Ionizing radiation induced degradation of salicylic acid in aqueous solution

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ABSTRACT

The radiation-induced degradation of salicylic acid (SA⁻) in aqueous solutions (1.0 and 0.1 mmol dm⁻³) saturated with N_2O or air or without oxygen were studied. Irradiation was carried out using a cobalt-60 source. With a 1 mmol dm⁻³ solution saturated with N_2O a seemingly total degradation occurred at about 18 kGy, although small quantities of 2,3-dihydroxybenzoic acid, catechol and 2,5-dihydroxybenzoic acid were present at that dose at concentrations of 67, 22 and 6 μmol dm⁻³ respectively. Under air and when free oxygen, the three radiolytic products were present at 18.54 kGy while SA⁻ was destroyed only to 90% and 62%, respectively. In the case of 0.1 mmol dm⁻³ SA⁻ solutions, the acid was degraded at 3.5 kGy if the solution contained N_2O, at 5.8 kGy in air and at 7 kGy without oxygen. The concentration of the radiolytic products increased with increasing dose and after a maximum they decreased. The oxidation was followed by measuring the chemical oxygen demand; the slopes were 0.48 and 0.11, 0.21 and 0.07, 0.15 and 0.03 mmol dm⁻³ kGy⁻¹ for 1.0 and 0.10 mmol dm⁻³ solutions saturated with N_2O or air or without oxygen, respectively.

1. Introduction

There are several studies that deal with the removal of organic compounds from water using different advanced oxidation processes (AOPs) based on in situ generation of a powerful oxidizing agent, such as ˙OH, at a sufficient concentration to effectively decontaminate water (Munter, 2001; Torun et al., 2014; Csay et al., 2014). These methods include heterogeneous photocatalysis using TiO_2 suspensions (Palmisano et al., 2007), photoelectro-Fenton reactions, using UVA and solar light (Flox et al., 2007), ozonolysis (O_3 + UV irradiation) and peroxonation (Zaviska et al., 2009), photo-Fenton processes using $H_2O_2/Fe^{2+}/UV$ (Brillas et al., 2009), and ultrasound in the presence of other oxidants (Ma, 2012). Other papers have described the oxidation and degradation-destruction of organic pollutants in water using ionizing radiation (Getoff, 1999; Peller and Kamat, 2005; Report of the 2nd RCM, 2012; Homlok et al., 2013; Wojnárovits and Takács, 2016).

Salicylic acid (SA) has been widely used as a medication mainly to treat skin ailments (Madan and Levitt, 2014). This acid acts as an antacid, mild antibiotic, bactericidal and antiseptic. SA is also used as a food preservative. However, it is ototoxic and causes diseases of the central nervous system. SA is also used in the production of other pharmaceuticals, such as acetylsalicylic acid (aspirin), 4-aminosalicylic acid sandulpiride, bismuth subsalicylate, etc. However, the pharmacological residues could have a negative impact on human health. Thus, it is important to determine pharmacological contaminants in water intended for human consumption. SA is an active metabolite of aspirin after it has been processed by the body. Microbial and chemical degradation of aspirin includes its conversion to SA. Aspirin has been found in wastewater in several countries. As an example, in Tokyo aspirin was the most abundant pharmaceutical in the influent of water processing plants, with an average concentration of 7300 ng dm⁻³ (Nakada et al., 2006). In order to degrade SA, different AOPs have been employed. An example is photoelectrochemical oxidation using TiO_2 nanotube arrays (Tian et al., 2009), where first-order kinetics and an 83% decomposition (30 ppm) oxidation were found over 2-h period. Guinea et al. (2008) studied the mineralization of SA by several electrochemical methods using platinum and boron-doped diamond as anodes. They found a quick destruction until totality with ˙OH produced at the boron-doped diamond anode. Zanta and Martínez-Huitle (2009) and Chen et al. (2010) showed that the Fenton process was the most effective under acid conditions of SA degradation requiring only a short time. In Garza-Campos et al. (2016) studied different AOPs and found that the best treatment to mineralize SA was obtained by coupling solar photoelectro-Fenton and solar heterogeneous photocatalysis, due to the additional oxidation by ˙OH at the TiO_2 surface.

The present study evaluates the use of ionizing radiation to degrade SA in water (salicylate SA⁻).

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2. Materials and methods

2.1. Reagents

SA⁻, dihydroxybenzoic acid (DHBA), catechol (CAT), and potassium ferrocyanide, all of the purest commercially available quality, methanol (HPLC grade) and acetic acid for analysis (99.7%) were all from Sigma-Aldrich. The gases N_2O (atomic absorption grade) and He (ultrahigh purity grade) were supplied by Praxair. For digestion, Hach Ultra-Low Range COD reagent (0.7–40 mg dm^{-3} O_2) was used. The water used in all irradiation experiments and for preparing the standard solutions was obtained using a Milli-Q Plus compact purifier from Millipore.

2.2. Sample preparation and irradiation

Aqueous solutions of 1.0 and 0.1 mmol dm^{-3} SA⁻ (138 and 13.8 mg dm^{-3} respectively) were prepared for irradiation as follows: a) 1 mmol dm^{-3} $K_3Fe(CN)_6$ was added to these solutions, which were then put into hermetically sealed vials and then saturated with N_2O using a needle; b) Aliquots of the solutions were placed in hermetically sealed vials and were saturated with N_2O; c) Aliquots of the solutions were placed in hermetically sealed vials and residual oxygen was eliminated from the solutions by bubbling helium. d) The solutions were placed in open tubes. The vials and tubes were irradiated with a ^{60}Co gamma-source (Gammabeam 651 PT, MDS Nordion) at different doses with a dose rate of 103 Gy min^{-1}, calibrated with a cupric-ferrous system (Spinks and Woods, 1990).

2.3. Analysis of the radiolytic products

The samples were analyzed immediately after irradiation with a HPLC chromatograph (Agilent Technologies Series 1100 System) coupled to a Chemstation for control and data acquisition. The chromatograph is equipped with both photodiode array and mass spectroscopy detectors. A Thermo Hypersil C18, 3 μm, 150 × 4.6 mm column was used for product separation. The products were eluted using 35:65 methanol:1% aqueous acetic acid. All products (peaks in the chromatogram) were identified by their retention times and their spectra, which were compared with authentic samples. In order to quantify the radiolytic products, the peaks from the chromatogram were integrated at their maximum wavelengths. The concentrations were determined from these areas using analytical curves obtained with reference sam-

ples, using the program Origin Pro 7.

2.4. Chemical Oxygen Demand (COD)

COD is a measure of the oxygen equivalent of the organic matter content a sample that is susceptible to oxidation by a strong chemical oxidant. In this work aliquots of 2 mL of the irradiated solutions were added to the Hach Ultra-Low Range solution for digestion, mixed and then heated for 2 h at 150 °C in a Hach reactor. Samples were cooled to room temperature and, when cool, were analyzed on an Agilent Technologies spectrophotometer with a diode array detector. A calibration curve was prepared from a Chemical Oxygen Demand standard solution (Hach) of 300 mg dm^{-3} of potassium acid phthalate.

Experiments were conducted in at least triplicate to ensure the reproducibility of the results for each tested dose.

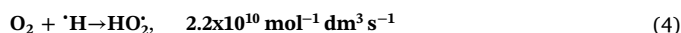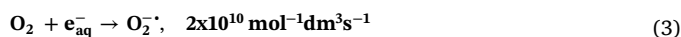## 3. Theoretical considerations

In the radiolysis of the water several species are generated (Spinks and Woods, 1990), principally $^\bullet OH$, e_{aq}^- and $H^\bullet$, which play the main role in the degradation of SA⁻:

$$H_2O \xrightarrow{\hspace{1cm}} e_{aq}^- + H^\bullet + {}^\bullet OH + H_2O_2 + H_2 \qquad (1)$$
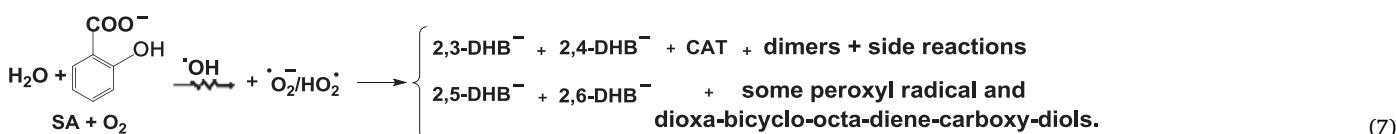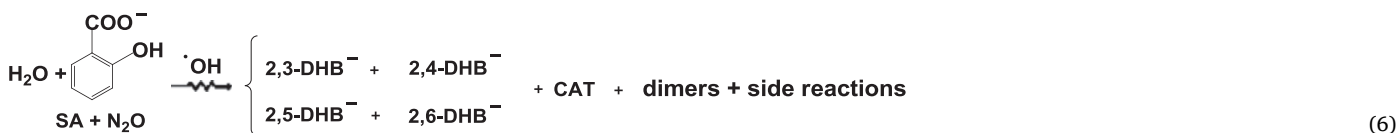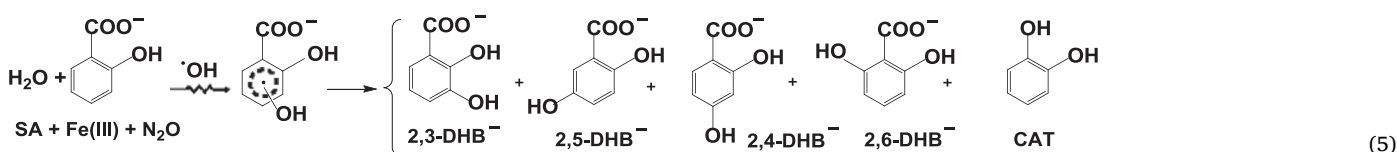
In addition, if water is treated prior to radiolysis with N_2O to saturate the solutions, e_{aq}^- is quantitatively converted to $^\bullet OH$ ($k = 9.1 \times 10^9$ dm^3 mol^{-1} s^{-1}) (Buxton et al., 1988) and the yield of the directly formed and the e_{aq}^- converted $^\bullet OH$ is G($^\bullet OH$) = 0.56 μmol J^{-1}, according to the following reaction (Janata and Schuler, 1982).

$$e_{aq}^- + N_2O + H_2O \rightarrow {}^\bullet OH + OH^- + N_2 \qquad (2)$$
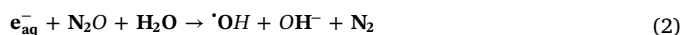
In solutions containing air the aqueous electron and the hydrogen atom, formed in the radiolysis of water, react with oxygen forming two new species according to reactions (3) and (4). The rate constants are given by Bielski et al. (1985).

$$O_2 + e_{aq}^- \rightarrow O_2^{-\bullet}, \quad 2x10^{10} \text{ mol}^{-1}\text{dm}^3\text{s}^{-1} \qquad (3)$$

$$O_2 + {}^\bullet H \rightarrow HO_2^\bullet, \quad 2.2x10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \qquad (4)$$

Thus, the free radicals formed in water radiolysis interact with SA⁻ in solution. The results depend on the conditions of the solution and the dose, according to the following reactions:

$$(5)$$

$$(6)$$

$$(7)$$