Journal of Radiation and Nuclear Applications
*An International Journal*

http://dx.doi.org/10.18576/jrna/050103

# Radiation Degradation of Aqueous Solutions of Phenolic Compounds and pH Dependence

*Salaheddin TAKRITI*

Arab Atomic Energy Agency, Cité El-Khadra 1003Tunis, Tunisia

Received: 21 Feb. 2019, Revised: 22 Mar. 2019, Accepted: 24 Mar. 2019.
Published online: 1 Jan. 2020.

**Abstract:** The effect of gamma radiation on the degradation of phenol (hydroxybenzene), resorcinol (1,3-dihydroxybenzene) and hydroquinon (1,4-dihydroxybenzene) existing in wastewater was investigated. The effect of concentrations of these pollutants as well as the pH effect was studied. The results showed that phenol is highly resistant against the irradiation compared to other phenol compounds. Phenol was also a product of radiolysis of resorcinol and hydroquinon. On the other hand, the acid phase of the irradiated samples increased with the degradation rate of pollutants. Spectrophotometer (UV-VIS) and chromatography (HPLC) were used to monitor the promotion of the radiation products. The results illustrated the existing of many substances with organic alcohol, aldehide, ketone and acidic functional groups as a final radiation products.
**Keywords:** *Radiation degradation, Phenolic compounds, Pollutants of wastewater, UV- spectrophotometer and HPLC-Chromatography.*

## 1 Introduction

Pollution is the introduction by man into the environment of substances or energy liable to cause hazards to human health, harm to living resources and ecological systems, damage to structures or amenity, or interference with legitimate uses of the environment [1-2].
In the last few decades the worldwide rapid industrial growth and population increase, have resulted in the release and accumulation of different pollutant materials in the environment with their subsequent adverse effect to the ecosystem and its natural habitat [3]. Industrial wastes in different forms represent one of the most serious problems of environmental pollution and necessitate strict control and appropriate treatment processes. These processes vary according to the nature of the pollutant material [4].
Since water is the limiting factor in the economic and social life, shortage of water is considered as one of the most significant obstacles against development in the Arab region. Agriculture consumes 75% of all water consumption in Syria. This obliges us to reuse the sewage wastewater after treatment to keep what is left from the natural resources [5].
Chlorination is widely used in water and wastewater treatment for disinfection and often seriously increases the level of toxic chlorinated organic compounds, for instance chlorophenols [6-7].
Radiation methods for purification and disinfection of wastewater are being developed comparatively widely [8]. The most important is the combined method such as gamma radiation, electron beam and ozone treatment [9]. In the last years irradiation treatment of the wastewater has become a good alternative to face the pollution problems caused by disposal of the wastes to rivers and grounds [10-12].
Radiolytic degradation of phenolic compounds for environmental purposes has been a subject of several papers. In the study of radiolysis of phenol with gamma radiation, formation of

*Corresponding author e-mail: stakriti@gmail.com

dihydroxybenzenes was observed [13]. Otherwise, the mechanism of the degradation of Radiation-induced degradation and the effect of scavengers was studied on benzene, monochlorobenzene and 1,2-dichlorobenzene in aqueous solutions [14].

The aim of this study was to investigate the effect of gamma radiation treatment on phenol, resorcinol and hydroquinone in wastewater. The effect of concentration of these pollutants and the solution pH on the final radiation products was illustrated.

## 2 Experimental Section

*2.1* Reagents

Phenol (hydroxybenzene), resorcinol (1,3-dihydroxybenzene) and hydroquinon (1,4-dihydroxybenzene) as well as the reference substances for UV, HPLC and expected irradiation products were purchased from Merck (extra pure) and Romil for $CH_3CN$ (99.9 %). These reagents were used without further purification. Sample solutions were made up in triply distilled water after passing on the anion-exchanging column. Water and eluents were degassed using ultrasonic.

*2.2* Apparatus

The investigation of the effect of gamma radiation on wastewater was carried out using $^{60}Co$ - gamma cell “Issledovatel – 10 kCi” at a dose rate of 2.5 kGy/h, which was determined by means of a modified Fricke dosimeter [15]. Samples were irradiated at 20 °C with doses ranging from 0 to 20 kGy.

Qualitative and quantitative analysis of the organic products were performed using UV-Vis Spectrophotometer (Shimadzu UV-Vis, A-120) and HPLC-High Performance Liquid Chromatography (Bio-Rad- AS-96C). The HPLC used ( ODS-2 , 4.6x 250 mm, 0.9µl , 45°C , 95 kg/cm$^3$ and $CH_3CN/H_2O$ 65/35) was equipped with a multiple wavelength UV-detector (Shimadzu-SPD-10AV). The individual compounds were detected by measuring their absorption at wavelength ranged between 200-450 nm, depending on the compounds.

The irradiation of samples was done using 10 ml sample solutions placed in sealed glass tube. To study the effect of air on the radiation degradation, some irradiation samples were irradiated in open glass tube.

## 3 Results and Discussion

In order to obtain better knowledge of the effect of γ-irradiation on phenolic compounds, three samples with different concentrations of phenol solution at pH=7 were selected and irradiated. The fraction of phenol degradation (variation of phenol initial concentration %) as a function of absorbed gamma dose (kGy) is presented in figure1. In this figure it is found that the high concentration of phenol (3.5 x $10^{-4}$ mol) needs 3 kGy of gamma dose to reach 50% of degradation, while 1 kGy and 0.75 kGy are needed for concentration of 1.5 x $10^{-4}$ mol and 0.5 x $10^{-4}$ mol, respectively. From these results a concentration of 1.5 x $10^{-4}$ mol is adopted to study all the phenolic substances.

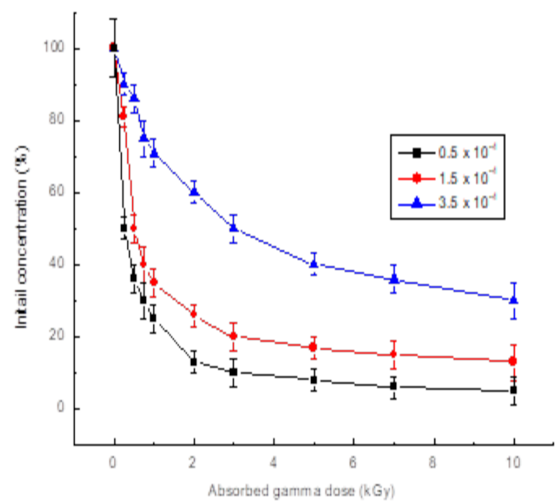



Fig.1 Radiation effect of phenol solution in different concentration as a function of gamma dose

The degradation fraction (initial content, %) of phenol, resorcinol and hydroquinon as a function of absorbed gamma dose (kGy) in different pH solutions is illustrated in figures 2, 3 and 4, respectively. The results showed that the phenolic substances degraded by radiation and the degradation rates depend on the substance and the pH of the solutions. It is also found that at pH=5 the degradation rate increased in comparison with pH=7 and pH=9. This increase could be due to the enrichment of the free radicals in irradiated solution [12]. The color of the resorcinol solution changed at pH=9 as a result of irradiation. Whereas, some salts were precipitated from hydroquinon solution.

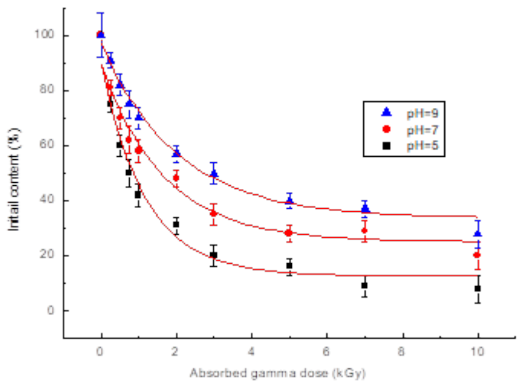


Fig.2 Variation of phenol concentration as a function of gamma dose

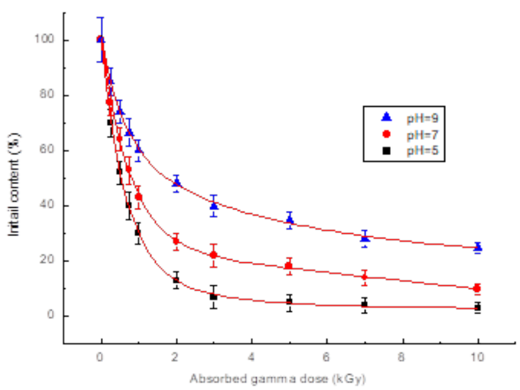


Fig.3 Variation of resorcinol concentration as a function of gamma doses.

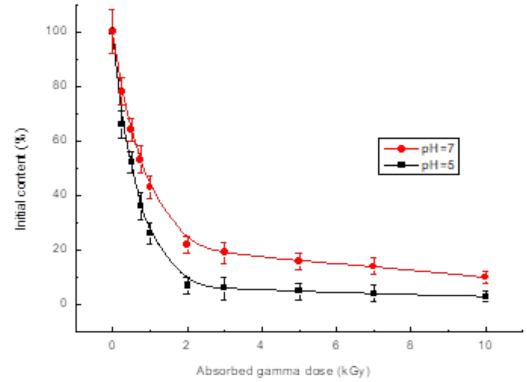


Fig.4 Variation of hydroquinon concentration as a function of gamma doses

In order to show the radiation resistance of phenolic compounds, the degradation fraction of phenol, resorcinol and hydroquinon as a function of absorbed gamma dose at pH=5 and pH=7 are shown in figures 5 and 6, respectively. The results showed that phenol is the most resistant for radiolytic degradation. While, the resorcinol and hydroquinon solutions require lower dose to be degraded. In addition, the position of the hydroxyl group influences the radiation degradation. It is found that the resorcinol (1,3-dihydroxybenzene) needs longer irradiation time than the hydroquinon (1,4- dihydroxybenzene). The γ-dose required for completing the decomposition of phenolic compounds is illustrated in Table 1. Getoff, [11] pointed out that radiation induced phenol degradation depends strongly on numerous factors such as substrate concentration, applied dose and availability of oxygen.

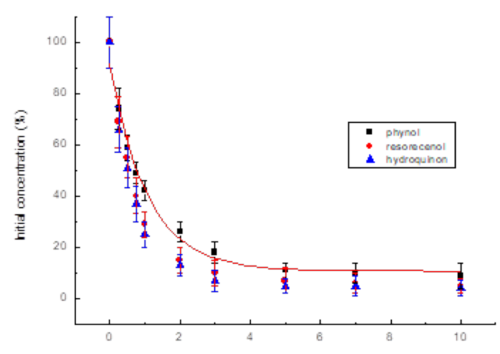


Fig. 5. Radiation effect of Phynol, Resorecinol and Hydroquinon in aqueous solution (pH=5)

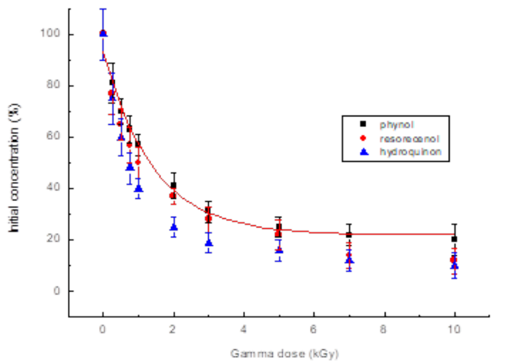



Fig. 6. Radiation effect of Phynol, Resorecinol and Hydroquinon in aqueous solution (pH=7)

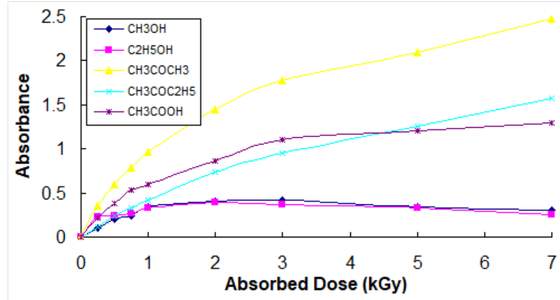



**Figure 7.** Species produced from radiation degradation of phenol

Table 1.The γ-dose required for decomposition of phenolic compounds

| Examined compound | γ-dose required for decomposition (kGy) | |
|---|---|---|
| | Started | Complete |
| Phenol (hydroxybenzene) | >0.5 | >15 |
| Resorcinol (1,3-dihydroxybenzene) | 0.25 | >10 |
| Hydroquinon (1,4-dihydroxybenzene) | <0.25 | 10 |

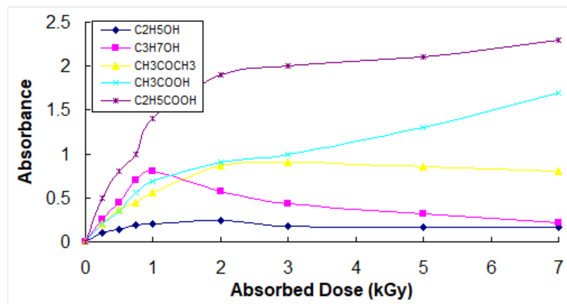



**Figure 8.** Species produced from radiation degradation of resorcinol

The difference between the UV spectra of the phenol, resorcinol and hydroquinon solutions before and after irradiation was used to determine the radiation products. The variation of initial content (%) of phenolic compounds as a function of gamma doses (kGy) was employed to determine the existence of other organic alcohol, aldehide, ketone and acidic functional groups. Figures 7 and 8 illustrated the variation of these functional groups as a function of gamma doses, respectively, where the increase of the absorbence is used as the increase of the radiation product concentrations. It is shown that the degradation of organic pollutants makes it possible to produce all the organic functional groups.

It was mentioned that the main process in radiation degradation of organic pollutants is the decomposition of pollutants [16] and the formation of organo-acid group [12] as the total organic carbon content in the irradiation solutions decreases [11] and for monochlorobenzen and 1,2 dichlorobenzen [17].

The irradiation of diluted aqueous solution is well known [12]. The solvent water mainly absorbs the energy of the ionizing radiation. This absorption leads to the formation of OH radicals, hydrated electrons and H atoms as reactive free radicals according to mechanism proposed by Takriti [17] as follow:

$$H_2O + \gamma \rightarrow H_2O^* \longrightarrow H^{\cdot} + OH^{\cdot}$$

$$H_2O + \gamma \rightarrow H_2O^+ + e^- \rightarrow e^-_{th} + n\,H_2O \longrightarrow e^-_{aq}$$

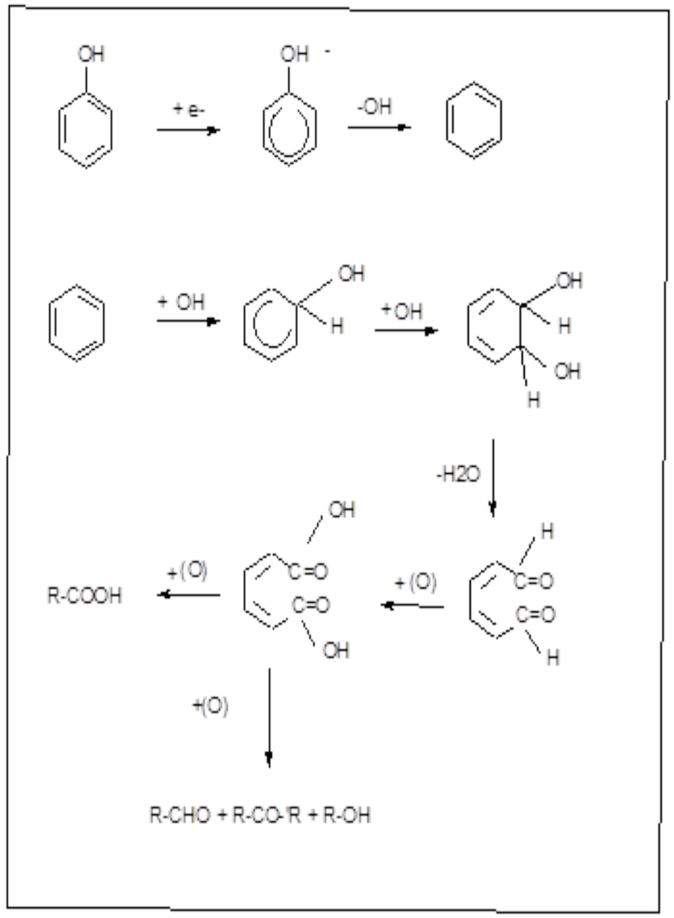
The radiation-chemical yields "G -value" (value x $10^{-7}$ mol/J) in aqueous solution at pH=7 are:

$$H_2O \rightarrow e^-_{aq}\ ,\ H\ ,\ OH\ ,\ H_2\ ,\ H_2O_2\ ,\ H^+\ ,\ OH^-_{aq}$$

$$(2.7)\ \ (0.6)\ \ (2.8)\ \ (0.45)\ \ (0.7)\ \ (3.2)\ \ (0.5)$$

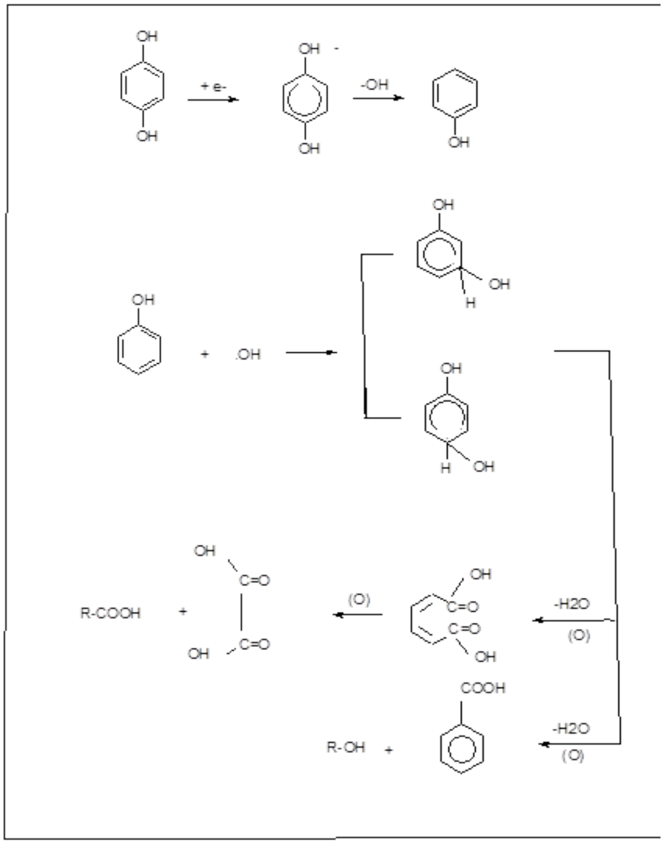
The general mechanisms for the reaction of ionizing radiation with aromatic compounds are known [7]. Therefore in the following schemes only those reactions, which elucidate the formation of the final products presented in figures 7 and 8, are considered.

The hydrated electrons exist in the irradiation solution attack the phenol into the benzene ring to form phenol radical. Benzene is then formed by hydroxyl elimination. Some of hydrated electrons may be converted into hydroxyl radicals. In this case, hydroxyl radicals can react with benzene by electron transfer forming phenol and dihydroxyphenol radicals. Aldehide is produced by water molecule elimination. The presence of oxidized group ($O^{\cdot}$ or $H_2O_2$) converts the formed aldehide to acidic substances and the following oxidizing process breaks the carboxyl chain to form other organic alcohol, aldehide, ketone and acidic final products ( Scheme 1).




Scheme 1. The possible reaction of OH radicals, hydrated electrons on phenol

In the case of dihydroxybenzene, hydroxyl radicals can react with phenol, which formed by hydroxyl elimination of dihydroxybenzen radical and transfer it to dihydroxyphenol radicals. When a water molecule is eliminated, aromatic acid can be formed in presence of oxidized group. Some aromatic acid has a chance to break down and to form organic alcohol and acidic as a final products ( Scheme 2).




Scheme 2. The possible reaction of OH radicals, hydrated electrons on dihydroxybenzene.

## 4 Conclusion

For most of the examined phenolic compounds it can be concluded that the phenolic species decompose by ionizing radiation. The increase of hydroxyl group linked to benzene ring requires a lower radiation dose for complete radiolytic degradation of studied species. The position of the hydroxyl group has affects the radiation degradation. The most resistant for radiolytic degradation is phenol, therefor dihydroxyphenol requires lower dose for complete degradation.

The radiation process in an open system helps to form the final products such as organic alcohol, aldehide, ketone and acidic.

## Acknowledgement

The author would like to thank Professor I. Othman, Director General of A.E.C.S., for his help. Many thanks are given to Ms. A. Al-kaid and Ms. G. Al-masri for their technical assistance.

## References

1- H. J. M. Bowen, Environmental chemistry of the elements, Academic press, London, 453 pp. (1979).
2- M. W. Holdgate, (1979) A perspective of Environmental Pollution, Cambridge university Press. Cambridge, 432 pp. (1979).
3- S. E. Jorgensen and I. Johsen, Principles of environmental science and technology, Elsevier. Amsterdam, 450 pp. (1989).
4- G. McKay, Use of adsorbents for the removal of pollutants from wastewaters. CRC Press Inc., London, 380 pp. (1996).
5- S. Takriti, A. Odah, and A. Al-Kaid, The effect of Gamma radiation on sewage wastewater of Damascus Plant. China, International Symposium on Radiation Technology in Emerging Industrial Application", 6-10 November, Beijing, 2000; IAEA-SM-365: 253-257 (2001).
6- A. El-Taher, A., Measurement of Radon Concentrations and Their Annual Effective Dose Exposure in Groundwater from Qassim Area, Saudi Arabia. Journal of Environmental Science and Technology, 5 (6) 475-481, (2012)
7- IAEA. Radiation technology for conservation of the environment, proceedings of a symposium, Session 3, Purification and decontamination of water, IAEA-TECDOC-1023, (1998).
8- D. T. Wait, C. N. Kurucz, W. J. Cooper, and D. Brown, Full scal EB systems for treatment of water, wastewater and medical waste. Radiation Technology for Concervation of the Environment (Proc. Symp. Zakopane), IAEA, Vienna,187:195. (1998).
9- S. L. Yue, Study on by-products generated in running water of Shanghai during the chlorination disinfecting. Chinese Journal of Water Supply and Drainage, 8: 8-15 (1998)..
10- N. Getoff, Purification of drinking waters

by irradiation. A review, Proc., Indian Acad. Sci., (Chem. Sci.); 105: 373-381 (1993).

11- N. Getoff, Radiation induced degradation of water pollutants, Radiat. Phys. Chem. 47: 581-539 (1996).

12- N. Getoff, Radiation Chemistry and the Environment, Proceeding of a symposium, Poland, 8-12 Sept. 1997, IAEA-TECDOC-1023: 432-432 (1997).

13- S. T. Hashimoto, W.M. Miyata, and W. Kawakumi, A liquid chromatographic study on the radiolysis of phenol in aqueous solutions. Env. Sci. Technol.; 13: 71-82 (1979).

14- H. Fricke, and E. J. Hart, In Radiation Dosimetry (Ed. F. H. Attix, W. C. Roesch and E. Tochilin), Academic Press, New York, 521 pp (1960).

15- M. Trojanowicz, A. Chudziak and T. Bryl-Sandelewska, Use of reversed-phase HPLC with solid-phase extraction for monitoring of radiolytic degradation of chlorophenols for environmental protection. Journal of Radioanalytical and Nucl. Chem. 224(1-2): 131-139 (1997).

16- S.Schmid, P. Krajnik, R. M. Quint and S. Solar, Degradation of monochlorophenols by gamma irradiation, Radiat. Phys.Chem. 50/5 : 493-500 (1997).

17- S. Takriti, Radiation-induced degradation and the effect of scavengers on benzene, monochlorobenzene and 1,2-dichlorobenzene in aqueous solutions Water Quality Research Journal of Canada.Vol. 39, No. 3, 247-253 (2004).