

PACS: 82.50.Rx

## RADIATION-CHEMICAL PROCESSES IN WATER SOLUTIONS OF PHENOLS AND CARBONIC ACIDS

U.A. Guliyeva, S.G. Mammadov, M.A. Gurbanov, Z.I. Iskenderova, E.T. Abdullayev

*Institute of Radiation Problems, ANAS*

[ulviyegulieva13@gmail.com](mailto:ulviyegulieva13@gmail.com)

**Abstract:** In this study the radiolytic conversion of phenol and its oxidation products— resorcinol, hydroquinone, oxalic and formic acid solutions in aqueous solutions under  $\gamma$ - irradiation was studied. The spectrum of the UV-absorption, Chemical Oxygen Demand (COD) and pH change was studied. In the  $13 \leq D \leq 38$  kGy dose range occurs radiolytic decomposition of phenol and in high doses decreasing of intensity and disappearance of absorption band shows the partial and complete transformation of dihydric phenols. The effective rate constants of brutto oxidation processes of phenol and its transformation products were calculated and it was determined that, the rate of phenol oxidation is greater than the rate of dihydric phenol oxidation, is smaller than oxidation of acids.

**Keywords:** phenol and its oxidation products, effective rate constants,  $\gamma$ - irradiation, radiation-chemical yield.

### 1. Introduction

Phenols, oxalic and formic acids are the intermediate products in the multistage phenol degradation into  $\text{CO}_2$  under the ionizing irradiation of aqueous solution [1]. Radiolysis of aqueous solutions of dihydric phenols has been previously investigated [2, 3], but they cover either the initial or late stages of dihydric phenols degradation. However, practically, there is no systematic investigation covering wide range of absorbed irradiation dose, which makes it difficult for proper understanding the mechanism of irradiation induced degradation of aqueous dihydric phenol solutions and consequently the mechanism of complete phenol degradation into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

In the current study the radiolysis of aerated aqueous solution of phenol and its oxidation products has been investigated at the wide range absorbed gamma irradiation dose covering its initial conversion as well as the final stage of deep oxidation.

### 2. Experimental

Aerated ( $[\text{O}_2]=2.7 \times 10^{-4}$  M) aqueous phenol, resorcinol, hydroquinone, formic and oxalic acid solutions ( $1 \times 10^{-2}$  M) were irradiated by  $\text{Co}^{60}$  gamma rays at the static condition in sealed glass vials at room temperature. The dose rate was 0.29-0.21 Gy/sec which was determined by ferrous sulfate dosimeter, pH with pH meter PHS-25, potassium permanganate ( $\text{KMnO}_4$ ) was used for measuring chemical oxygen demand (COD), hydrogen peroxide by the methodic CTB ISO 8467, ultraviolet spectrum of products were taken by spectrophotometer Varian-Carry-50 at the wavelength ( $\lambda$ ) range of 200-800nm.  $\text{CO}_2$  was analyzed by a gas chromatography.

### 3. Results and discussion

The optical absorption spectra of aqueous phenol, dihydric phenols and organic acid solutions with different dose are presented in Figure 1-3.

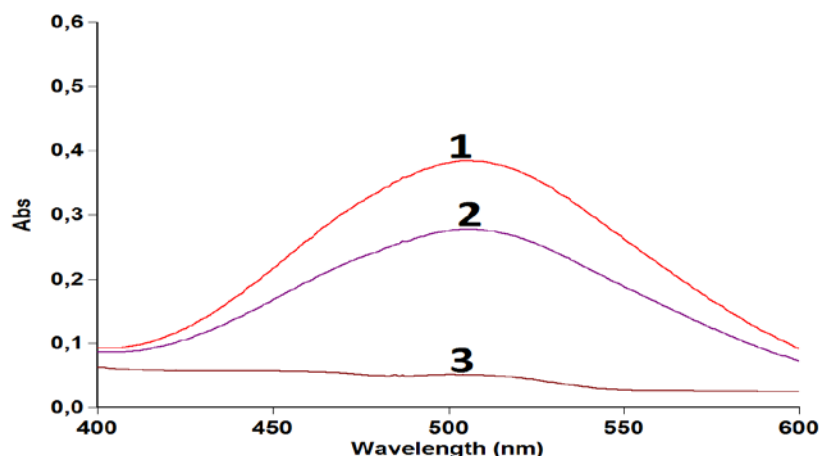


Fig.1. UV absorption spectrum of aqueous phenol solutions ( $1 \times 10^{-2} M$ ) absorbed at different doses:  $D=13$  kGy (1);  $D = 38$  kGy (2);  $D=380$  kGy (3)

In the  $13 \leq D \leq 38$  kGy dose range occurs radiolytic decomposition of phenol and in high doses decreasing of intensity and disappearance of absorption band shows the partial and complete transformation of dihydric phenols. The intensity of the absorption bands corresponds phenols are decreases to 38 kGy, at high doses observed low picks with respect phenol transformation.

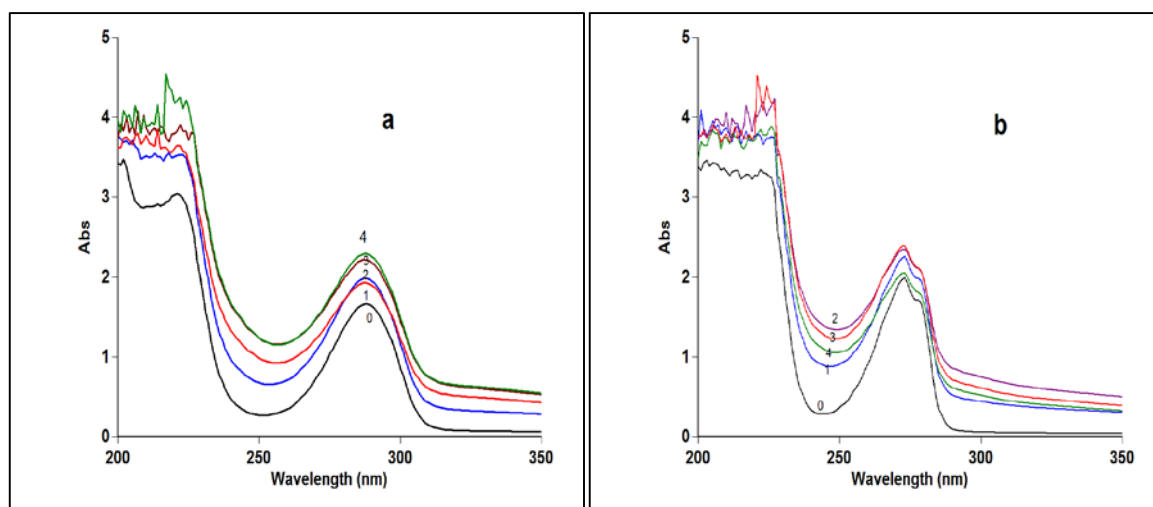


Fig.2. UV absorption spectrum of aqueous hydroquinone (a) and resorcinol (b) solutions ( $1 \times 10^{-2} M$ ) absorbed at different doses:  $D=0$ (0);  $D=27$ kGy (1);  $D = 55$ kGy (2);  $D=82$ kGy (3);  $D=109$ kGy (4)

As shown in the spectrum, the absorption maximum (Abs) of resorcinol observed at 200-225 nm and 273nm, while the hydroquinone is observed at 200-225 nm and 290nm, The intensity of the absorption bands in the spectrum of resorcinol increases with increasing absorbed dose and we observe hyper chromic effects at 55 kGy. The further increasing the dose results in a decrease in band intensity. Absorption band at 273 nm and 290nm corresponds to the absorption of the aromatic nucleus, and increasing the absorption in this area is associated with the appearance of structures of polymer molecules. The absorption bands in the 203-222 nm (resorcinol) and 200-230 nm (hydroquinone) associated with the formation of the oxidation products of resorcinol and hydroquinone, which is associated with the formation of organic acids. Additional evidence for

this is reducing the pH of solutions which is decreasing from 6.5 to 2.8 in the case of resorcinol and 6.5 to 2.7 in the case of hydroquinone with increasing absorbed dose to 27 to 109 kGy.

Thus, the radiolytic transformation of hydroquinone under gamma irradiation occurs in two directions: Polymerization and oxidation.

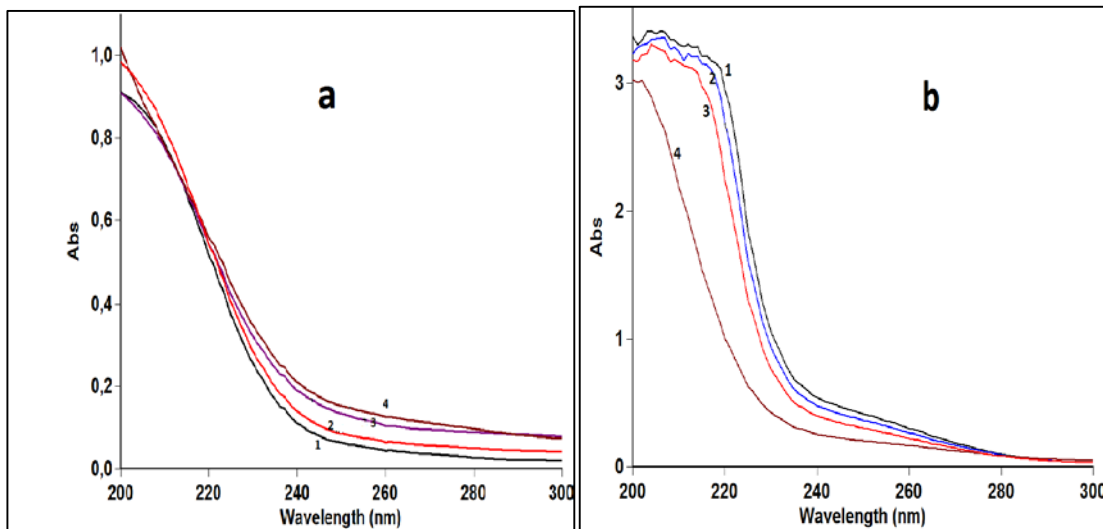


Fig.3. UV absorption spectrum of aqueous formic (a) and oxalic (b) solutions ( $1 \times 10^{-2} M$ ) absorbed at different doses:  $D=2 kGy$  (1);  $D = 6kGy$  (2);  $D=13kGy$  (3);  $D=27kGy$  (4)

In figure 3 is given adsorbtion spectrum of aqueous oxalic and formic solutions in 2-27 kGy dose range ( $\lambda=200-300 nm$ ). As shown in the spectrum of aqueous formic (a) solution optical absorbance increases within the dose range 2 to 27kGy, but for the oxalic acid solution the absorbance decrease with absorbed dose. So that, in all cases absorption is observed less than  $\sim 250 nm$ .

COD was recalculated into the unit of molar concentration using the following formula:

$$COD=(C/F_w) \times (RWO) \times (32)$$

Where C is a concentration of oxydizable compound in the sample;  $F_w$  – formula weight of the oxydizable compound in the sample; and RWO is a ratio of the mole numbers of oxygen to number of moles oxydizable compound in their reaction to  $CO_2$  and  $H_2O$ .

Chemical oxygen demand (COD) was measured at the different irradiation doses which shows the decrease of the COD (mg O/L) with increasing of irradiation dose. Accordingly, irradiation of aerated dihydric phenols solution leads to decreasing of total organic compounds.

Brutto degradation processes can be described as:  $A \xrightarrow{k_1} B \xrightarrow{k_2} C$  [5], where A are the initial components – hydroquinone and resorcinol, B is the organic intermediates and C is the final substrates ( $CO_2$  and  $H_2O$ )/ the pathways from A to C represents the complex reaction,  $k_i$  is the apparent rate constant ( $sec^{-1}$ ). If all reactions can be simplified to pseudo-first-order kinetics then by applying the kinetic equation to the COD date we obtain the following equation for the describing the reduction of COD with reaction time.

$$\ln \frac{COD_0}{COD} = (k_1 + k_2)t$$

Where,  $COD_0$  is the original organic compound. From the linear dependence the  $(k_1 + k_2)$  can be calculated (Fig. 4).

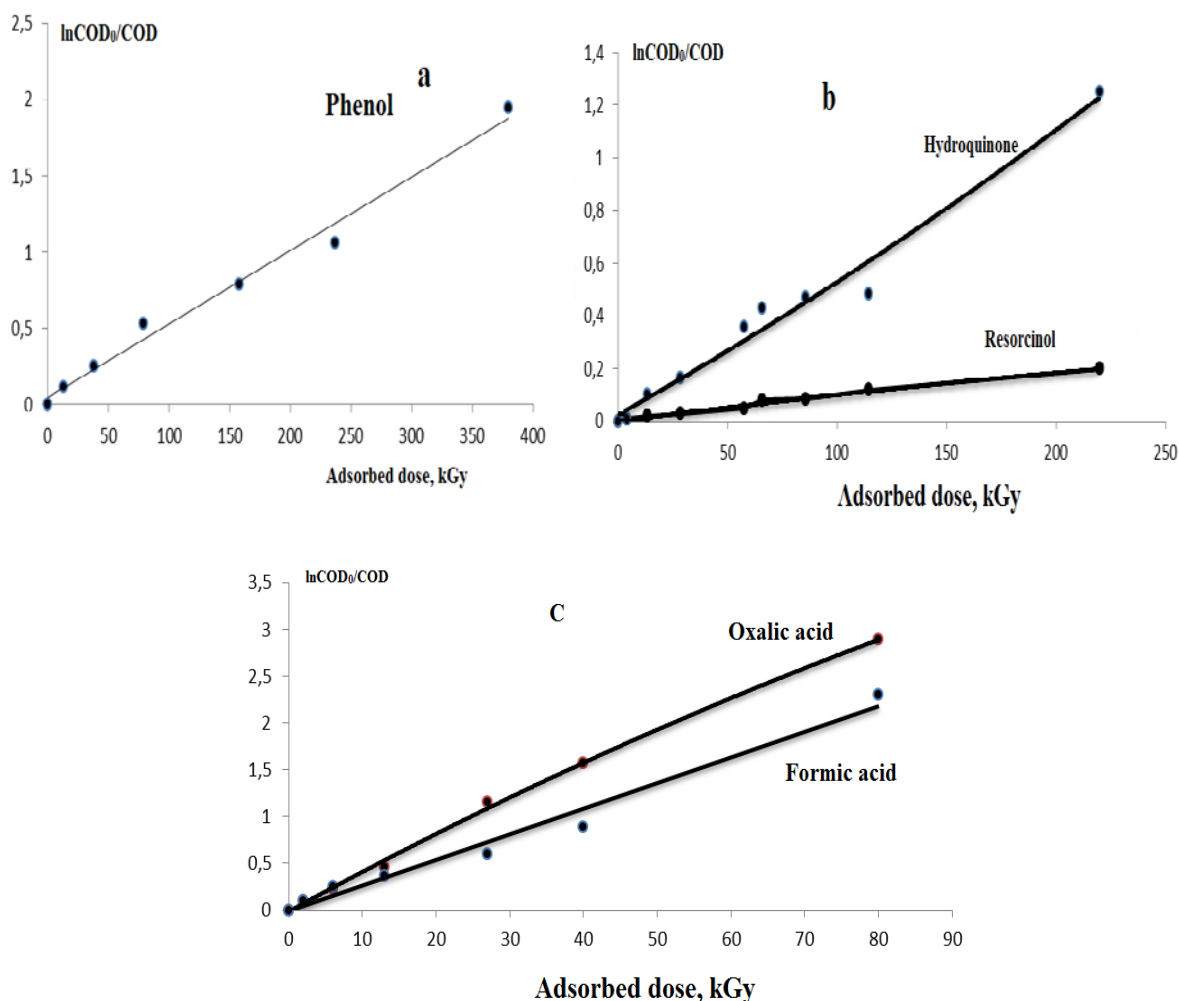


Fig.4. Dependence of  $\ln COD_0/COD$  from adsorbed dose. Phenol (a), resorcinol, hydroquinone (b), oxalic and formic acid (b).  $D=0,29-0,20$  Gy/sec

From the Fig. 4 the following values of the total apparent rate constants were obtained: These data shows that the rate of phenol oxidation is greater than the rate of dihydric phenol oxidation, is smaller than oxidation of acids.

Table1. The effective rate constants of brutto oxidation processes of phenol and its transformation products

Products	K(1/s)
Phenol	$1,2 \cdot 10^{-6}$
Hydroquinone	$1 \cdot 10^{-6}$
Resorcinol	$2 \cdot 10^{-7}$
Oxalic acid	$7 \cdot 10^{-6}$
Formic acid	$5 \cdot 10^{-6}$

#### 4. Conclusions

1. The intensity of absorption bands increase with the increasing of absorbed dose (hyper chromic effect), indicating to the formation of organic acids and aldehydes, that confirms with the decreasing of pH under gamma irradiation.
2. The polymerization of dihydric phenols under gamma irradiation was observed, the Abs of aromatic nuclear is increasing with rising of adsorbed dose.
3. With increasing absorbed dose the COD decreases, that indicates reducing of organic part in irradiated solutions. The apparent rate constant for the brutto oxidation reaction is equal to  $1,2 \cdot 10^{-6} \text{ s}^{-1}$  for phenol,  $2 \cdot 10^{-7} \text{ s}^{-1}$  for resorcinol,  $1 \cdot 10^{-6} \text{ s}^{-1}$  for hydroquinone,  $7 \cdot 10^{-6} \text{ s}^{-1}$  and  $5 \cdot 10^{-6} \text{ s}^{-1}$  respectively for oxalic and formic acids.

#### References

1. Nikola Getoff Radiation-Induced Degradation Of Water Pollutants-State Of The Art// Radiat. Phys. Chem. Vol. 47,pp 581-593(1996),
2. Kazuo Sato, Kazuto Takimoto, Saturo Tsuda , Degradation of aqueous phenol solution by gamma irradiation. Environmental Science and Technology.Vol.12, No9,pp 1043-1046 (1978)
3. A.N.M. Bagyo, W. A. Lindu, S. Sadjirun et al. Radiation-induced degradation of organic pollutants in wastewater. Centre for the Application of Isotopes and Radiation, National Nuclear Energy Agency, Jakarta, Indonesia. XA0101546 pp140
4. Hashimoto, S., Miyata, T. Kawakami, W. Radiation induced decomposition of phenol in flow system, Radiat.Phys.Chem.vol.16, pp59(1980)
5. HE Feng, Le-Cheng. Degradation kinetics and mechanisms of phenol in photo-Fenton process. Journal of Zhejiang University Science, vol. 5 (2),pp198-205,(2004)

### РАДИАЦИОННО-ХИМИЧЕСКИЕ ПРОЦЕССЫ В ВОДНЫХ РАСТВОРАХ ФЕНОЛОВ И КАРБОНОВЫХ КИСЛОТ

У.А. Кулиева, С.Г. Мамедов, М.А. Курбанов, З.И. Искендерова, Э.Т. Абдуллаев

**Резюме:** Исследовано радиолитическое превращение фенола и его продуктов окисления -резорцин, гидрохинон, щавелевой и муравьиной кислоты в водных растворах при  $\gamma$ - облучении. Изучено спектры УФ-поглощения, химическое потребление кислорода (ХПК) и изменение pH. В диапазоне  $13 \leq D \leq 38$  кГр подложенной дозе фенол радиолитически разлагается, и при высоких дозах с снижением интенсивности и исчезновением полосы поглощения показывает частичную и полную трансформацию двухатомных фенолов. Рассчитаны эффективные константы скорости брутто окислительных процессов фенола и продуктов его трансформации. Установлено, что скорость окисления фенола больше, чем скорость окисления двухатомного фенола, меньше чем окисление кислот.

**Ключевые слова:** фенол и его продукты окисления, эффективные константы скорости,  $\gamma$ - облучения, радиационно-химический выход.

## FENOLLARIN VƏ KARBON TURŞULARININ SULU MƏHLULLARDA BAŞ VERƏN RADIASIYA-KİMYƏVİ PROSESLƏRİ

Ü.A. Quliyeva, S.Q. Məmmədov, M.Ə. Qurbanov, Z.İ. İskəndərova, E.T. Abdullayev

**Xülasə:** Fenol və onun oksidləşmə məhsullarının – hidroxinon, rezorsin, oksalat və qarışqa turşularının suda məhlullarının  $\gamma$ -şüalarının təsiri altında radiolitik çevrilmə prosesi tədqiq edilmişdir. UB-udma spekrləri, oksigenə olan kimyəvi tələbat (OKT) və pH-ın dəyişməsi öyrənilmişdir.  $13 \leq D \leq 38$  kQr udulma dozasında fenolun radiolitik parçalanması baş verir. Böyük dozalarda intensivliyin azalması və zolağın yox olması uyğun olaraq ikiatomlu fenolların qismən və tam çevrilməsini göstərir. Fenolun və onun radiolitik çevrilmə məhsullarının brutto oksidləşmə proseslərinin effektiv sürət sabitləri hesablanmış və müəyyən edilmişdir ki, fenolun oksidləşmə sürəti ikiatomlu fenolların oksidləşmə sürətindən çox, turşuların oksidləşmə sürətindən isə kiçikdir.

**Açar sözlər:** fenol və onun oksidləşmə məhsulları, effektiv sürət sabiti,  $\gamma$ -şüalanma, radiasiya-kimyəvi çıxım