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STUDY OF RADIATION DEGRADATION OF PHENOL IN AQUEOUS SOLUTION BY UV SPECTROSCOPY

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Abstract: The absorption spectrum of phenol and degradation products in radiolysis of its water solutions (0.1 M) in the range 200-800 nm was studied by UV-spectroscopy. It was found that, with increasing absorbed dose the concentration of phenol decreases and Abs of the relevant λ_{\max} increase.

Keywords: Adsorbed dose, degradation of phenol, radiation-chemical yield, adsorption spectrum

1. Introduction

Phenols are widespread pollutants in aquatic environment and components of the waste water from many industries. The radiation method is an effective method for cleaning water from phenol, by which phenol degradation with intermediate particles of water radiolysis (OH, H, e-, HO₂, etc.) to CO₂ and H₂O occurs [1]. Although there is a number of works on study of the products in the initial stage of the radiolytic degradation of phenol, such as dihydric phenols, -OH radical adducts to phenol molecules [2,3], the mechanism of the formation of the final degradation products and products of deeper oxidation of phenol is less clear. In this aspect, the UV absorption spectrum can provide additional information about the mechanism of deep oxidation of phenol.

2. Experimental

In this work the UV absorption spectrum of degradation products of phenol at different absorbed doses is studied. Irradiation was carried out by gamma radiation from the isotope ⁶⁰Co at room temperature, the absorbed dose rate was 30 Rad/hour.

The phenol content was determined by standard method [4] using 4-aminoantipyrine in the presence of hexaneferrate (III) at pH = 10,0 ± 0,2 based on formation of colored compounds of phenol with a spectrophotometer UV-Visible Spectrophotometre Cary-50 in the range $\lambda = 200-800$ nm based on calibration curve.

The liquid products were determined by spectrophotometry at the same spectrophotometry methods in the range of $\lambda = 200-800$ nm. Gaseous products were determined by the chromatography "Gazohrom" 3101 (column-activated carbon AG-3, the carrier gas-air) and chromatography SVET-102 (column-activated carbon K-3, a carrier gas-helium). pH is measured with pH-meter PHS-25.

3. Results and discussion

The absorption spectrum of phenol and degradation products in radiolysis of its water solutions (0.1 M) in the range 200-800 nm was studied. The UV- absorption spectrum of the

phenol complex at 400-600 nm ($\chi_{\max} = 510$ nm) and the absorption spectrum of products ($\Delta\chi = 200-300$ nm) at different absorbed doses are shown in figures 1 and 2 .

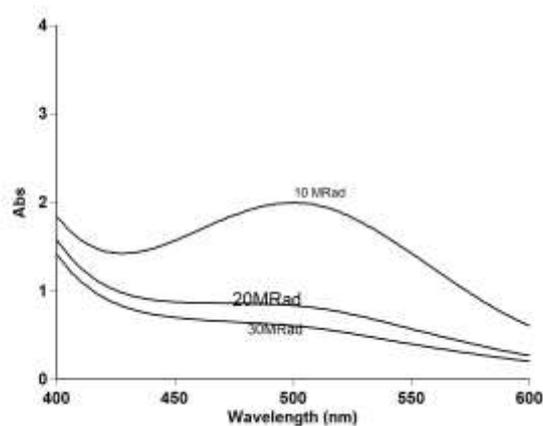


Fig. 1 UV- absorption spectra of the complex of phenol at different absorbed doses

From the absorption spectrum the concentration of phenol have been determined which is given in the table 1.

Table 1 Depends of phenol concentration on absorbed doses

Absorbed dose (MRad)	Concentration of phenol, M
0	$1 \cdot 10^{-2}$
10	$6 \cdot 10^{-3}$
20	$4.3 \cdot 10^{-3}$
30	$4.1 \cdot 10^{-3}$

Radiation-chemical yield of phenol degradation, which was 4 mol/100eV calculated on the basis of kinetic data. The obtained value is consistent with literature data on radiation-chemical decomposition of phenol by irradiation of aerated phenol solutions [5].

Fig. 2 shows the UV absorption spectrum of products at range $\Delta\chi = 200-300$ nm at different absorbed doses.

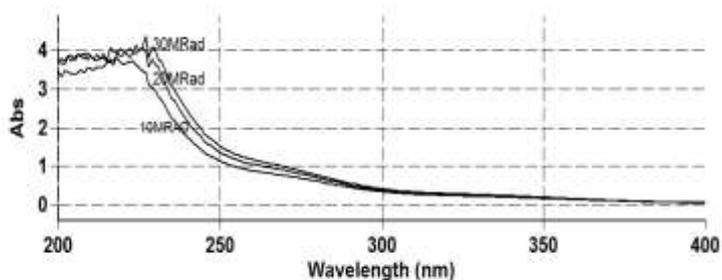


Fig. 2 UV absorption spectra products of phenol

In the investigated dose range the increase of the intensity peaks of products with increasing absorbed dose was observed. The calculated absorption coefficients (Abs) are shown in Table 2.

Table 2. Absorption (Abs) of products at different absorbed doses

λ_{\max} , nm	Absorbed dose, MRad		
	10	20	30
	A b s		
228,94	3,051	3,764	4,098
227,06	3,423	3,958	4,361
225,96	3,460	4,056	4,073
216,07	3,704	3,764	4,072
217,95	3,811	3,897	3,954
211,99	3,568	3,756	3,901
209,00	3,551	3,873	3,928
200,98	3,324	3,686	3,716
201,93	3,458	3,647	3,782

According to the literature assumes that the products are of the absorption band, respectively dihydric phenols- pyrocatechol $\lambda=214-276$ nm, resorcinol- $\lambda=216-273$ nm, hydroquinone $\lambda=225-295$ nm, aldehydes $\lambda=210-290$ nm and quinones $\lambda=400-500$ nm [6]

The mechanism of deep oxidation of phenol is presented in a series of works, devoted to electrolysis [7], oxidation of phenol with ozone [8], oxidation with hydrogen peroxide [9], in the presence of Fenton's reagent [10] and in the presence of catalysts [11].

The intermediate molecular products of deep oxidation depends on conditions of the oxidation process at the oxidation by ozone found traces of oxalic acid [12] was found, during the oxidation by hydrogen peroxide, muconic acid, [13], and under the action of Fenton's reagent, muconic acid, maleic acid and oxalic acid [14] were found.

The process of deep catalytic ($MnO_2/Al_2O_3, Fe_2O_3/Al_2O_3, Cu/Al_2O_3, Ce/TiO_2$ and oth.) phenol oxidation is complex and is accompanied by the formation of a large number of intermediate compounds: o-, p-benzoquinones, o-, p-hydroquinone, p-hydroxy-benzoic acid tetrahydro-p-benzoquinone, maleic acid, malic acid, fumaric acid, succinic acid, acetic, oxalic, glyoxylic, and formic acid insoluble polymer products and carbon dioxide [15].

The additional confirmation on acid formation is pH dependence on the absorbed dose presented in Fig. 3.

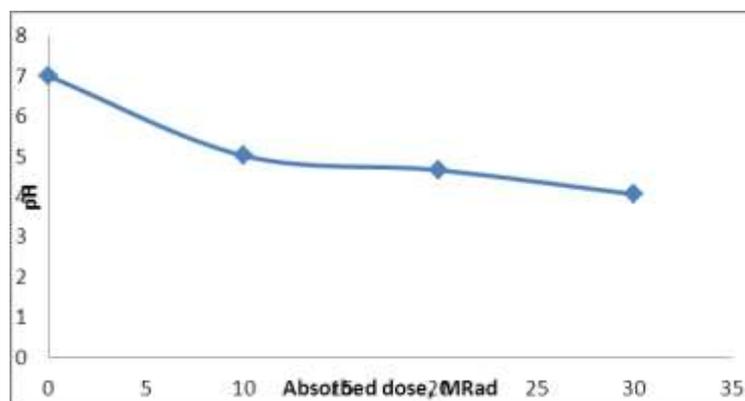


Figure 3. pH dependence of solution on the absorbed dose

By the dose increasing up to 30 Mrad, the pH decreases up to 4.1. Formation of gaseous products such as CO₂, CO and H₂ are observed by chromatography analysis.

4. Conclusions

1. The absorption spectrum of phenol and degradation products in gamma radiolysis of its water solutions (0.1 M) in the range 200-800 nm was studied. Established that, with raising absorbed dose the Abs of the relevant λ_{\max} is increasing.
2. It was found that, with increasing absorbed dose the concentration of phenol decreases from $1 \cdot 10^{-2}$ M to $4.1 \cdot 10^{-3}$ M. Radiation-chemical yield of phenol degradation is equal to 4 mol/100eV
3. The absorbed dose increases up to 30 Mrad, the pH decreases up to 4.1.

References

1. А.О.Аллен.“Радиационная химия воды и водных растворов”. М.,Атомиздат, 1963, 23 с.
2. Toyooki Miyazaki, Yosuke Katsumura, Mingzhang Lin and oth.,”Radiolysis of phenol in aqueous solution at elevated temperatures”, Radiation Physics and Chemistry. 75, 2006, p.408-415,
3. И.И.Поздняков, Ю.А.Соседова, В.Ф.Илюснин и др., ”Оптические спектры и кинетические характеристики радикалов, возникающих при фотолизе водных растворов комплекса $\text{FeOH}_{\text{aq}}^{2+}$ и фенола”,Институт Академии Наук, №12, 2004, с.1-8
4. Ю.Ю.Лурье, А.И.Рыбникова. Химический анализ производственных сточных вод. Москва. 74-77, 1966, с.259,
5. А.К.Пикаев.”Современная радиационная химия твердое тело и полимеры. Прикладные аспекты” Москва, 1987, 371 С.
6. www.chem.asu.ru. Ультрафиолетовая (электронная) Спектроскопия. Спектры поглощения основных классов органически соединений, 31 с.
7. Т.Н.Волгина, О.С.Кукурина, В.Т.Новиков, Химия в интересах устойчивого развития. 13, 2005, с.41-44
8. S.J.Niegowski.Destruction of phenols by oxidation with ozone.Industrial and engineering chemistry. vol.45, N3
9. Подзорова Е.А., Бычков Н.В. Фоторадиационное окисление фенола в водных растворах в присутствии H₂O₂ . Химия Высоких Энергий, том 15, №6, 1981, с.501 – 503,
10. М.Нарманкава,G.Gunduz,Tr.J.ofEngineeringand Environmental Sciences. 22, 1998, p.9-15
11. Chen C.Y., Lu C.L.Sci.Total Environ. vol. 289, N 140, 2002, p.13
12. Н.Б.Сократова, Н.С.Фунтикова, Д.С.Стародубцев, Кокс и Химия. 4, 1982, p.37
13. И.Ю.Литвинцев, Ю.В.Митник, А.И.Михайдюк и др. Кинетика и катализ, 34, 1982, p.37
14. M.Sudoh, T.Kodera, K.Sakai et al., J.Chem.Eng.Jap., 19, 1986, 6513
15. Cybulski A., Trawczynski J. Applied Catalysis B: Environmental vol.47, 2004, p.1