



Gamma irradiation-induced complete degradation and mineralization of phenol in aqueous solution: Effects of reagent



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HIGHLIGHTS

- Ionizing radiation effectively mineralizes phenol in aqueous solution.
- Radiolytic system improves when O_3 , H_2O_2 , N_2O , O_2 , or $S_2O_8^{2-}$ is combined with γ -rays.
- Radiation chemical yield, dose constant, and dose for 90% degradation are discussed.
- Removal/mineralization yields increase with initial concentration of H_2O_2 or $S_2O_8^{2-}$.
- Initial pH and inorganic salts have an impact on phenol degradation.

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ABSTRACT

This study aims to gain new insight into phenol degradation and mineralization in aqueous solution using ionizing radiation to control its radiolytic elimination under various experimental conditions and to present the different radical reactions involved in water radiolysis. The most obvious finding of this study is that the combination of a reagent, i.e., O_3 , H_2O_2 , N_2O , O_2 , or $S_2O_8^{2-}$, with γ -rays effectively enhances the radiolytic system for phenol degradation or mineralization. Radiolytic yield is higher with H_2O_2 than with $S_2O_8^{2-}$. For the γ -ray/free O_2 , γ -ray/ H_2O_2 , γ -ray/ $S_2O_8^{2-}$, γ -ray/ N_2O , and γ -ray/ N_2 systems, the absorbed doses for 90% phenol elimination are 1.7, 0.85, 1.65, 1.2, and 6.4 kGy, respectively; in contrast, phenol can be decomposed totally and directly via reaction with molecular ozone. The lowest dose constant for phenol removal is determined for γ -ray/ HCO_3^- . 89% of mineralization is reached for an absorbed dose of 10 kGy with a γ -ray/ $S_2O_8^{2-}$ combination.

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1. Introduction

Since the 1970s, ionizing radiation has been considered as a means for treating aqueous effluents [1]. Across many fields, increasing attention has been paid to non-power applications of nuclear energy. Ionizing radiation is being explored for green environmental remediation e.g., the treatment of air pollutants [2], effluents from the textile dyeing industry [3], industrial wastewater [4,5], and municipal wastewater and sewage sludge [6–8] and for power plant clean-up [9].

High-energy radiation produced by γ -rays or electron beam accelerators is considered a unique advanced oxidation process (AOP) technology owing to the simultaneous formation of mainly approximately amounts of highly reactive oxidizing species

(hydroxyl radicals, $\bullet OH$; $E^\circ = 1.9V$; [10]) and reducing species (hydrated electron, e_{aq}^-) in aqueous solutions (Eq. (1), Table 1) and the indirect effect of this energy on a moderate concentration of solute ($\leq 0.1 M$) present in aqueous solution [11,12]. Other advantages of this technology are that it can be effectively used at room temperature and often does not require the presence of unsafe chemical additives.

The high-energy radiation absorbed by water molecules effectively leads to the phenomenon of water radiolysis (Eq. (1), Table 1). Usually, e_{aq}^- and H atoms are scavenged rapidly by oxygen (Eqs. (11) and (13), Table 1). Many studies have shown that the combination of hydrogen peroxide (H_2O_2) and persulfate anions ($S_2O_8^{2-}$) dissolved in aqueous solution with high-energy radiation greatly enhances process efficiency [13–16]. Alkhuraji and Leitner [13] reported that the addition of $S_2O_8^{2-}$ or H_2O_2 can greatly promote the removal efficiency of 2-naphthalenesulfonate during electron beam irradiation. Similar results have demonstrated the capability of this combination to increase the efficiency of degradation

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Table 1
Main reactions and rate constants for pure water radiolysis [25,26].

Reaction No.	Reaction	k (M ⁻¹ s ⁻¹)
(Eq. 1)	H ₂ O $\xrightarrow{\gamma}$ •OH, e _{aq} ⁻ , H•, H ₃ O ⁺ , H ₂ , H ₂ O ₂	
G-value (species/100 eV)	2.7, 2.6, 0.6, 2.6, 0.45, 0.7	
(Eq. 2)	•OH + •OH → H ₂ O ₂	5.5 × 10 ⁹
(Eq. 3)	•OH + H ₂ O ₂ → HO ₂ •	2.7 × 10 ⁷
(Eq. 4)	•OH + O ₂ ⁻ → O ₂ + OH ⁻	8.0 × 10 ⁹
(Eq. 5)	•OH + HO ₂ • → H ₂ O + O ₂	6.0 × 10 ⁹
(Eq. 6)	HO ₂ • + HO ₂ • → O ₂ + H ₂ O ₂	8.3 × 10 ⁵
(Eq. 7)	HO ₂ • + O ₂ ⁻ → O ₂ + H ₂ O ₂ + OH ⁻	9.7 × 10 ⁷
(Eq. 8)	HO ₂ • + O ₂ ⁻ + H ⁺ pka = 4.8	
(Eq. 9)	•OH + •OH → H ₂ O pka = 11.9	
(Eq. 10)	H• + H• → H ₂	7.8 × 10 ⁹
(Eq. 11)	H• + O ₂ → HO ₂ •	2.1 × 10 ¹⁰
(Eq. 12)	H• + O ₂ ⁻ → HO ₂ •	4.5 × 10 ¹⁰
(Eq. 13)	e _{aq} ⁻ + O ₂ → O ₂ ⁻	1.9 × 10 ¹⁰
(Eq. 14)	e _{aq} ⁻ + •OH → OH ⁻	3.0 × 10 ¹⁰
(Eq. 15)	e _{aq} ⁻ + H ₂ O ₂ → •OH + OH ⁻	1.1 × 10 ¹⁰
(Eq. 16)	e _{aq} ⁻ + H ⁺ → H•	2.3 × 10 ¹⁰
(Eq. 17)	e _{aq} ⁻ + O ₂ ⁻ /HO ₂ • → O ₂ ²⁻ /HO ₂ ²⁻	1.3 × 10 ¹⁰

or mineralization of hazardous organic compounds, e.g., pharmaceutical and endocrine disruptors [17–19], carboxylic acid [14,20], phenol [15,21], pesticides [22], refractory compounds [23], and hydrophilic linear polymers [24]. The e_{aq}⁻ formed during water radiolysis reacts rapidly with S₂O₈²⁻ or H₂O₂ to generate the sulfate radical (SO₄^{•-}, E⁰ = 2.43 V; [10]) or to increase the amount of •OH radical, respectively (Eqs. (15) and (31)). In the same manner, there is interest in combining high-energy radiation with catalysts or oxidants, such as TiO₂, N₂O, or O₃, in order to improve the efficiency and reduce the absorbed dose needed to eliminate the target pollutants.

Phenol (known as carbolic or phenic acid; [27]) is a phenolic compound widely used for both industrial and domestic purposes. It was one of the first compounds recorded on the list of priority organic pollutants by the US Environmental Protection Agency (US EPA) [28]. Phenol and its derivatives were found to be refractory organic pollutants [27]. US EPA prescribed a phenol discharge limit of less than 1 mg/L in wastewater [29], whereas the European Community Directive specified a legal tolerance level of 0.5 µg/L for some phenolic compounds in water intended for human consumption [30]. Worldwide, phenol is produced at a rate of about 6 million tons/year, with a highly significant increasing production trend [27]. Due to its wide range of industrial applications and high solubility, the presence of phenol in certain effluents has been demonstrated, leading to negative ecosystem impacts [27]. Many studies have been performed for eliminating phenol in aqueous media using AOPs. Chitose and co-workers [31] found that the energy of the ionizing radiation (γ-ray and electron beam) needed for removing phenol was much lower than that of UV/TiO₂. Additionally, the degradation of phenol by ionizing radiation was more efficient than the ozonation process [21]. The degradation of phenol was more effective when TiO₂ was combined with UV [32]. Comparisons of different AOPs for phenol degradation were investigated by Esplugas et al. [33], Beltrán et al. [34], and Suzuki et al. [35].

This study contributes to the existing literature regarding the irradiation of aqueous solutions of phenol (C₆H₆O) under various experimental conditions. Also, our study summarizes all possible radiolytic reactions that may occur during water radiolysis with or without solute. The data obtained may serve as baseline information for the water radiolysis of phenol pollutants.

2. Experimental

2.1. Reagents and chemicals

All chemical reagents used in this study were of high-purity analytical grade and used without any further purification.

Phenol (water solubility at room temperature = 9.3 g/100 mL [27]) was selected as the model industrial organic pollutant for this study; this was supplied by Merck (≥99%).

2.2. Solution preparation and experimental setup

Aqueous solutions of phenol with initial concentration of 200 ± 11 µM were prepared by diluting a standard 1 mM phenol solution in deionized water (Milli-Q device, Elix Technology inside Integral 5 Millipore) and placed in 40 mL or 2 mL vials having airtight caps with Teflon-based silicon septa. The prepared solutions were irradiated in these vials over the range 0.1–50 kGy. Measurements were performed immediately after the irradiation. Irradiation of samples was conducted using Co-60 Gamma Cell 220 from MDS-Nordion, Canada. The dose rate was 4.1 kGy/h. The initial solution concentration of dissolved oxygen was 7.3 ± 0.9 mg/L and the initial pH was 6.2 ± 0.4. For certain experiments, solutions of phenol to be irradiated were bubbled with nitrogen (N₂), ozone (O₃), or nitrous oxide (N₂O). Ozone was generated from pure oxygen dried by a Longevity (Canada resources) model ozone generator, with an ozone output of 10 g/h assumed for each dose. The phenol solution was ozonized in a 250 mL cylindrical Pyrex reactor by bubbling ozone inside the solution to be irradiated through a sintered glass filter with a pore size of 50–80 µm at a fixed pure oxygen flow rate of 0.25 L/min. The experiments and analysis were performed at room temperature without adjustment. Pressure was not controlled. To insure the reliability and reproducibility, some experiments were performed twice.

2.3. Analytical methods

The concentrations of phenol were determined by ultra-performance liquid chromatography (UPLC-Nexera X2, SHIMADZU). UV detection was undertaken at 211 nm. The column was a RaptorTM ARC-18 (5 µm, 150 × 4.6 mm; Restek), the flow rate was 1 mL/min, the injection volume was 50 µL, and the mobile phase contained 20% methanol and 80% ultra-pure water acidified with 0.1% orthophosphoric acid. The TOC content was determined using a Shimadzu TOC-L analyzer connected to an ASI-L auto-sampler system. Dissolved oxygen and pH were measured by a Cello 325 oxygen probe (WTW model 740) and a Sentix 81 pH electrode, respectively.

3. Results and discussion

3.1. Gamma irradiation of phenol solutions

Gamma irradiation of pure water or dilute aqueous solutions leads to the primary species •OH, e_{aq}⁻, H•, H₃O⁺, H₂, and H₂O₂ (Eq. (1), Table 1). Their G_{values}, together with the radical reactions following pure water irradiation and their k , are indicated in Table 1. Fig. 1a shows the effect of initial concentration on phenol degradation (γ-ray/free O₂) as a function of absorbed dose. The residual concentrations of phenol dramatically decrease with the absorbed dose.

For the concentrations of 100, 200, and 300 µM, 90% phenol degradation is found at absorbed doses of 0.7, 1.7, and 3 kGy, respectively. The three main species that could degrade phenol are •OH, e_{aq}⁻, and H• radicals (Table 2). However, comparing the rate constants of their reactions with phenol suggests that the highly oxidizing and non-selective electrophilic •OH radical, which undergoes hydroxylation of phenol leading to its destruction. The elimination rate of phenol decreases with increasing initial concentration. This decrease is effectively due to an increase in the concentration of organic carbon of the phenol and its by-products,

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