



Influence of persulfate ions on the removal of phenol in aqueous solution using electron beam irradiation

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ABSTRACT

The removal of phenol ($C_0 = 100 \mu\text{M}$) during electron beam irradiation was studied in pure water and in the presence of HCO_3^- and Br^- ions. It was found that the introduction of $\text{S}_2\text{O}_8^{2-}$ ions (1 mM), by generating $\text{SO}_4^{\bullet-}$ radicals increases the radiation yield of phenol removal. 90% removal of phenol was obtained with radiation doses 600 and 1200 Gy with and without $\text{S}_2\text{O}_8^{2-}$ ions respectively. This system induced smaller oxygen consumption with smaller concentration of catechol and hydroquinone found in the solution. HCO_3^- and Br^- have an inhibiting effect in the presence as in the absence of $\text{S}_2\text{O}_8^{2-}$. In most cases, the introduction of $\text{S}_2\text{O}_8^{2-}$ ions in water radiolysis system can advantageously increase the yield of organic compounds removal by oxidation.

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1. Introduction

With the aim of degrading a wide variety of organic compounds in aqueous effluents, various free radical based processes were developed at the end of last century. These processes that use the strongly oxidizing hydroxyl radical (OH^\bullet) include $\text{H}_2\text{O}_2/\text{UV}$, $\text{H}_2\text{O}_2/\text{Fe}^{\text{II}}$, $\text{H}_2\text{O}_2/\text{O}_3$, O_3 , TiO_2/UV , sonolysis or electron beam technologies. The chemistry of primary interest in the high-energy electron beam process is the fact that ionizing radiation produces both oxidizing and reducing species simultaneously in approximately the same concentration. One of the many applications of the electron beam process is the treatment of aqueous effluents containing organic pollutants [1–4]. The degradation of organic pollutants occurs under the action of reactive species (OH^\bullet , e_{aq}^- , H^\bullet) formed during the transfer of energy from accelerated electrons in the aqueous phase (Eq. (A.1), Table 1) [5,6]. The radical species thus formed by the radiolysis of water can initiate oxidation reactions of compounds dissolved in water. The treatment of aqueous solutions by electron beam irradiation can decrease the concentration of certain pollutants, provided that the energy absorbed (dose) is sufficient. To improve the efficiency of pollutant removal or decrease the radiation dose applied, a number of

published papers propose the addition of a catalyst [3,7–10] or reactive oxidants [11–13] before treatment with the electron beam. The introduction of ozone, which leads to increased production of OH^\bullet radicals has also been shown to be particularly useful [13]. In the present study, the authors will look at the effect of another oxidant: persulfate. Radiolysis studies of aqueous solutions of persulfate ions [14–16] reported the formation of the sulfate radical ($\text{SO}_4^{\bullet-}$) by the direct action of the solvated electron (e_{aq}^-) on the persulfate (Eq. (B.1) – Table 2). This radical is an oxidant reactive towards many organic and inorganic compounds. Its redox potential of 2.43 V [17], being close to that of the hydroxyl radical OH^\bullet ($E = 2.80 \text{ V}$), ranks it among the most oxidizing species.

In this paper, wherein the system combining an electron beam and the persulfate is investigated, the degradation of phenol was studied as a model organic pollutant. The action of the hydroxyl radical on this compound, widely discussed in the literature and including some studies relating to radiolytic processes [1,3,18–20], will be linked to the contribution of sulfate radicals.

2. Materials and methods

2.1. Electron beam irradiation

The irradiation experiments were conducted using a vertical electron beam from a Van de Graaff accelerator (Vivirad S.A.). The maximum electron energy was 3 MeV. Depending on doses applied, the beam current was fixed at 25 or 50 μA . In the bench scale device

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Table 1
Main reactions and rate constants for pure water radiolysis.

Reaction number	Reaction	k ($M^{-1} s^{-1}$)	Ref.
(A.1)	$H_2O \rightsquigarrow OH^\bullet, e_{aq}^-, H^\bullet, H_3O^+, H_2, H_2O_2$		[6]
	G-value (species/100 eV)	2.7; 2.6; 0.6; 2.6; 0.45; 0.7	
(A.2)	$e_{aq}^- + O_2 \rightarrow O_2^{\bullet-}$	1.9×10^{10}	[6,22]
(A.3)	$e_{aq}^- + OH^\bullet \rightarrow OH^-$	3.0×10^{10}	[6,22]
(A.4)	$e_{aq}^- + H_2O_2 \rightarrow OH^\bullet + OH^-$	1.1×10^{10}	[6,22]
(A.5)	$e_{aq}^- + H^+ \rightarrow H^\bullet$	2.3×10^{10}	[6,22]
(A.6)	$e_{aq}^- + O_2^{\bullet-}/HO_2^\bullet \rightarrow O_2^{2-}/HO_2^{2-}$	1.3×10^{10}	[6,22]
(A.7)	$OH^\bullet + OH^\bullet \rightarrow H_2O_2$	5.5×10^9	[6,22]
(A.8)	$OH^\bullet + H_2O_2 \rightarrow HO_2^\bullet$	2.7×10^7	[6,22]
(A.9)	$OH^\bullet + O_2^{\bullet-} \rightarrow O_2 + OH^-$	8.0×10^9	[6,22]
(A.10)	$OH^\bullet + HO_2^\bullet \rightarrow H_2O + O_2$	6.0×10^9	[6,22]
(A.11)	$H^\bullet + H^\bullet \rightarrow H_2$	7.8×10^9	[6,22]
(A.12)	$H^\bullet + O_2 \rightarrow HO_2^\bullet$	2.1×10^{10}	[6,22]
(A.13)	$H^\bullet + O_2^{\bullet-} \rightarrow HO_2^\bullet$	4.5×10^{10}	[6,22]
(A.14)	$HO_2^\bullet + HO_2^\bullet \rightarrow O_2 + H_2O_2$	8.3×10^5	[6,22]
(A.15)	$HO_2^\bullet + O_2^{\bullet-} \rightarrow O_2 + H_2O_2 + OH^-$	9.7×10^7	[6,22]

Table 2
Reactions and rate constants for radiolysis persulfate aqueous solution.

Reaction number	Reaction	k ($M^{-1} s^{-1}$)	Ref.
(B.1)	$S_2O_8^{2-} + e_{aq}^- \rightarrow SO_4^{\bullet-} + SO_4^{2-}$	1.1×10^{10}	[25]
(B.2)	$S_2O_8^{2-} + OH^\bullet \rightarrow OH^- + S_2O_8^{\bullet-}$	$<1.0 \times 10^6$	[6]
(B.3)	$S_2O_8^{2-} + H^\bullet \rightarrow SO_4^{\bullet-} + SO_4^{2-} + H^+$	1.4×10^7	[28]
(B.4)	$S_2O_8^{2-} + HO_2^\bullet \rightarrow SO_4^{\bullet-} + SO_4^{2-} + O_2 + H^+$	2.2×10^4	
(B.5)	$S_2O_8^{2-} + O_2^{\bullet-} \rightarrow SO_4^{\bullet-} + SO_4^{2-} + O_2$	2.4×10^3	
(B.6)	$S_2O_8^{\bullet-} + O_2 \rightarrow O_2S_2O_8^{\bullet-}$		[37]
(B.7)	$S_2O_8^{\bullet-} \rightarrow 2SO_4^{2-}$		
(B.8)	$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + OH^\bullet$	1.4×10^7	[29]
(B.9)	$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet-}$	6.6×10^5	[30]
(B.10)	$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-}$	7.6×10^8	[30]
(B.11)	$SO_4^{\bullet-} + OH^\bullet \rightarrow HSO_4^- + (1/2)O_2$	1.0×10^{10}	[30]
(B.12)	$SO_4^{\bullet-} + H_2O_2 \rightarrow SO_4^{2-} + HO_2^\bullet + H^+$	2.0×10^7	[31]
(B.13)	$SO_4^{\bullet-} + HO_2^\bullet \rightarrow SO_4^{2-} + O_2 + H^+$	3.5×10^9	[30]
(B.14)	$SO_4^{\bullet-} + H^\bullet \rightarrow SO_4^{2-} + H^+$	1.0×10^{10}	[6,30]
(B.15)	$SO_4^{\bullet-} + O_2^{\bullet-} \rightarrow SO_4^{2-} + O_2$	3.5×10^9	[38]
(B.16)	$SO_4^{2-} + e_{aq}^- \rightarrow$	$<1.0 \times 10^6$	[32]
(B.17)	$OH^\bullet + SO_4^{2-}/HSO_4^- \rightarrow SO_4^{\bullet-} + OH^-/H_2O$	3.5×10^5	[39]
(B.18)	$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + OH^\bullet + H^+$	$360 s^{-1}$	[30,39]

of the University of Poitiers, solutions were exposed to the vertical scanned beam in a continuous flow reactor (depth: 1.5 cm, width: 3 cm, volume under the beam: 45 cm³). Doses up to 1.5 kGy were obtained by varying the flow rate from 360 to 1800 Lh⁻¹ that corresponds to a rate under the beam of between 0.2 and 1.1 m s⁻¹ respectively. Fig. 1 shows the hydraulic device developed for the routing of the solutions under the electron beam. The absorbed

dose (in gray, 1 Gy = 1 J kg⁻¹) is determined from the relation:

$$D(\text{Gy}) = \frac{\text{Beam current}(\mu\text{A}) \times \text{Voltage}(\text{MV})}{\text{Flow rate}(\text{L s}^{-1})}$$

In dilute aqueous solutions i.e. the experimental conditions of this study, the concentration of organic compounds is far smaller than the solvent. Water is present as the major compo-

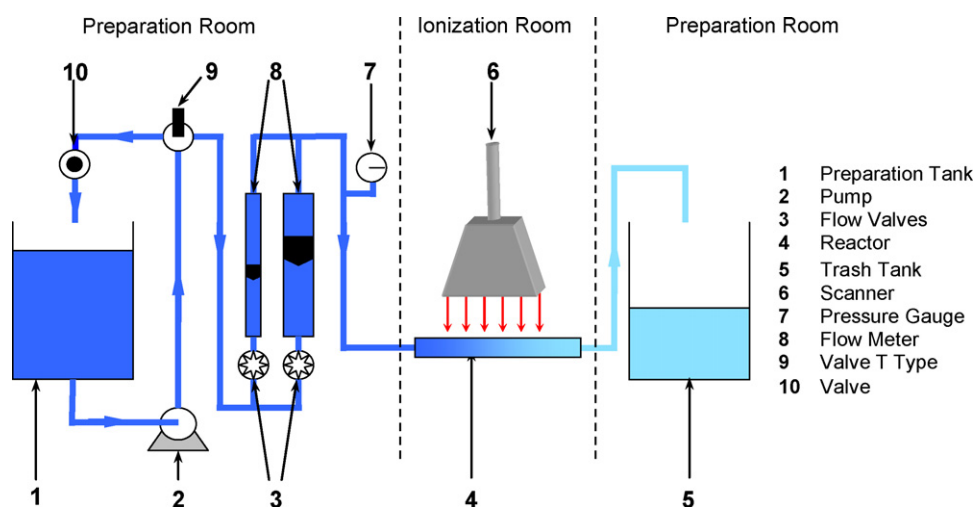


Fig. 1. Hydraulic device developed for the treatment of aqueous solutions under the electron beam.

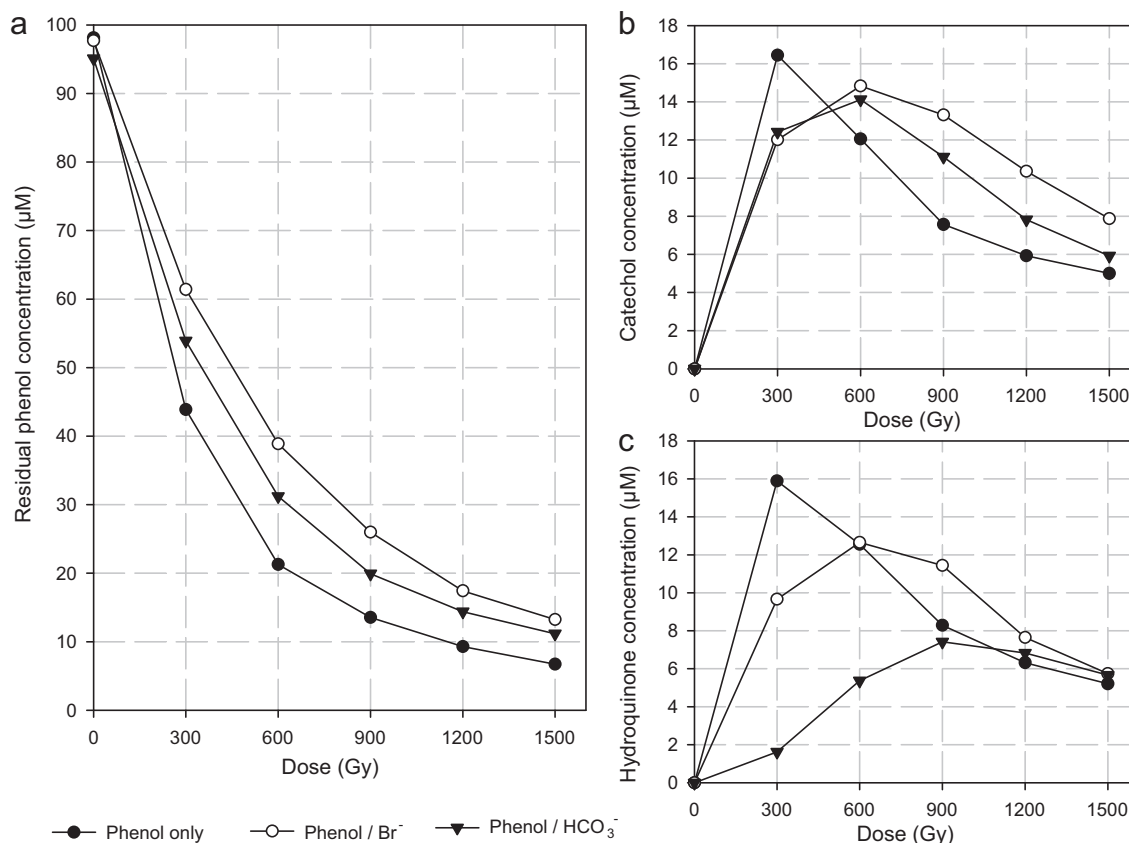


Fig. 2. Removal of phenol in aqueous solution by electron beam irradiation in presence or not of Br⁻ (0.6 mM) and HCO₃⁻ (5.0 mM).

ment, so that the radiation dose is mostly absorbed by the water molecules.

2.2. Chemicals and solution preparation

In this study all reagents were used without further purification. Phenol (C₆H₅OH, 99.5%) and sodium persulfate (Na₂S₂O₈, 98%) were obtained from Fulka Chimika. Sodium bromide (NaBr, 99%) and sodium bicarbonate (NaHCO₃, 99.7%) were purchased from Sigma.

All the solutions were prepared in deionized water which was purified with a Milli-Q device (Millipore). The initial concentration of phenol in the solutions before irradiation was 100 µM. Other compounds (Na₂S₂O₈, NaBr and/or NaHCO₃) were introduced into the phenol solution and stirred for 15 min before the irradiation. In all the experiments, the solutions were initially saturated with air before irradiation. The radiation doses were applied at uncontrolled temperatures falling within the range 15–25 °C.

2.3. Analysis

The concentration of phenol and some of the by-products was determined by high performance liquid chromatography (HPLC) with an Interchrom column C₁₈ Uptisphere. The HPLC system is equipped with a gradient pump (Waters 600), an auto sampler (Waters 717) and a PDA detector (Waters PDA 996 Detector). The elution was performed with H₂O/Methanol (65/35, v/v) acidified by 0.1% (v/v) H₃PO₄. The flow rate was 1 ml min⁻¹ and the injection volume was 100 µL. The wavelength of the UV detection was 215 nm for phenol.

Hydrogen peroxide (H₂O₂) was analysed by the TiCl₄ colorimetric method [21]. Dissolved oxygen was measured before and after irradiation by a WTW Inolab oximeter model 740.

3. Results and discussion

3.1. Irradiation of aqueous solutions of phenol

In pure water, entities formed by the radiolysis of water (Eq. (A.1), Table 1) initiate many reactions with compounds present or formed (O₂, H⁺, and H₂O₂). Recombination reactions between the active species can also occur. Table 1 shows the dominant reactions of the system regarding the rate constants and the concentrations in the solution.

In the presence of organic compounds in dilute solution (concentration less than 1 mol L⁻¹), the ionization of the compound is minimal compared to the radiolysis of the aqueous solvent. Accordingly, the species produced by the reaction (A.1) can react with the solute. In order to study the contribution of the reactions involved in the presence of organic compounds, the concentration of the organic molecule phenol chosen for this study has been followed. The concentration of phenol in aqueous solution (100 µM), as a function of the dose applied during the irradiation in the absence of reagents, is shown in Fig. 2a. In deionized water, from the application of the first dose, a reduction of 55.3% phenol is observed, with an overall radiolytic yield, G_{300 Gy}, equal to 0.18 µmol J⁻¹. This G-value is the same order of magnitude as the one cited in the literature. Indeed Lin et al. [1] have obtained an output value G_{500 Gy} = 0.17 µmol J⁻¹ for an initial concentration of phenol of 106 µM [1], while Pellizzari et al. [18] arrived at a value for G_{300 Gy} = 0.205 µmol J⁻¹ for an initial phenol concentration of 160 µM. A removal of 90% of phenol was obtained for an applied dose of 1200 Gy. Three main active entities (H[•], e_{aq}⁻, OH[•]) generated in the radiolysis of water can be responsible for the degradation of phenol in solution (Eqs. (C.1)–(C.8) shown in Table 3).

Table 3Reactions and rate constants for degradation of phenol and the reactions with HCO_3^- and Br^- .

Reaction number	Reaction	k ($\text{M}^{-1} \text{s}^{-1}$)	Ref.
(C.1)	$\text{C}_6\text{H}_5\text{OH} + \text{OH}^* \rightarrow \text{CAT} + \text{HYD}$	1.8×10^{10}	[3,6,22]
(C.2)	$\text{C}_6\text{H}_5\text{OH} + \text{OH}^* \rightarrow [\text{C}_6\text{H}_5(\text{OH})_2]^*$	1.4×10^{10}	[3,6,22]
(C.3)	$\text{C}_6\text{H}_5\text{OH} + e_{\text{aq}}^- \rightarrow \text{products}$	3.0×10^7	[3,6,22]
(C.4)	$\text{CAT} + \text{OH}^* \rightarrow \text{products (trihydroxybenzene)}$	1.1×10^{10}	[6]
(C.5)	$\text{HYD} + \text{OH}^* \rightarrow \text{products (trihydroxybenzene)}$	2.1×10^{10}	[6]
(C.6)	$[\text{C}_6\text{H}_5(\text{OH})_2]^* + \text{O}_2 \rightarrow \text{C}_6\text{H}_4(\text{OH})_2 + \text{HO}_2^*$		[24]
(C.7)	$\text{Trihydroxybenzene} + \text{OH}^* \rightarrow \text{by-products}$	1.0×10^{10}	[6,33]
(C.8)	$\text{C}_6\text{H}_5\text{OH} + \text{H}^* \rightarrow \text{C}_6\text{H}_5(\text{OH})\text{H}^*$	1.7×10^9	[3,6,22]
(C.9)	$\text{C}_6\text{H}_5\text{OH} + \text{SO}_4^{\cdot-} \rightarrow \text{products}$	8.8×10^9	[34]
(C.10)	$\text{HCO}_3^- + \text{OH}^* \rightarrow \text{CO}_3^{\cdot-} + \text{H}_2\text{O}$	8.5×10^6	[6]
(C.11)	$\text{HCO}_3^- + e_{\text{aq}}^- \rightarrow \text{products}$	1.0×10^6	[22]
(C.12)	$\text{HCO}_3^- + \text{SO}_4^{\cdot-} \rightarrow \text{SO}_4^{2-} + \text{CO}_3^{\cdot-} + \text{H}^*$	2.8×10^6	[35]
(C.13)	$\text{Br}^- + \text{OH}^* \rightarrow \text{BrOH}^-$	1.1×10^{10}	[6]
(C.14)	$\text{Br}^- + \text{SO}_4^{\cdot-} \rightarrow \text{SO}_4^{2-} + \text{Br}^*$	3.5×10^9	[36]

The rate constants for the reaction of phenol with OH^* and e_{aq}^- at pH 7, are respectively $1.8\text{--}6.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $2.7\text{--}3.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ [1,3,6,22]. The rate constant for the reaction of H^* with phenol cited in the literature is $1.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ [1,3,6,22]. Under conditions of oxygen concentration close to equilibrium with atmospheric oxygen, it is generally accepted that, with regard to high kinetics of solvated electrons and hydrogen atoms with oxygen ($k = 1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $k = 2.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ respectively – Eqs. (A.2) and (A.12) in Table 1), these reactions are favored. They lead to the formation of superoxide and hydroperoxy radicals which are not very reactive with phenol. The radical OH^* is thus the entity responsible for the decomposition of phenol in the radiolysis of an aqueous solution [1,3,18,23]. The reactivity of phenol and OH^* radicals in an oxygenated medium has been discussed at length in the literature. OH^* radicals will induce the degradation of phenol and that of its by-products, as is indicated by Eqs. (C.1)–(C.7) in Table 3 [6,22]. In a first step where most of the phenol remains in solution when low doses (<600 Gy) are applied, the OH^* radical attacks especially the phenol on the ortho and para positioned carbons to form catechol (CAT) and hydroquinone (HYD). Fig. 2b and c shows the catechol and hydroquinone concentrations measured during irradiation of the phenol solution. For a dose of 300 Gy, these two by-products are dominant and their concentration reaches a maximum. For the highest dose absorbed (>600 Gy), catechol and hydroquinone then compete with phenol leading to the formation of trihydroxybenzene. Finally, the reaction is marked by the opening of the aromatic ring at high doses, leading to the formation of aldehydes and carboxylic acids (glyoxal and formic acid) [1,23]. In parallel to these oxidation reactions, a weak pH decrease is observed (from pH 5.5 to 4.6 for a radiation dose value of 600 Gy).

3.1.1. The influence of bicarbonate and bromide ions

The removal of phenol by electron beam irradiation is also possible in deionized water in the presence of HCO_3^- or Br^- ions. However, the addition of bicarbonate ions (5.0 mM) or bromide ions (0.6 mM) to the system shows an abatement of phenol which is less than that for phenol system alone (Fig. 2a). In fact, in terms of Eqs. (C.10) and (C.13) in Table 3, bicarbonates and bromides react with the hydroxyl radical. Thus there is competition between phenol and the bicarbonate (or bromide) which leads to an inhibition of the reaction between phenol and the OH^* radical. Concentrations of catechol and hydroquinone are not greatly influenced by the presence of Br^- ions and the maximum is reached for a higher dose (600 Gy). On the other hand, in the presence of HCO_3^- ions, the formation of hydroquinone is lower.

3.1.2. Variation of the physico-chemical parameters

For the three irradiated solutions (phenol alone, phenol/ HCO_3^- and phenol/ Br^-), the oxidation of phenol is accompanied by a reduction in dissolved oxygen concentration as a function of the applied dose (Fig. 3). The take up of dissolved oxygen is greater when the phenol removal is greater. During the irradiation of a solution of phenol in pure water, the total consumption of oxygen is 2.6 mol per mole of phenol eliminated for a dose of 1200 Gy, corresponding to 90% removal of phenol. It should be noted that no significant oxygen consumption was observed during the irradiation of pure water in the absence of phenol. In this case the reaction of e_{aq}^- (produced during the radiolysis of water) with the dissolved oxygen is followed by recombination reactions leading to the release of oxygen (Eqs. (A.9), (A. 10), (A.14) and (A.15) of Table 1). Oxygen consumption by the mechanisms of radical oxidation of organic compounds is very frequently observed. In the case of phenol, the action of the OH^* radical on phenol leads to the formation of the radical dihydroxycyclohexadienyl. This reacts with dissolved oxygen to form the peroxy radical [24] (Eqs. (C.2) and (C.6) of Table 3). This radical intermediate lies at the origin of the consumption of oxygen and the formation of catechol and hydroquinone. The further oxidation of these by-products also consumes oxygen.

During the experiments, the production of hydrogen peroxide was demonstrated (Fig. 4). For doses below 1000 Gy, the values of the radiolytic yield of hydrogen peroxide formation ($G_{\text{H}_2\text{O}_2}$ values between 0.12 and $0.25 \mu\text{mol J}^{-1}$) are much greater than the theoretical value resulting from the radiolysis of water ($G_{\text{H}_2\text{O}_2} = 0.7 \text{ species}/100 \text{ eV} = 0.07 \mu\text{mol J}^{-1}$ [5]). For these same doses, the yield of radiolytic production of hydrogen peroxide in the case of irradiation of the phenol solution alone is superior to the other two systems phenol/ HCO_3^- and phenol/ Br^- ($G_{300 \text{ Gy}}$ is of the order of $0.25 \mu\text{mol J}^{-1}$ for the phenol solution and of 0.18 for the phenol/ HCO_3^- and phenol/ Br^- solutions). The production of hydrogen peroxide is greater as the elimination of phenol is increased. The formation of hydrogen peroxide results from the recombination of radicals $\text{O}_2^{\cdot-}/\text{HO}_2^*$ released by organic peroxy (Eqs. (A.14) and (A.15) of Table 1, Eq. (C.6) of Table 3). The hydrogen peroxide concentration reaches a maximum and then decreases as the hydrogen peroxide competes with the phenol in reactions with active species of radiolysis.

3.2. Orientation of reactions in the presence of $\text{S}_2\text{O}_8^{2-}$ ions

The solvated electrons formed during the radiolysis of water do not participate in the degradation of phenol. The advantage of producing an active species, the sulfate radical from the reaction with this reductive entity has been discussed. In pure water, the irra-

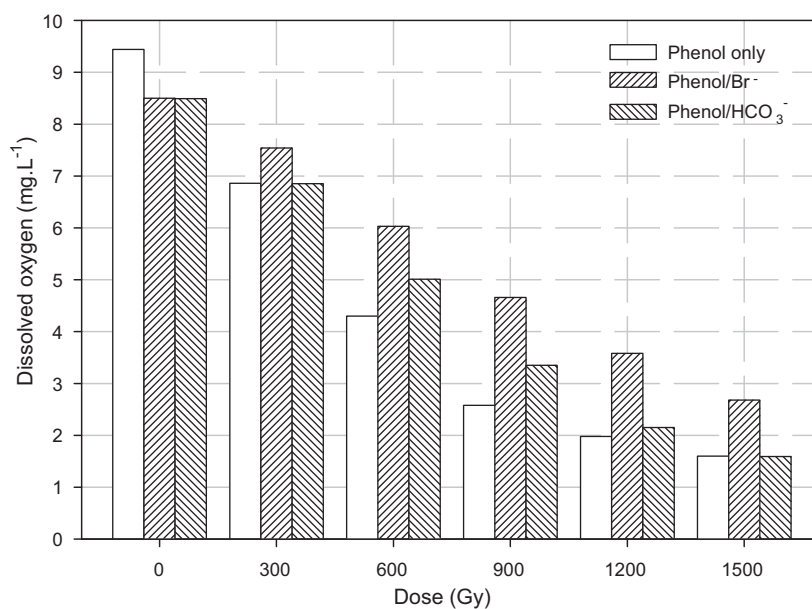


Fig. 3. Evolution of dissolved oxygen during irradiation of phenol solution (100 μM) with or without Br^- (0.6 mM) and HCO_3^- (5.0 mM).

diation of aqueous solutions of persulfate ions leads to additional reactions (Eqs. (B.1)–(B.18) presented in Table 2. In the reaction system, the sulfate radical formed from persulfate ions can react with phenol (Eq. (C.9) of Table 3). It is noted that the reaction between persulfate ions and phenol is negligible. In the presence of persulfate (1 mM) added to the phenol solution before irradiation, a significant improvement in the phenol degradation was thus observed. The radiolytic yield calculated for the dose of 300 Gy is $G_{300\text{Gy}} = 0.24 \mu\text{mol J}^{-1}$. The removal of more than 95% of phenol is observed for an applied dose of 1200 Gy (Fig. 5a). In the experimental conditions of this study, kinetic constants indicate that the concentration of $\text{S}_2\text{O}_8^{2-}$ chosen leads to the reaction of solvated electrons mainly with the $\text{S}_2\text{O}_8^{2-}$ ions (Eq. (B.1) in Table 2). In this system of reactions, it is the reducing species from the radiolysis of water (mainly solvated electrons) that react with the persulfate, leading to the formation of active radical species, especially the

sulfate radical $\text{SO}_4^{\bullet-}$ (Table 2). The latter is known to be a strong oxidant (2.43 V) and its high reactivity in relation to organic compounds ($k = 2.4\text{--}3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for benzene [25,26]). Nevertheless, the sulfate radical is less reactive and more selective than the hydroxyl radical. In a reaction mixture containing phenol and persulfate, the reaction between phenol and sulfate radicals formed, in addition to hydroxyl radicals, would explain the improvement in the degradation of phenol.

The radiolysis of a solution containing persulfate (persulfate alone or phenol/persulfate) induced a very noticeable decrease in pH (from pH 5.2 to 3.6 in the presence of phenol for a radiation dose of 300 Gy) in agreement with data of Table 2. The reaction of the persulfate with the solvated electrons, as well as all the reactions involving the sulfate radicals apart from phenol (Eqs. (B.1), (B.8), (B.9), (B.11)–(B.15) and (B.18) of Table 2), contributes to a decrease in pH. These reactions are accompanied by the release of SO_4^{2-} ions

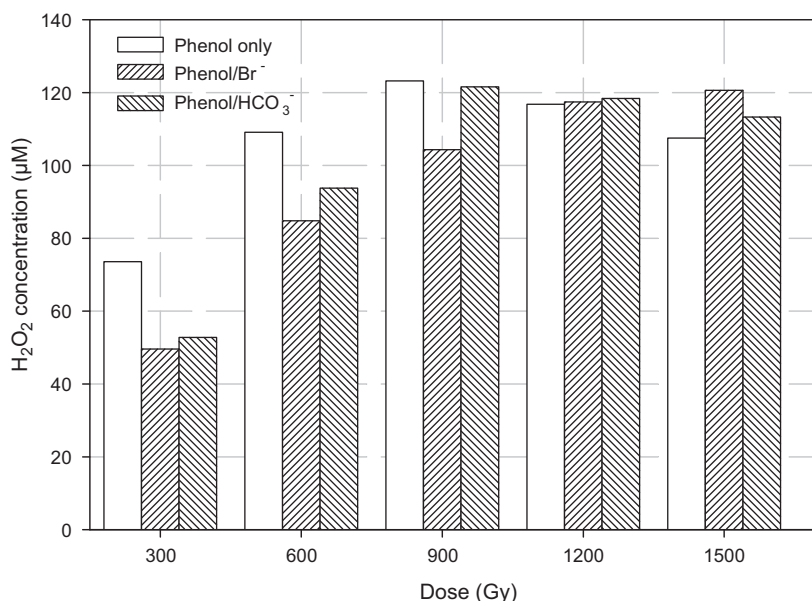


Fig. 4. Evolution of Hydrogen peroxide during irradiation of phenol solution (100 μM) with or without Br^- (0.6 mM) and HCO_3^- (5.0 mM).

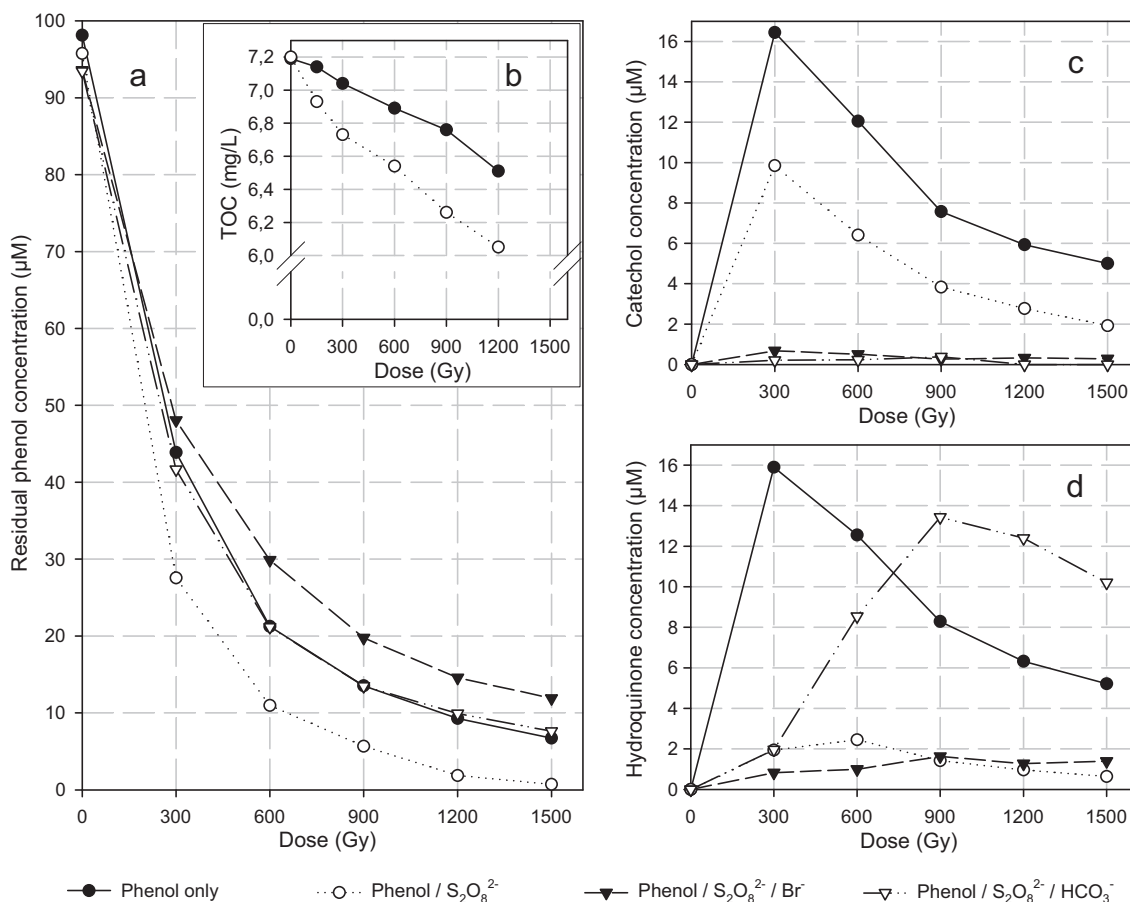


Fig. 5. Removal of phenol in aqueous solution by electron beam irradiation in presence or not of $S_2O_8^{2-}$ (1 mM), Br^- (0.6 mM) and HCO_3^- (5.0 mM).

(322 μM for a radiation dose of 300 Gy applied to a solution of phenol/persulfate) which do not constitute an undesirable element. Moreover, only weak scavenging of the OH^\bullet radicals by SO_4^{2-} ions is expected regarding the rate constant of this reaction (Eq. (B.17); $k = 3.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) and the concentration of SO_4^{2-} ions.

3.2.1. Adding of bicarbonate or bromide to the phenol/persulfate system

As in the case where persulfate ions are absent, the presence of HCO_3^- and Br^- in phenol and persulfate solutions leads to lower removal efficiencies of phenol. The degradation of phenol is still greater in the presence of $S_2O_8^{2-}$ ions. Whereas the presence of Br^- ions has no effect on the pH change observed previously, only small pH decrease occurs in presence of HCO_3^- (from pH value of 8.4 to 8.3 and 8.3 to 7.8 in absence and presence of $S_2O_8^{2-}$ ions respectively). Under these weakly basic conditions the reaction of sulfate radical with hydroxide ions (Eq. (B.8)) is not significant [27]. The HCO_3^- and Br^- ions thus do not seem to scavenge on the $SO_4^{\bullet-}$ radicals. The reaction between the $SO_4^{\bullet-}$ radicals and phenol remained significant even in the presence of Br^- ions. Given the values of rate constants indicated in the literature ($k_{SO_4^{\bullet-}/phenol} = 2.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{SO_4^{\bullet-}/Br^-} = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, Eqs. (C.9) and (C.14) respectively), the Br^- ions do not completely prevent the reaction between the $SO_4^{\bullet-}$ radicals and phenol. The rate constants of HCO_3^- and Br^- with the $SO_4^{\bullet-}$ radicals ($k = 2.8 \times 10^6$ and $3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ respectively) are lower than those involving the OH^\bullet radicals ($k = 1.0 \times 10^7$ and $1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ respectively).

As in the case of irradiation of a solution of phenol only, catechol and hydroquinone are two aromatic by-products identified during

the irradiation of a solution of phenol in the presence of persulfate. However, it should be noted that the concentrations of each of these by-products measured during the irradiation are lower under this latter condition than those measured during the irradiation of a solution containing only phenol (Fig. 5c and d). When persulfate ions are present, catechol is the major by-product. But only small concentrations are detected with bromides or bicarbonates in solutions. Hydroquinone was also found in low concentrations (<3 μM), probably due to oxidation of this compound by $S_2O_8^{2-}$ ions except in the presence of HCO_3^- ions. TOC measurements (Fig. 5b) showed that the mineralization in the radiolysis system in the presence of persulfate is greater than that obtained without persulfate (18 and 10% mineralization respectively for a radiation dose of 1200 Gy). However, the carbon mass balance with respect to the residual phenol and resulting by-products (catechol and hydroquinone) is far from being verified. In this case the competition between phenol and the two by-products relating to the active radicals (OH^\bullet and $SO_4^{\bullet-}$) certainly led to the opening of the aromatic ring. Some additional pathways should occur from the reaction with the $SO_4^{\bullet-}$ radicals.

3.2.2. Variation in dissolved oxygen and hydrogen peroxide in the radiolysis of solutions containing persulfate

As in the experiments performed on solutions not containing persulfate, the results showed a decrease in dissolved oxygen concentration in the radiolysis experiments for all solutions containing persulfate (Fig. 6). However, this decline is less compared to the results obtained for the equivalent solutions not containing persulfate. In the reaction system in the presence of persulfate ions, oxygen acts as a reagent (in the mechanism of radical oxidation

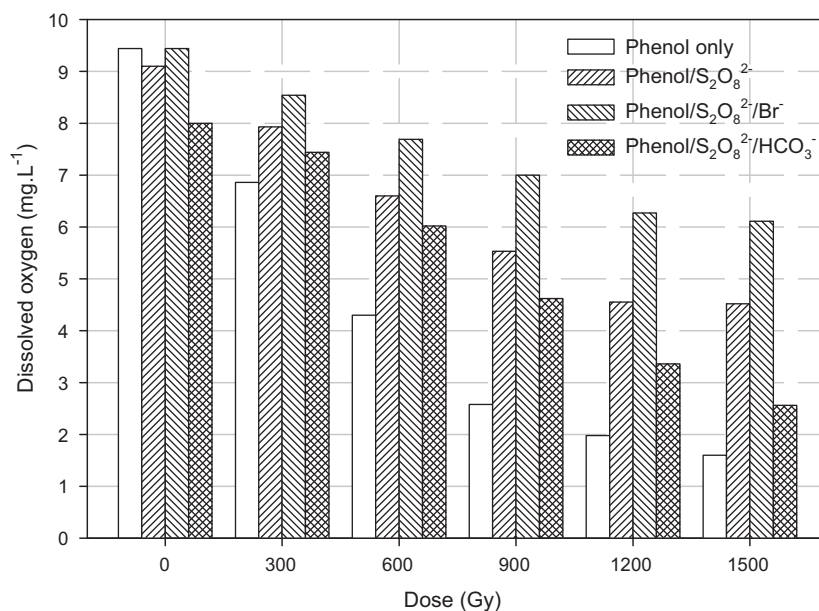


Fig. 6. Evolution of dissolved oxygen during irradiation of phenol solution (100 μM) with or without $\text{S}_2\text{O}_8^{2-}$ (1 mM), Br^- (0.6 mM) and HCO_3^- (5.0 mM).

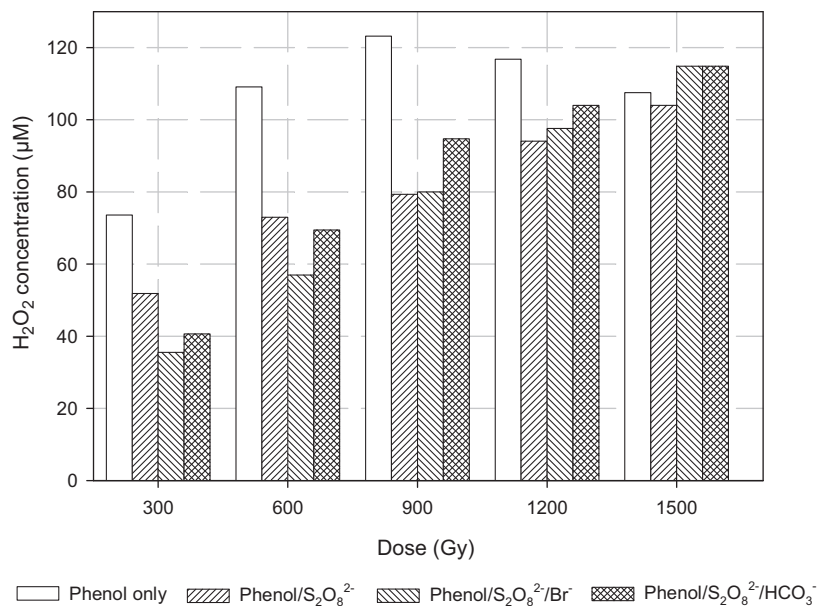


Fig. 7. Evolution of hydrogen peroxide during irradiation of phenol solution (100 μM) with or without $\text{S}_2\text{O}_8^{2-}$ (1 mM), Br^- (0.6 mM) and HCO_3^- (5.0 mM).

of organic compounds) but also as the product of the reaction (Table 2). The presence of persulfate ions increases the release of oxygen and results in a significantly weaker global decrease. Changes in the concentration of dissolved oxygen are the result of the reactions in terms of both production and consumption. Regarding the production of hydrogen peroxide, concentrations obtained during the irradiation of solutions containing persulfate are lower than the equivalent solutions without persulfate (Fig. 7). To explain these results one must consider, as stated previously, that the major routes of production of hydrogen peroxide arises from the reaction between HO_2^\bullet and $\text{O}_2^{\bullet-}$. In the presence of persulfate, in addition to the hydroxyl radical, the radical intermediate sulfate also reacts with hydroperoxyl radicals and the hydrogen peroxide formed during the radiolysis (Eqs. (B.12) and (B.13) of Table 2). This could explain the lower concentration of hydrogen peroxide measured.

4. Conclusion

The presence of $\text{S}_2\text{O}_8^{2-}$ ions in aqueous solutions under ionizing radiations can lead to the generation of the $\text{SO}_4^{\bullet-}$ radicals originated from reaction with solvated electrons in addition to the highly oxidative OH^\bullet radicals. This system enables significant improvement of organic compound oxidation like phenol with smaller oxygen consumption. Inorganic compounds such as bicarbonates and bromide ions have inhibiting effects also towards $\text{SO}_4^{\bullet-}$ radicals but to a small extent and the system remains advantageous in the presence of $\text{S}_2\text{O}_8^{2-}$ ions. When reducing species like solvated electrons are generated as in the water radiolysis systems, the power requirement can be significantly lowered by the formation of the additional $\text{SO}_4^{\bullet-}$ active species. Further investigations of the ionizing radiation/ $\text{S}_2\text{O}_8^{2-}$ combined system for aqueous solution treatment are now performed on various organic compounds.

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