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# Reaction pathway of the degradation of the *p*-hydroxybenzoic acid by sulfate radical generated by ionizing radiations

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## HIGHLIGHTS

- *p*-Hydroxybenzoic acid (HBA) is easily removed by e-beam irradiation.
- The sulfate radicals formed from persulfate induce loss of the benzoic acid skeleton.
- The dissolved oxygen concentration is a limiting parameter of the HBA degradation.
- The effect of pH is minimized in presence of persulfate.

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## ABSTRACT

The degradation of *p*-hydroxybenzoic acid (HBA) in aqueous solutions by ionizing radiation was studied. The phenolic pollutant was easily removed by the electron beam irradiation, as more than 80% of the initial 100 μM introduced was degraded for a dose of 600 Gy. It was shown that the addition of persulfate, producing the sulfate radical as additional reactive species, induced a change in the reaction pathway. LC–MS analyses were performed in order to identify the different by-products formed. In the absence of persulfate, the main by-product formed was 3,4-dihydroxybenzoic acid, while in presence of persulfate, 1,4-benzoquinone was detected and the hydroxylated by-products were not present. A reaction pathway of HBA degradation by hydroxyl and sulfate radicals was proposed from the identification of the chemical structure of the different by-products detected.

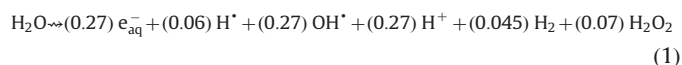
The influences of pH and dissolved oxygen were also studied. A high decline of HBA degradation was observed at pH 11 compared to pH 4.5, this decrease was minimized in the presence of persulfate. The dissolved oxygen concentration was found to be a limiting parameter of HBA degradation, however an excess of dissolved oxygen in solution did not improve the degradation to a large extent.

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## 1. Introduction

Advanced oxidation processes (AOPs) are commonly used for the treatment of refractory compounds in waters of different origins. AOPs typically involve the formation of hydroxyl radical as the reactive species; this radical is usually formed from ozone, hydrogen peroxide decomposition or ultraviolet irradiation. Among the different existing AOPs, the water treatment by ionizing radiation generates different radical species from water radiolysis. In opposition to many AOPs, ionization of water produces in the same time oxidative (OH<sup>•</sup>, HO<sub>2</sub><sup>•</sup>, H<sub>2</sub>O<sub>2</sub>) and

reductive (e<sub>aq</sub><sup>-</sup>, H<sup>•</sup>) species; hydrated electron and hydroxyl radical are the two main reactive species. The radiolysis of pure water could be described by the global equation (Eq. (1)) with yields (*G*-values=number of molecules formed or decomposed per absorbed energy unit) expressed in μmol J<sup>-1</sup> at pH 7 (Spinks and Woods, 1990).



While OH<sup>•</sup> is available for the degradation of target pollutant, e<sub>aq</sub><sup>-</sup> is in large part scavenged by dissolved oxygen in solution; the O<sub>2</sub><sup>-•</sup> radical formed from this reaction is much less reactive. Numerous applications have been described in literature, such as, the degradation of phenol (Boukari et al., 2011), pesticides (Basfar et al., 2009; Kwon et al., 2009; Liu et al., 2005), pharmaceutical compounds (Sanchez-Polo et al., 2009; Yu et al., 2008; Homlok et

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al., 2011; Zhang et al., 2011; Yu et al., 2013) or dye effluents (Vahdat et al., 2010; Zhang et al., 2005; Paul et al., 2011).

Industry or domestic activities often generate aqueous effluents containing phenolic compounds in large amounts. These organic pollutants present an inhibition character to the anaerobic digestion due to their poor biodegradability and/or toxicity for the microorganisms (Gonzalez et al., 1990); among those *p*-hydroxybenzoic acid (HBA) is typically found in waste from olive oil industry (Beltran de Heredia et al., 2001).

This study focused on the degradation of *p*-hydroxybenzoic acid which was selected as a representative compound of phenolic pollutants present in waste waters. It is considered especially toxic and refractory to common biological treatment (Creanga Manole et al., 2007). Moreover, the impact of several parameters on the ionizing radiation process was studied: persulfate addition, modification of pH and dissolved oxygen concentration. Additionally, a better understanding of the process was achieved by the identification of the by-products, thus a reaction pathway was proposed in this study.

## 2. Methods

### 2.1. Electron accelerator

Irradiation experiments were carried out with a vertical electron accelerator. The electron beam generator consisted of a 3 MeV Van de Graaff accelerator which enables the treatment of a continuous flow up to 3600 L h<sup>-1</sup>. In the bench scale device, solutions were exposed to the vertical scanned beam (2.7 MV; 99 μA) in a continuous flow reactor (depth: 1.2 cm; width 3.0 cm) (Follut and Karpel Vel Leitner, 2007). For the experiments performed, the different doses ranging from 150 to 600 Gy were obtained by modifying the flow rate of the solution i.e. the residence time under the beam. All the irradiation experiments were made at ambient temperature. A solution of ceric sulfate was periodically used as dosimeter to control the calibration of the irradiation device (Follut et al., 2007).

### 2.2. Chemicals

All solutions were prepared in deionised water provided by a MilliQ water system (TOC < 0.2 mgC L<sup>-1</sup>). *p*-hydroxybenzoic acid (Fulka), sodium persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, Aldrich), cerium sulfate (Riedel de Haën, 98%), sulfuric acid (SDS, 95%), were used as supplied. Alcian Blue (Acros Organics) was used for the persulfate analysis. Phosphoric acid (Fisher Scientific), acetic acid (Riedel de Haën, > 99%) and MeOH (Fluka, LC-MS grade) were used for HPLC analysis.

### 2.3. Analyses

The quantification of HBA (pKa=4.7; 9.4) and of the main by-products formed (1,4-benzoquinone and 3,4-di-hydroxybenzoic acid) was performed by HPLC analysis. The Waters liquid chromatograph with a photodiode array detector (Waters PDA 996) was equipped with a C<sub>18</sub> column (ModuloCart QS Uptisphere; Interchrom 250 × 4.6 mm). The elution was performed with H<sub>2</sub>O/MeOH (70/30 v/v) acidified by H<sub>3</sub>PO<sub>4</sub> (1%). The flow rate was 1 mL min<sup>-1</sup> and the injection volume was 100 μL. The identification and quantitative analysis of HBA and by-products were based on comparison of their retention times and their UV spectra with standards. The integration of areas was performed at the maximum of absorbance for each product.

The identification of by-products formed during the radiolysis of HBA solutions was performed by LC-MS analysis. A Thermo

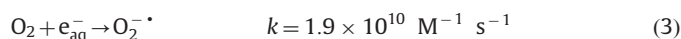
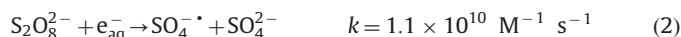
chromatographic system (pump+thermostated autosampler Surveyor) equipped with a diode array detector (Surveyor) and an ion trap mass spectrometer DECA XP Ion max was used. The column was an Uptisphere HDO C<sub>18</sub> column (3 × 250 mm) packed with 5-μm spherical particles. A H<sub>2</sub>O/MeOH mixture (85/15 v/v) acidified by acetic acid (1%) was used as the mobile phase with a flow-rate of 0.3 mL min<sup>-1</sup>. Total scan UV chromatogram (210–600 nm) were plotted. Mass spectrometry has been performed with an electrospray ionisation (ESI) in negative mode, source voltage, -5.0 kV; capillary temperature, 275 °C; nitrogen sheath gas flow rate, 17.3 L min<sup>-1</sup>. Full scanning analyses were performed by scanning *m/z* range from 50 to 250 in profile mode. MS<sup>2</sup> analysis of selected ions was performed in the ion trap; MS<sup>*n*</sup> ion isolation widths, relative activation amplitudes and activation Q<sub>s</sub> were optimised to obtain high response and stability of the base peak fragment ion.

Quantification of Total Organic Carbon was performed with a TOC thermal analyser (Shimadzu VCSH). Persulfate analysis was performed using the Alcian Blue colorimetric method developed by Villegas et al. (1963). pH and dissolved oxygen were measured with, respectively, a pH electrode Sentix 81 and an oxygen probe Cellox 325 (WTW).

## 3. Results

### 3.1. Effect of persulfate

The impact of persulfate addition on the degradation of aqueous solutions of *p*-hydroxybenzoic acid by ionizing radiation was studied. The persulfate was added to the solutions to favour the reaction of aqueous electron with persulfate (Eq. (2)) instead of its reaction with dissolved oxygen (Eq. (3)). The reaction of aqueous electron with persulfate forms the sulfate radical as an additional reactive species in solution (Eq. (2)).



In opposite to the O<sub>2</sub><sup>·-</sup> radical formed from the reaction of aqueous electron with oxygen (Eq. (3)), the sulfate radical is very reactive (E°=2.43 V (Stanbury, 1989)). It was shown in previous studies that the addition of persulfate enhanced the degradation of carboxylic acids (citric and acetic) during the treatment by ionizing radiation (Criquet and Karpel Vel Leitner, 2011a,b, 2012). Fig. 1 presents the evolution of the concentration of HBA (C<sub>0</sub>=100 μM)

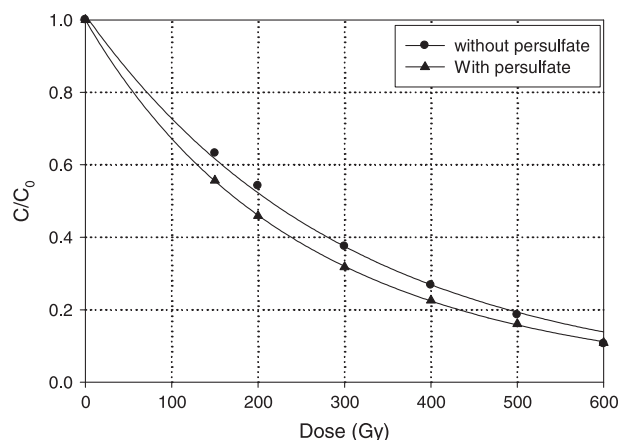


Fig. 1. Degradation of *p*-hydroxybenzoic acid and effect of persulfate addition. Without persulfate: [HBA]<sub>0</sub>=95 μM; [O<sub>2</sub>]=290 μM; pH=4.5. With persulfate: [HBA]<sub>0</sub>=100 μM; [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>]<sub>0</sub>=2000 μM; [O<sub>2</sub>]=285 μM; pH=3.8.

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