

Research Article

Radiation Induced OH[•] Free Radicals Degradation Process of Phenol in Aqueous Solutions – Environmental Implications

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Abstract

The presence of the phenol, an organic refractory pollutant, in wastewater is one of the biggest environmental issues for both human health and life in aquatic ecosystems. In this study, gamma radiation induced degradation of phenol has been investigated. The radiolitically produced hydroxyl free radical OH[•] initiates the degradation via its addition to the phenol ring. After one hour, the phenol degradation was found 98% at a dose of 9 kGy. The initial major aromatic ring byproducts were identified as catechol, hydroquinone and benzoquinone. Further oxidation of these intermediates compounds via ring openings and bond breaking leads to a set of carboxylic acids and finally to a complete mineralization of phenol. The degradation rate decreased with increasing initial phenol concentration and followed first order kinetics. The influence of the pH on this degradation was also investigated. Increasing the pH from 6.6 to 12 decreased the phenol degradation efficiency from 95 to 73 %, respectively. Overall, the results showed that oxygen gas plays a key role in phenol degradation.

Keywords: Gamma Radiation; Hydroxyl Radical; Phenol Degradation; Oxidation; Radiation Induced

Introduction

A broad range of organic contaminants such as phenolic compounds (phenol, chlorophenols, and nitrophenol) are discharged in the water system from industrial, pharmaceutical and agricultural activities [1]. The US Environmental Protection Agency considers the contamination by these compounds of the hydric resources as a major environmental issue for both humans and life in aquatic ecosystems and prescribed a discharge limit in wastewater of less than 1 mg/L and a concentration of less than 1µg/L for drinking water [2]. Besides being highly irritating to the skin and eyes, phenol or its derivative contaminated drinking, cooking or bathing water can be

one of the biggest risks to human health due to their toxicity to vital organs [3], mutagenic and carcinogenic effects [4]. Hence, removal of phenols from wastewater before its reuse or discharge to the environment is a vital issue.

Phenol is a colorless-to-white aromatic organic solid compound highly soluble in water. The hydroxyl group –OH is bound to the cyclic phenyl group –C₆H₅. Phenol and phenol compounds are known as refractory organic pollutants [5], which resist conventional biological degradation [6], ozonation [7], adsorption [8], solvent extraction [9] and electrochemical processes [10].

In the last few years, radical-based advanced oxidation processes proved significant importance for the alleviation of recalcitrant toxic pollutants in wastewaters. They involve the generation of some very reactive oxidizing species mainly the hydroxyl free radical (OH^\bullet) which reacts unselectively at nearly diffusion control rates, $\sim 10^9 \text{ mol dm}^{-3} \text{ s}^{-1}$, with aromatic hydrocarbons, unsaturated compounds and aliphatic alcohols and degrade them [11]. Oxidation of phenols and their derivatives by OH^\bullet radicals generated by $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ Fenton and $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ Fenton-like reactions have been extensively studied [12]. This oxidation requires the presence of hydrogen peroxide and ferric or ferrous ions in the solutions to generate OH^\bullet .

To the best of our knowledge, the radiation induced oxidation of phenols was seldom investigated. The objective of the present laboratory study was to assess the advanced oxidation process of phenol with the gamma (γ) radiation induced OH^\bullet . The effect of pH and initial phenol concentration on the removal percentage of phenol were investigated.

Materials and Methods

Phenol solutions of purity higher than 99 % was supplied by British Drug Houses (BDH) Chemicals and were used without any further purification. Phenol stock solutions of different concentrations were prepared using purified and deionized water by Millipore milli-Q system (resistivity $\sim 18 \text{ M}\Omega\text{-cm}$). In our work *tert*-butanol of analytical grade from BDH was used as received. The pH of solutions was measured with Electronic Instruments Ltd (EIL) 7200 glass electrode pH-meter calibrated before use. The deoxygenated solutions were obtained by bubbling phenol solutions with pure nitrous oxide gas (N_2O) for around 15 min. The oxygenated solutions were prepared by bubbling with pure oxygen gas. The concentrations of phenol and its oxidation products were determined by the Hewlett-Packard 1090 high performance liquid chromatography (HPLC) equipped with a diode-array detector (DAD) and a reverse column Zorbax C_{18} (150 x 4.6 mm) column. The mobile phase in the reverse phase column consisted of a mixture of water and methanol (40:60, v/v) with an elution rate of 0.8 mL min^{-1} . The eluate from the column was monitored at 280 nm. To monitor the removal of the phenol, irradiations were stopped periodically for the solution to be analyzed. All experiments were performed in a 100 cm^3 Perspex beaker batch reactor at room temperature. The pH of the dilute phenol solution was found to be around 6.6. When necessary, the pH adjustments of the solutions were done by the addition of perchloric acid or borax.

Irradiation facility

Steady state irradiations were carried out using a ^{60}Co γ -ray source (of activity 2000 Ci nominal activity) of average energy of 1.25MeV fixed at the end of a rod and shielded by a block of steel mounted on a concrete base for radiation protection purposes (Fig. 1). The source is moved to the irradiation position

by pushing manually the rod in position "in". A ruler was used to position the sample in the irradiation compartment in a determined distance from the source for a dose rate of 9 kGy/hr which was used throughout this work. The design of the irradiation unit is such as the leaded access door remains locked when the rod is in the irradiation mode (Fig. 1a) and can be open only at the end of the irradiation time when the rod is pulled out (Fig. 1b).

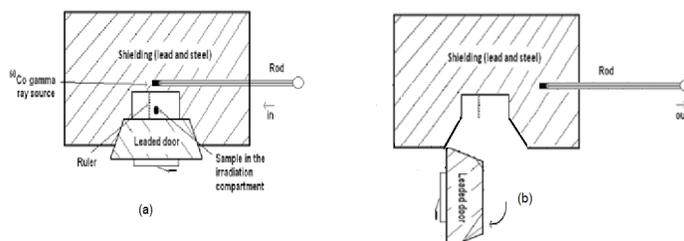


Figure 1: Top view of the irradiation compartment with the irradiated sample, (a): irradiation mode, (b): sample taken out.

Dosimetry

Dosimetry was performed using the dichromate chemical dosimeter at pH 9.2 [13]. It is based on measuring the amount of disappearance of chromate ion CrO_4^{2-} at 370 nm, namely the net change in optical density due to irradiation. The dose is calculated according to the expression

where ΔOD is the change in optical density of the chromate ion at 370 nm, γ is the reduction yield of this ion, D is the density of the dosimeter solution, ϵ is the extinction coefficient of the chromate ion at 370 nm and l is the cell optical pathlength. By taking $\gamma = 0.20 \text{ }\mu\text{mol J}^{-1}$, $D = 1 \text{ kg dm}^{-3}$, $\epsilon = 4820 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ and $l = 1 \text{ cm}$ [13], the radiation dose in Gray is given by

Phenol solution irradiation

Irradiation of pure water with low energy transfer (LET) γ -radiation gives rise to transient species and stable byproducts homogeneously distributed in the bulk solution [11]



Table 1 gives the typical yields in $\mu\text{mol J}^{-1}$ of these species and stable byproducts. A series of recombination reaction can occur between them as shown in Table 2.

Table 1: G-values of radiation induced species in pure water [11].

Species	G-value (in $\mu\text{mol J}^{-1}$)
H_2	0.047
H_2O_2	0.078
e_{aq}^-	0.280
H^\bullet	0.062

OH•	0.280
H•	0.027
OH ⁻	0.044

Table 2: Recombination reactions following pure water irradiation [11].

Reaction	k (mol dm ⁻³ s ⁻¹)
$e_{aq}^- + OH^\bullet \rightarrow OH^-$ (4)	3.0×10^{10}
$e_{aq}^- + H^+ \rightarrow H^\bullet$ (5)	2.3×10^{10}
$e_{aq}^- + O_2 \rightarrow O_2^{\bullet-}$ (6)	1.8×10^{10}
$H^\bullet + O_2 \rightarrow HO_2^\bullet$ (7)	2.1×10^{10}
$e_{aq}^- + e_{aq}^- \rightarrow H_2 + OH^-$ (8)	7.0×10^9
$HO_2^\bullet \rightleftharpoons O_2^{\bullet-} + H^+$ (9)	$pK_a = 4.88$
$OH^\bullet + OH^\bullet \rightarrow H_2O_2$ (10)	5.5×10^9
$OH^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O$ (11)	2.5×10^9
$OH^\bullet + O_2^{\bullet-} \rightarrow O_2 + OH^-$ (12)	9.4×10^9
$HO_2^\bullet + OH^\bullet \rightarrow O_2 + H_2O$ (13)	6.6×10^9
$HO_2^\bullet + HO_2^\bullet \rightarrow O_2 + H_2O_2$ (14)	8.3×10^5
$HO_2^\bullet + H_2O_2 \rightarrow OH^\bullet + H_2O + O_2$ (15)	3.0
$H^\bullet + H^\bullet \rightarrow H_2$ (16)	7.8×10^9

In dilute phenol solution the transient radicals react with phenol. The $O_2^{\bullet-}$ and HO_2^\bullet transient free radicals formed in the water radiolysis are much less reactive with phenol than OH^\bullet , H^\bullet and [14]. In the literature, the reported rate constant between $O_2^{\bullet-}$ and phenol is $5.8 \times 10^2 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ [15]., H^\bullet and OH^\bullet are competing for phenol as shown in Table 3.

Table 3: Reactions of phenol with OH^\bullet , H^\bullet and transient species [11].

Transient species	Rate constant ($10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$)
$OH^\bullet + \text{phenol} \rightarrow \text{Product 1}$ (17)	6.6
$H^\bullet + \text{phenol} \rightarrow \text{Product 2}$ (18)	1.7
$+ \text{phenol} \rightarrow \text{Product 3}$ (19)	0.02

Results and Discussions

As shown in Table 3, phenol is oxidized by hydroxyl radicals and reduced by hydrogen atom and the hydrated electrons. This results in its removal from the solution. The removal percentage at time of irradiation t , was calculated from the following equation

$$\%R(t) = \frac{C_0 - C_t}{C_0} \times 100 \quad (20)$$

where C_0 is the initial phenol concentration (mol dm⁻³) and C_t is the

phenol concentration at time of irradiation t . The fractions of phenol reacting with OH^\bullet , H^\bullet and e_{aq}^- are respectively given by the expressions

$$f(OH^\bullet, Ph) = \frac{k_{17}[OH^\bullet][Ph]}{k_{17}[OH^\bullet][Ph] + k_{18}[H^\bullet][Ph] + k_{19}[e_{aq}^-][Ph]} \quad (21)$$

$$f(H^\bullet, Ph) = \frac{k_{18}[H^\bullet][Ph]}{k_{17}[OH^\bullet][Ph] + k_{18}[H^\bullet][Ph] + k_{19}[e_{aq}^-][Ph]} \quad (22)$$

$$f(e_{aq}^-, Ph) = \frac{k_{19}[e_{aq}^-][Ph]}{k_{17}[OH^\bullet][Ph] + k_{18}[H^\bullet][Ph] + k_{19}[e_{aq}^-][Ph]} \quad (23)$$

By using data from Table 1 and Table 3, these fractions are 94.3%, 5.4% and 0.3% respectively. This indicates that the hydroxyl radical is the primary species in the radiation induced degradation of phenol.

Phenol removal: effect of tert-butanol

Tert-butanol (2-methyl-2-propanol) is a good OH^\bullet scavenger in aqueous solution [16]. The reaction proceeds by H^\bullet abstraction and yields the relatively unreactive radical $\cdot CH_2C(CH_3)_2OH$



$$k = 6 \times 10^8 \text{ mol dm}^{-3} \text{ s}^{-1}$$

Fig. 2 shows clearly that the degradation of phenol is greatly inhibited by the presence of this OH^\bullet scavenger. For instance the degradation percentage was reduced from 95% to around 43% in the presence of 1 mM of *tert*-butanol at an absorbed dose of 4 kGy. In the presence of 1 mM of *tert*-butanol, around 40% of phenol was still detected after 1 hour of irradiation while in the absence of this scavenger all the phenol was degraded. This finding clearly indicates that hydroxyl radical is the primary degrading agent of phenol in aqueous solutions.

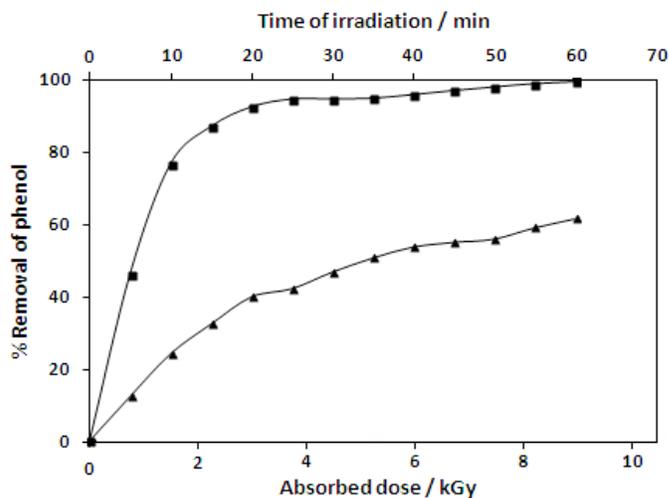
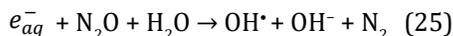


Figure 2: Effect of *tert*-butanol hydroxyl scavenger on phenol deg-

radiation: initial phenol concentration: 0.40 mM, dose rate: 9 kGy/hr. (■) without *tert*-butanol, (▲) with 0.01 M *tert*-butanol.

Effect of gas bubbling

Fig. 3 shows that the radiation induced degradation of phenol in solution saturated with oxygen was increased nearly 9-fold when compared to N₂O-saturated solution. When bubbled with N₂O, hydrated electrons are quickly scavenged and converted into OH[•] [11]



Although the yield of OH[•] increases in the N₂O-saturated solution, $G(OH^\bullet)_{tot} = G(OH^\bullet) + G(O) = 0.28 + 0.28 = 0.56 \mu\text{mol J}^{-1}$, the degradation of phenol decreased but is not completely suppressed as small amount of radiolytically produced O₂ builds up in the solution (reactions 10 – 13 in Table 2) and contribute to the oxidation of phenol with a low yield compared to the yield for O₂-saturated solution. Sato and his co-workers [17] showed that the phenol decomposition yield was six-fold higher for γ -radiolysis in aerated solution than in deaerated one. The absence of oxygen inhibits the degradation of phenol and the buildup of its by-products.

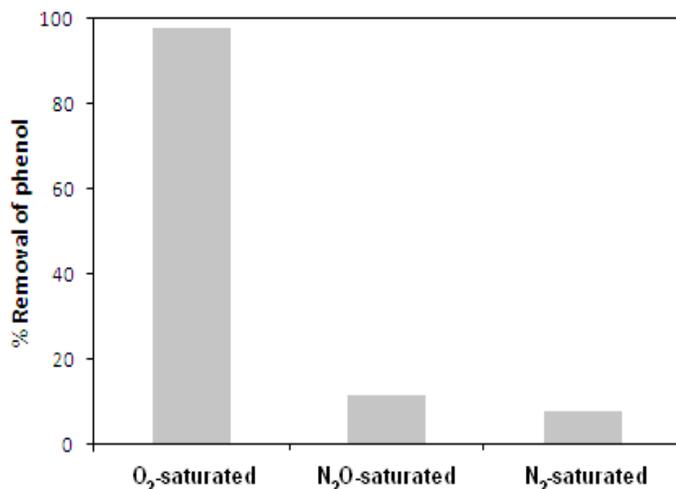


Figure 3: % Removal of phenol for different gases saturated solution. Initial phenol concentration: 0.40 mM, irradiation time: 1 hour, dose rate: 9 kGy/hr.

Kinetics of phenol degradation

Our experimental data for radiation induced removal of phenol in the absence of *tert*-butanol were found to fit a first order equation with respect to time as used previously by other authors [18]

$$[C] = [C_0]e^{-kD} \quad (26)$$

where C is the remaining phenol concentration (mol L⁻¹) at time t , is the initial concentration of phenol and k is the rate constant of the phenol removal (Gy⁻¹). Taking the logarithm of its both sides, equation (26) can be linearized to:

$$\ln\left(\frac{[C]}{[C_0]}\right) = -kD \quad (27)$$

The rate constant of the phenol removal k was determined from linear plot of versus dose of irradiation and was found to be equal to 0.79 kGy⁻¹ with a coefficient of correlation $R^2 = 0.9972$ as shown in Fig. 4.

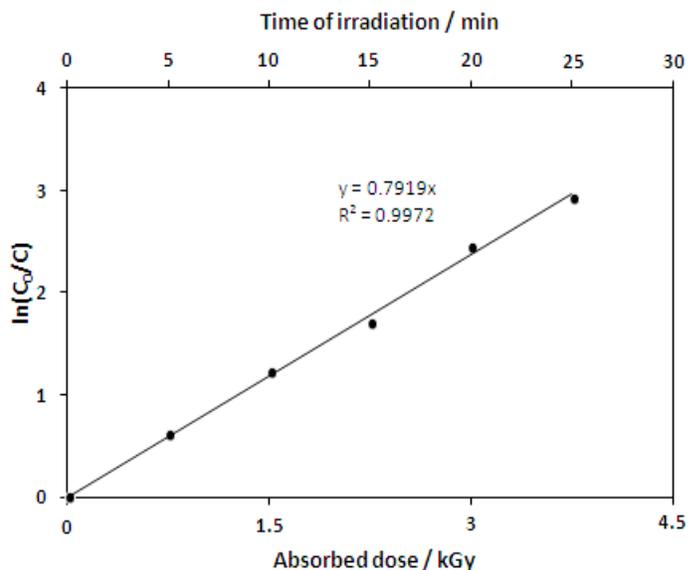


Figure 4: Plot of $\ln(C_0/C)$ as function of absorbed dose. Initial phenol concentration: 0.40 mM, irradiation time: 1 hour, dose rate: 9 kGy/hr.

The amount of degraded phenol per unit absorbed radiation energy, $G(-Ph)$, calculated at each absorbed dose is expressed by [19]

$$G(-Ph) = \frac{\Delta(Ph)}{D} \times 10^6 \quad (\mu\text{mol J}^{-1}) \quad (28)$$

where $\Delta(Ph)$ is the change in concentration of the phenol (mol L⁻¹) and D is the absorbed dose (Gy). Table 4 shows that $G(-Ph)$ decreases with increasing absorbed dose. This is probably due to the competition between the phenol and its increasing byproducts (catechol and hydroquinone) for OH[•] radicals as confirmed by previous work [20].

Dose (kGy)	$G(-Ph)$ ($\mu\text{mol J}^{-1}$)
0.75	0.246
2.25	0.154
3.75	0.100
5.25	0.072

Table 4: Effect of dose on the degradation yield of phenol. Initial phe-

nol concentration fixed at 0.40 mM.

Table 5 shows that for a fixed dose of 2.25 kGy, increases with increasing initial concentration of phenol although the removal percentage increased with the decrease in initial phenol concentration. The highest percentage phenol degradation was obtained when irradiating the solution with the lowest initial phenol concentration. Again this can be explained by the competition between the phenol and its byproducts for hydroxyl radicals.

Table 5: Variation of k and the percentage removal of phenol with the initial phenol concentration. Dose of irradiation: 2.25 kGy.

[Phenol] mmol L ⁻¹	%R	($\mu\text{mol J}^{-1}$)
0.1	99.32	0.044
0.4	86.96	0.154
0.8	64.55	0.230
1.2	45.32	0.241
1.8	34.13	2.773

The effect of the initial phenol concentration

To assess the effect of initial phenol concentration on its degradation, various initial phenol solutions of concentrations 0.1, 0.4, 0.8, 1.2 and 1.8 mM at near neutral pH, were irradiated at the same dose rate of 9 kGy/hr. As it is depicted in Fig. 5 and Table 6, the degradation of phenol decreases with increasing initial phenol concentration and was found to follow first order kinetics. The absorbed dose required to remove 90%, of the initial phenol concentration was computed using the following equation

Table 6: Dose and kinetic parameters obtained for the radiation induced degradation of phenol, pH = 6.6, dose rate: 9 kGy hr⁻¹.

(mM)	(kGy)	(kGy ⁻¹)
0.1	1.58	1.453
0.4	2.54	0.906
0.8	3.24	0.710
1.2	4.31	0.534
1.8	5.04	0.456

The experimental values of k obtained from equation 29 were fit into the power function of the initial concentration with non linear least-squares method with the two parameters α and β as adjustable parameters. The values providing the best fit are 0.600 and -0.401 respectively with a coefficient of correlation $R^2 = 0.9844$. The decrease of the removal efficiency of phenol with increasing its initial concentration is probably due to the increase in the concentration of the intermediates by-products which compete with the phenol for the radiation induced free

radicals OH[•] available in solution.

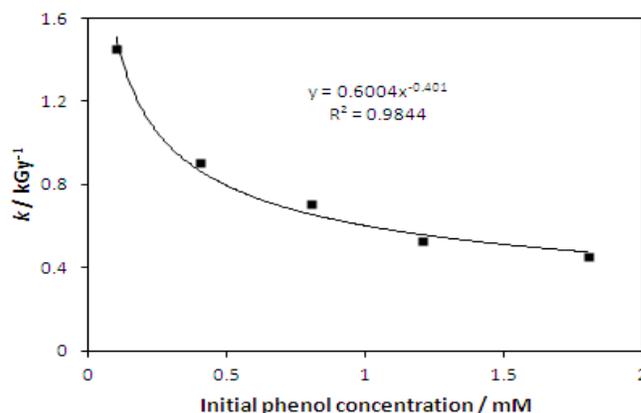
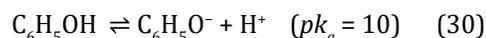


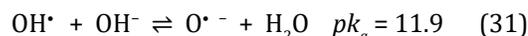
Figure 5: Initial phenol concentration vs. k profile for the radiation removal of 90% of initial phenol concentration: pH = 6.5, dose rate: 9 kGy hr⁻¹.

pH influence on the phenol degradation

The G -values of the transient species produced when irradiating water, the equilibrium OH[•] / O^{•-} and the degree of ionization of the phenol are all depending on the pH of the solution. Fig. 6 shows that the percentage degradation of phenol is higher at acidic than at alkaline pH. The higher rate of degradation was obtained at near neutral pH. These results are in agreement with some previous studies [21]. This pH dependence is probably related to the partially deprotonation of the hydroxyl group of the phenol in alkaline solution to form its conjugate base phenoxide ion [22]:



and the hydroxyl radical abstracts hydrogen atom from the hydroxide ion to form the oxyl anion radical O^{•-} [11]



Being nucleophilic species the O^{•-} is less prone to attack the electron rich aromatic ring due to their lower redox potential vs SHE (1.73 V) compared to that of hydroxyl radical (2.73 V) [23]

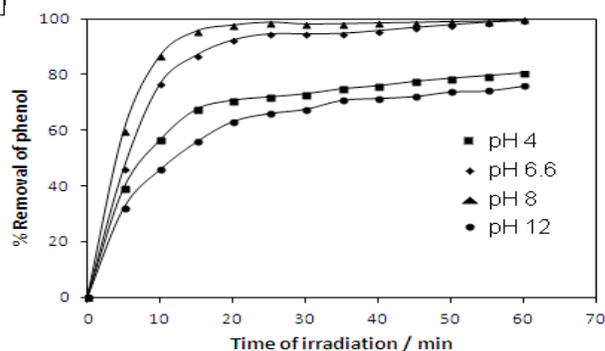


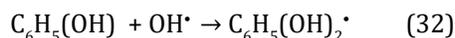
Figure 6: Influence of pH initial concentration on the percentage deg-

radiation of phenol. Initial phenol concentration: 0.40 mM, dose rate: 9 kGy/hr.

Mechanism of phenol degradation

Fig. 7 shows the formation and degradation of the three major by-products catechol, hydroquinone and *p*-benzoquinone. Being particularly unstable, [24], the *o*-benzoquinone was not detected in our experiments. Similar byproducts were also observed by some authors [25 - 27] using other advanced oxidation processes. This demonstrates that the very strong and non-selective electrophile free radical OH^\bullet [28] attacks the *ortho*-position and the *para*-position of the phenol ring much faster than it will at other positions.

The $-\text{OH}$ group attached to the phenol through the sp^2 hybridized orbital of carbon atom, makes this aromatic compound highly reactive toward electrophilic addition because one of the oxygen lone pairs in the $-\text{OH}$ group contributes to the electron density of the delocalized electron ring. Pulse radiolysis studies of the aqueous phenol solution have shown that the initial products formed when OH^\bullet radical reacts with phenol are the OH -adducts *ortho*-dihydroxycyclohexadienyl and *para*-dihydroxycyclohexadienyl transient intermediates [29]:



This initial phenolic ring hydroxylation is in good agreement with the theoretical work done by Wu et al. [30] and Kiliç and his co-workers [31] who showed that the activation energies are in the order $E_{ortho} < E_{para} < E_{meta}$ which favors the *ortho*- and *para*- addition over the *meta*- one. The *para*-dihydroxycyclohexadienyl and *ortho*-dihydroxycyclohexadienyl transient intermediates are then oxidized by either molecular oxygen O_2 present in the solution (route 1 of Fig. 8) to yield hydroquinone and catechol, respectively with splitting off HO_2^\bullet radicals.



or by OH^\bullet (route 2 of Fig. 8) to yield again hydroquinone and catechol

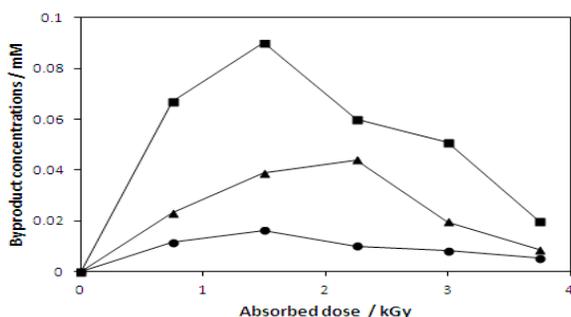


Figure 7: Formation and degradation of phenol byproducts during

the radiation induced phenol oxidation of 0.4 mM, at dose rate 9 kGy/hr. (■) catechol, (▲) *p*-benzoquinone, (●) hydroquinone.

Hydroquinone and catechol were also subsequently oxidized either by molecular oxygen O_2 or by free radical OH^\bullet to *p*-benzoquinone and the unstable *o*-benzoquinone respectively [32] (Fig. 8). It has also been reported [33] that, depending on the pH of the solution, the hydroperoxyl free radical HO_2^\bullet and its conjugate base superoxide radical $\text{O}_2^{\bullet-}$, although they are much less reactive with phenol than OH^\bullet , can further oxidize the hydroquinone and catechol to *p*-benzoquinone and *o*-benzoquinone respectively.

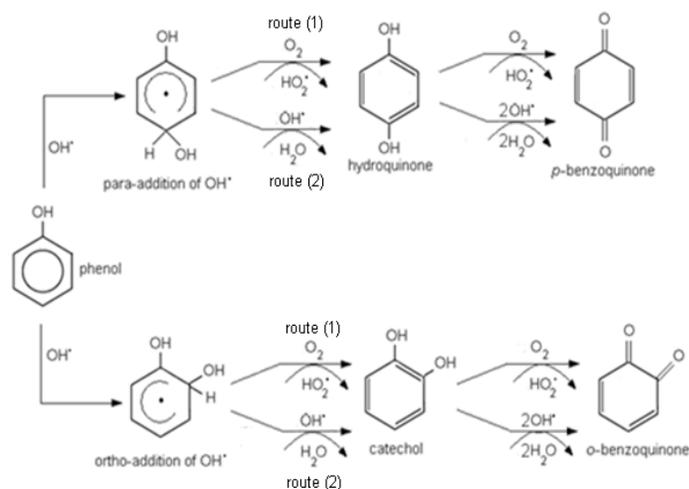


Figure 8: Reaction pathways for the radiation induced degradation of phenol.

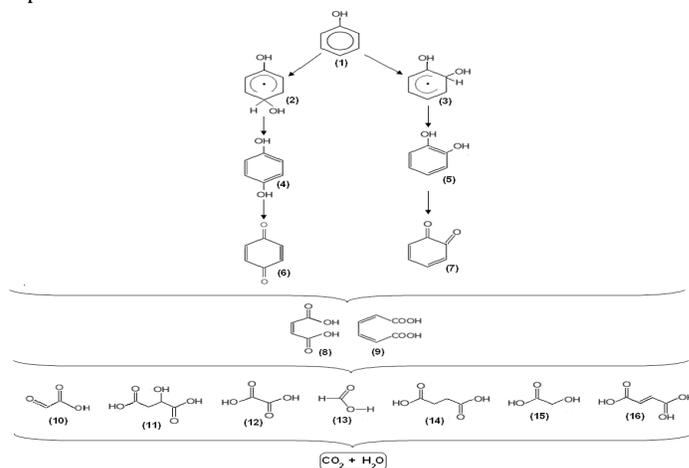


Figure 9: Proposed and simplified radiation induced degradation pathways of phenol: (1) phenol, (2) *p*-, (3) *o*-, (4) hydroquinone, (5) catechol, (6) *p*-benzoquinone, (7) *o*-benzoquinone, (8) maleic acid, (9) muconic acid, (10) glyoxylic acid, (11) malic acid, (12) oxalic acid, (13) formic acid, (14) succinic acid, (15) glycolic acid, (16) fumaric acid.

These primary byproducts present maxima where their subsequent degradation starts by aromatic ring opening and C–C, C=C, C–O and C–H bond cleavages. This leads to numerous unsaturated carboxylic acids, as shown in Fig. 9, detected in traces and resulting in a slight decrease in the solution pH. They were identified as: maleic, fumaric, succinic, glyoxylic, oxalic, formic, acetic, muconic and malonic acids. These findings confirm the results of some other authors [34,35].

Conclusions

This work showed that the hydroxyl free radical OH[•] initiates the degradation of aqueous phenol. This degradation depends on the absorbed dose and the pH of the solution and proceeds in three sequences

Phenol → OH-phenol adduct → ring products → aliphatic acids

The initially high yield of hydroquinone and catechol supports the evidence that OH[•] radical attacks the *ortho*- and *para*- position of phenol. The molecular oxygen present in solution plays a key role in this radiation induced degradation of phenol as it degrades the OH-phenol adduct to catechol and hydroquinone and further oxidizes these latter into *o*-benzoquinone and *p*-benzoquinone respectively. The highest radiation induced degradation was found at near neutral pH and alkaline environment is less prone to induce phenol degradation. Oxidation of these byproducts leads to a series of potentially less harmful aliphatic acids which do not need further mitigation.

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