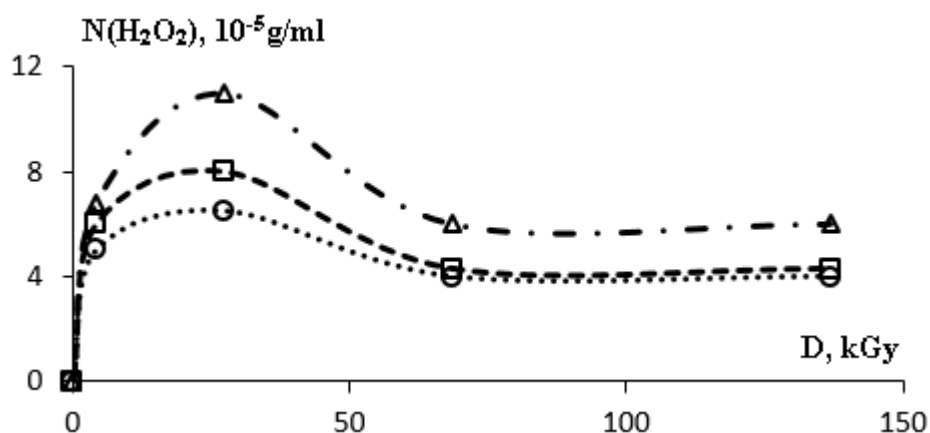


Fig. 1. Dependence of the concentration H₂O₂ on absorption dose in the radiolysis of two-phase system of transformer oil (5ml), containing 5-40 ppm polychlorobiphenyl + water (10 ml)

○ - 5 ppm PCB + 10 ml water, □ - 15 ppm PCB + 10 ml water, △ - 40 ppm PCB + 10 ml water

As it is seen from fig. 1, the concentration of H₂O₂ increases and reaches a stationary value with the increase of absorption dose. A further growth in the dose leads to a decrease in the concentration that indicates a leakage of secondary reaction of H₂O₂ consumption. The radiation-chemical yields of H₂O₂ have been calculated and the values have been presented in Table 2.

Table 2. Radiation-chemical yields of H₂O₂ and CO₂ in the radiolysis of a system of PCB + transformer oil (5 ml) + water (10 ml) at different initial concentrations of PCBs.

N, ppm	G, molecule/100 eV	
	H ₂ O ₂	CO ₂
0	0.8	0.18
5	3.5	0.4
15	4.2	0.38
40	4.7	0.244

As it can be seen, an increase in the initial concentration of PCBs leads to a growth in the radiation-chemical yield of hydrogen peroxide. It should be noted that the obtained values of radiation-chemical yields are ~ 5 times higher than the radiation-chemical yields of H₂O₂ in radiolysis of water that indicates the presence of additional channels for the formation of H₂O₂ during the radiolysis of this two-phase system [3].

In this work, the radiation-chemical yields of CO₂ formation, of which values are presented in Table 2, were also determined. As it is seen, the increase in the concentration of PCBs in the oil leads to a growth in the CO₂ yield from 0.18 to 0.24 molecules/100 eV in the concentration range of PCB 5 -40 ppm. It was of interest to compare the yields of H₂O₂ in the radiolysis of a two-phase system of PCB-oil-water with the yield of H₂O₂ in the radiolysis of a homogeneous system of PCB-oil. The dependence of radiation-chemical yield of H₂O₂ on the concentration of PCB in the transformer oil during the radiolysis of a homogeneous mixture has been presented in Fig. 2.

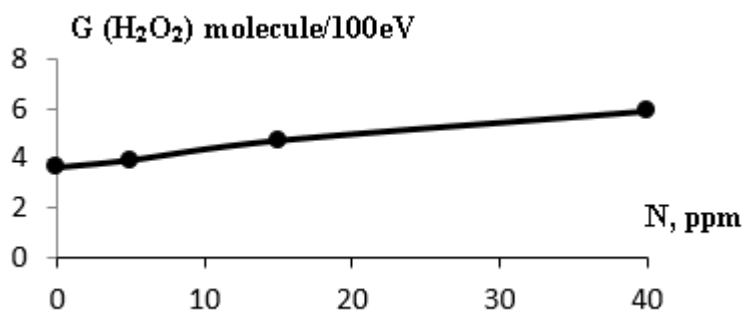


Fig. 2. Dependence of the radiation-chemical yield of H₂O₂ on the concentration of PCB in the radiolysis of the mixture of PCB-transformer oil

As it is seen, although the nature of the dependence of G(H₂O₂) on the concentration of PCB is similar with this dependence in the radiolysis of a two-phase system, there is observed a stronger influence of PCB concentration on the yield of H₂O₂ in the former case.

For obtaining additional information on the radiation-chemical transformation of PCBs in water, the UV spectroscopy method was used. In fig.3, it has been presented UV absorption spectra of the samples of aqueous medium in the system of transformer oil (5 ml) + water (10 ml) (curve 1) and in system of transformer oil (5 ml) + water (10 ml) + PCB at the contents 5, 15, 40 ppm.

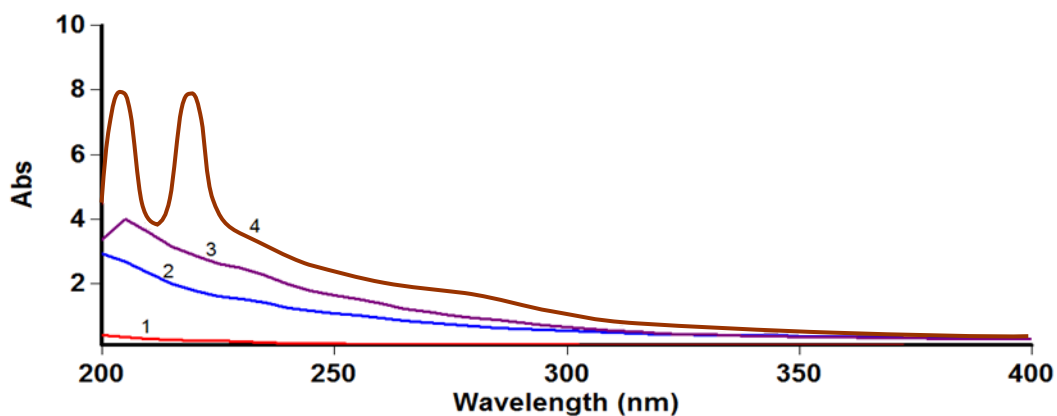


Fig. 3. Absorption spectra of samples: 1. Transformer oil + water (waterpart), 2. 5ppm PCB in 5ml transformer oil + 10 ml water (waterpart), 3. 15ppm PCB in 5ml transformer oil + 10 ml water (waterpart), 4. 40ppm PCB in 5ml transformer oil + 10ml water (waterpart)

As it is seen, a growth in the content of PCB in a two-phase system leads to an increase of the absorption and a shift of absorption in the direction of short wavelength. In addition, the absorption band, of which intensity increases by the increase of content of PCB in the system, appears in the range of $\lambda \leq 220$ nm.

UV absorption spectra of the samples irradiated at different absorption doses have been shown in the figure 4.

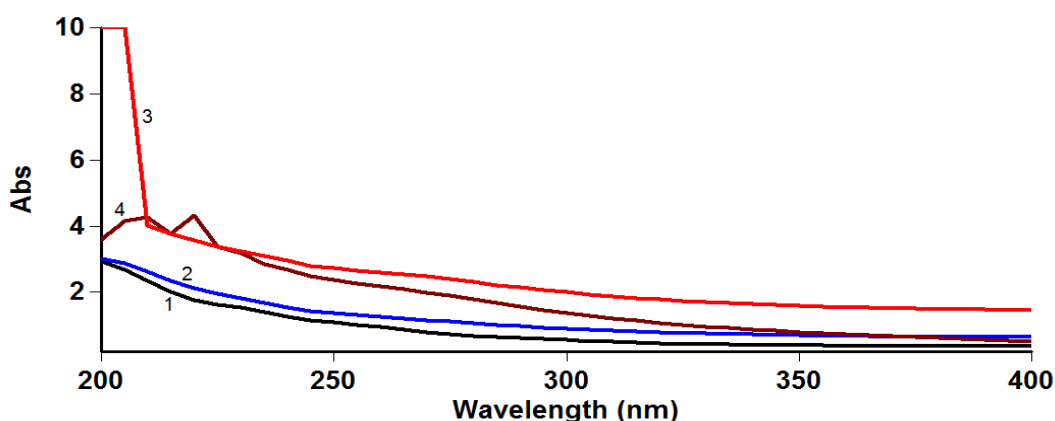


Fig. 4. Absorption spectra of irradiated samples (in water parts) of the system. 5ppm PCB in 5ml transformer oil +10ml water (200-400nm) 1. $D=0$; 2. 4.1 kGy; 3. 27.4 kGy; 4. 68.4 kGy

As it is seen, the value of Abs increases from 3 to ~ 10 by the growth of absorption dose in radiolysis systems, containing 5 ppm PCB. A further increase in the dose up to 68.4 kGy leads to decrease of Abs up to ~ 3.6 . A similar picture is also observed in relatively high PCB contents in the change under consideration.

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РАДИАЦИОННО-ХИМИЧЕСКАЯ ДЕГРАДАЦИЯ ПОЛИХЛОРБИФЕНИЛОВ В ВОДНОЙ СРЕДЕ

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Резюме: Изучены закономерности изменения рН-индикатора, химического потребления кислорода (ХПК) и образования перекиси водорода и углекислого газа, а также УФ спектры поглощения при радиоллизе двухфазных систем трансформаторного масла, содержащего 5-40 ppm полихлорбифенилов с водой под действием γ -излучения.

Установлено, что рост начальной концентрации ПХБ приводит к увеличению радиационно-химического выхода перекиси водорода до 4,7 молекул/100 эВ. Рост концентрации ПХБ в масле приводит к увеличению выхода CO_2 от 0,18 до 0,24 молекул/100 эВ в интервале концентрации ПХБ 5-40 ppm в масле.

Показано, что с ростом поглощенной дозы значения A_{bc} увеличиваются от 3 до ~ 10 при радиоллизе системы, содержащей 5 ppm ПХБ. Дальнейшее увеличение дозы до 68,4 кГр приводит к уменьшению A_{bc} до ~ 3,6.

Ключевые слова: Полихлорбифенилы, γ - излучение, деградация, УФ спектры поглощения, радиационно-химический выход

POLİXLORBİFENİLLƏRİN SU MÜHİTİNDƏ RADİASIYA-KİMYƏVİ DEQRADASIYASI

Z.İ. İskəndərova, M.A. Qurbanov

Xülasə: Tərkibində (5-40)ppm polixlorbifenil olan ikifazlı transformator yağı su sisteminin γ -süaların təsiri altında radiolizi zamanı pH-göstəricisinin dəyişməsi, oksigenə kimyəvi tələbat (OKT), hidrogen peroksidin və karbon qazının əmələ gəlməsi və UB-udma spektrlərinin qanunauyğunluqları öyrənilmişdir.

PXB-nin ilkin qatılığı artdıqca hidrogen peroksidin radiasiya-kimyəvi çıxımı artaraq 4,7 molekul\100ev olur.

Yağda PXB-nin qatılığının artması (5-40)ppm CO_2 -nin radiasiya-kimyəvi çıxımının 0,18-dən 0,24 molekul\100eV-a qədər artmasına səbəb olur.

Tərkibində 5ppm PXB olan transformator yağı və su sisteminin radioloji zamanı udulan doza artdıqca A_{bc} –nin 3-dən 10-a qədər artması müşahidə olunur. Dozanın sonrakı artımı 68,4kGr-də A_{bc} -nin 3,6-ya qədər azalmasına gətirir.

Açar sözlər: Polixlorbifenil, γ -süalamna, deqradasiya, UB-udulma spektrləri, radiasiya kimyəvi çıxım