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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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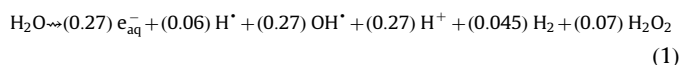
The degradation of *p*-hydroxybenzoic acid (HBA) in aqueous solutions by ionizing radiation was studied. The phenolic pollutant was easily removed by the electron beam irradiation, as more than 80% of the initial 100  $\mu\text{M}$  introduced was degraded for a dose of 600 Gy. It was shown that the 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.

## 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 ( $\text{OH}^\bullet$ ,  $\text{HO}_2^\bullet$ ,  $\text{H}_2\text{O}_2$ ) and

reductive ( $e_{\text{aq}}^-$ ,  $\text{H}^\bullet$ ) 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  $\mu\text{mol J}^{-1}$  at pH 7 (Spinks and Woods, 1990).



While  $\text{OH}^\bullet$  is available for the degradation of target pollutant,  $e_{\text{aq}}^-$  is in large part scavenged by dissolved oxygen in solution; the  $\text{O}_2^{\bullet -}$  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

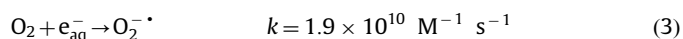
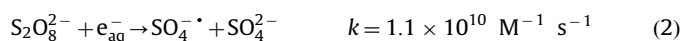
chromatographic system (pump+thermostated autosampler Surveyor) equipped with a diode array detector (Surveyor) and an ion trap mass spectrometer DECA XP Ion max was used. The column was an Uptisphere HDO C<sub>18</sub> column (3 × 250 mm) packed with 5-μm spherical particles. A H<sub>2</sub>O/MeOH mixture (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).

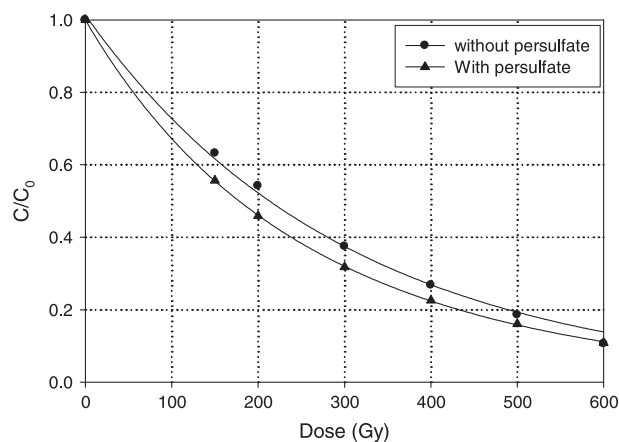
## 3. Results

### 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.

during the radiolysis in absence and in presence of persulfate ( $C_0=2000\ \mu\text{M}$ ) as a function of the absorbed dose.

According to Fig. 1, the degradation of HBA occurred for low doses. More than 80% of the initial  $100\ \mu\text{M}$  HBA introduced was degraded for a dose of 600 Gy (for comparison, a dose of 5000 Gy was needed for the degradation of the same amount of acetic acid (Criquet and Karpel Vel Leitner, 2011a)). The addition of persulfate resulted in only a small improvement in the degradation of HBA. The evolution of TOC was also monitored; for a dose of 600 Gy, the initial TOC was reduced by 14 and 20%, respectively, in absence and in presence of persulfate. Despite the great elimination of HBA for low doses, the elimination of TOC was small. In fact the transformation of HBA occurred rapidly, but the dose absorbed was not sufficient to convert the organic compounds into  $\text{CO}_2$ . Higher doses would be necessary to degrade the intermediate organic compounds formed.

The analysis of the concentration of persulfate showed that the persulfate was only partially degraded for the doses absorbed. Effectively the degradation of persulfate was below 15% for a dose of 600 Gy. This weak degradation could explain the small difference noticed between the experiments performed in absence and in presence of persulfate. The pH of the solution decreased with increasing absorbed dose. In absence of persulfate, the decrease observed was smaller than 0.2 pH unit but in presence of persulfate, the decrease was higher; the initial pH of 3.8 dropped to 3.3 for a dose of 600 Gy applied. The comparison of the evolution of dissolved oxygen concentration in absence and in presence of persulfate (from 290 to 120  $\mu\text{M}$ , and from 285 to 190  $\mu\text{M}$ , respectively, in absence and in presence of persulfate) showed that the consumption was more important in the absence of persulfate. In absence of persulfate, the aqueous electron reacts with dissolved oxygen inducing a decrease of the concentration of this later (Eq. (3)). Moreover, it is well known that oxygen participates to many radical mechanisms. On the other hand, it has been shown in a previous study, that the radiolysis of persulfate solution induced an increase of dissolved oxygen in solution (Criquet and Karpel Vel Leitner, 2011b). Then, the formation of oxygen in presence of persulfate partly balanced the oxygen consumption by the oxidation reactions.

Fig. 2 presents the degradation of HBA in presence of persulfate for different initial concentrations of dissolved oxygen in solution (1.8; 9.0  $\text{mg L}^{-1}$  and saturation i.e. 22.5  $\text{mg L}^{-1}$ ) obtained by  $\text{N}_2$  or  $\text{O}_2$  bubbling. The linearization of results by the logarithmic representation permits to calculate the dose constant,  $k$ , for the

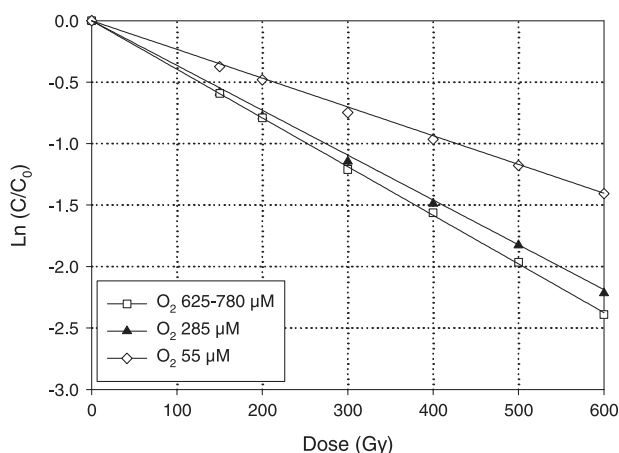


Fig. 2. Impact of initial dissolved oxygen concentration in presence of persulfate.  $[\text{HBA}]_0=100\ \mu\text{M}$ ;  $[\text{S}_2\text{O}_8^{2-}]_0=2000\ \mu\text{M}$ ;  $\text{pH}=3.9$ . Dissolved oxygen concentration obtained by  $\text{O}_2$  or  $\text{N}_2$  bubbling.

different experimental conditions according to Eq. (4).

$$\ln\left(\frac{C}{C_0}\right) = -kD \quad (4)$$

with

$D$ : absorbed dose (Gy),  $C$ : HBA concentration for the absorbed dose  $D$  ( $\mu\text{mol L}^{-1}$ ),  $C_0$ : HBA initial concentration ( $\mu\text{mol L}^{-1}$ ),  $k$ : apparent dose destruction constant ( $\text{Gy}^{-1}$ ).

From the slopes in Fig. 2, the apparent dose constants determined for the degradation of HBA were  $2.4 \times 10^{-3}$ ,  $3.7 \times 10^{-3}$  and  $4.0 \times 10^{-3}\ \text{Gy}^{-1}$ , respectively, for the dissolved oxygen concentrations of 55, 285  $\mu\text{M}$  and saturation. This figure shows the beneficial impact of the presence of dissolved oxygen on the degradation of HBA by ionization. The decrease of oxygen concentration from 285 down to 55  $\mu\text{M}$  had a large influence on the HBA degradation (Fig. 2). In fact, for a dose of 600 Gy the concentration of HBA determined for the highest dissolved oxygen concentration was less than half of the residual concentration obtained in absence of a significant dissolved oxygen concentration. Dissolved oxygen seems to be a limiting parameter for the degradation of HBA solution by irradiation. Oxygen at various concentrations is a necessary component in the system for the oxidation to proceed from the formation of organic peroxide radicals. However when it was present, the increase of dissolved oxygen concentration up to the saturation did not show a significant beneficial effect on the HBA concentration. In the range of oxygen concentration studied, the reaction of aqueous electron with persulfate (Eq. (2)) remained predominant. In absence of oxygen, by products different from those formed in presence of oxygen could compete with HBA for the oxidizing radicals ( $\text{OH}^\cdot$ ,  $\text{SO}_4^{\cdot-}$ ). Moreover, the recombination of aqueous electron with the organic radicals derived from HBA oxidation could not be neglected and could induce the regeneration of the initial HBA molecule (Quici et al., 2008).

The persulfate analysis for each sample irradiated showed that the presence of oxygen in varying concentration had no influence on the persulfate degradation in the range of concentrations and doses studied. The degradation of persulfate was small; below 15% for a dose of 600 Gy.

### 3.2. Effect of pH

pH adjustment was made by sodium hydroxide addition before irradiation. The effect of the initial pH of the solution on the degradation of HBA in presence or absence of persulfate is shown in Table 1. In basic media the pH remained relatively stable. A decrease of 0.3 unit was measured for a dose of 600 Gy.

According to the radiolytic yields ( $G$ -values) presented in Table 1, the degradation of HBA was highly reduced in basic media. On the contrary to the yields observed at acidic pH, the yields of HBA degradation at pH 11.0 were significantly different in presence and in absence of persulfate. In absence of persulfate, the yield was dramatically reduced, reaching approximately only one third of the value observed at free pH. These observations are in agreement with the work of Swoboda and Solar (1999) who reported the decrease of the radiolytic yield ( $G(\text{HBA})$ ) with the increase of pH. The presence of persulfate at pH 11.0 improved the degradation of HBA, as its degradation approximately doubled for

Table 1  
Radiolytic yield of *p*-hydroxybenzoic acid degradation for a dose of 600 Gy. Comparison of the effect of persulfate for different pH.

		pH 3.8–4.5	pH 11.0
$G(\text{HBA})_{600\ \text{Gy}}\ (\mu\text{mol J}^{-1})$	Without persulfate	0.086	0.031
	With persulfate	0.089	0.057

a dose of 600 Gy. As a consequence, the addition of this reactant to the solution before irradiation limits the loss of activity towards HBA in basic solution.

From the two pKa values of the molecule of *p*-hydroxybenzoic acid (4.7 (carboxyl group) and 9.4 (phenolic group)), it results that at pH 11.0 the compound has two negative charges. The rate constants of reaction of the different forms of the compound are only partially known:  $k_{OH^\bullet/HBA} = 2.19 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (Beltran de Heredia et al., 2001);  $k_{OH^\bullet/HBA^-} = 6.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (Swoboda and Solar, 1999). The rate constant of reaction of hydroxyl radical with the dianion is not known. Considering the high reactivity of hydroxyl radical with phenolic compound, and the small difference noticed between the rate constants of reaction with the different ionic forms of HBA or other phenolic compounds (Buxton et al., 1988), it could be suggested that the kinetics are relatively similar, whatever the ionic form considered. Consequently, the smaller degradation observed at pH 11 would be explained by the different repartition of the reactive species at this pH compared to the neutral pH. In fact, above pH 10, the yield of formation of hydroxyl radical slightly decreases (at pH 11:  $G(OH^\bullet) = 0.24$  instead of 0.27). Moreover, in basic media, the  $OH^\bullet$  radical is partly present as  $O^{\bullet-}$  (pKa=11.5 (Poskrebyshev et al., 2002)) which is less reactive. On the contrary, the yield of production of aqueous electron is higher at pH 11 ( $G(e_{aq}^-) = 0.30$  instead of 0.27 at pH 7); this higher yield could induce a higher production of sulfate radical, and therefore enhance the degradation of the target compound at this pH in the presence of persulfate ( $k_{SO_4^{\bullet-}/HBA^-} = 2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (Neta et al., 1988)). The analysis performed showed that the degradation of persulfate at pH 11.0 was similar to those at free pH.

### 3.3. By-product identification

#### 3.3.1. In absence of persulfate

Transformation products in irradiated HBA solutions were characterized by mass spectrometry analysis (LC-MS and MS<sup>2</sup>). Fig. 3 represents the chromatogram of a HBA solution irradiated in absence of persulfate (dose of 300 Gy). Additionally, the overall UV, MS and MS<sup>2</sup> data for each compound detected in the irradiated solution are gathered in Table 2.

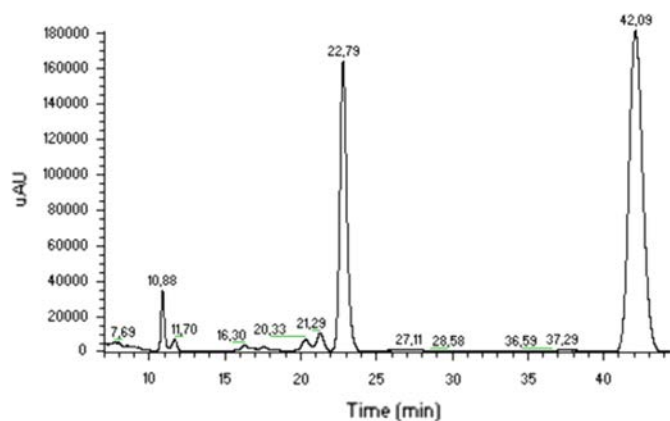
As shown in Fig. 3, the degradation of HBA by water radiolysis induced the formation of several by-products; based on the UV absorbance, one product (V) seemed to be predominant.

According to the data of MS and MS<sup>2</sup> spectra given in Table 2, structures for the by-products were suggested.

The mass spectra of HBA included several characteristics that were also observed for the by-products. A peak at *m/z* 137.0 corresponding to the deprotonated molecular ion was detected as the main fragment. Additional fragment ions were present at *m/z* 196.6 and 274.7 corresponding to an acetic acid adduct and a dimerization of HBA, respectively. The MS<sup>2</sup> fragmentation spectrum indicated a loss of CO<sub>2</sub> (−44) from the molecular ion which was characteristic to the carboxylic acid group present on the aromatic ring. The major product detected by UV absorption (V) showed two main fragments at *m/z* 153.1 (molecular ion) and 306.7 (dimer). The molecular ion showed a difference of mass of +16 compared to the HBA molecular ion; this indicates the hydroxylation of the aromatic ring. Moreover the MS<sup>2</sup> spectra of the molecular ion exhibited a fragment of *m/z* 109.1 which corresponds to a CO<sub>2</sub> loss (−44) (also present in a small proportion in the MS spectra), confirming that the carboxylic group was

**Table 2**  
Data from UV spectra and LC-MS<sup>2</sup> chromatograms for the by-products formed in irradiated HBA solutions in absence of persulfate.

Compounds	Retention time	$\lambda_{\max}$ (nm)	Observed fragment ions at <i>m/z</i> value (relative abundance)			Proposed structure	
			MS	Corresponding fragment - compared to HBA	MS <sup>2</sup>		
HBA	42.1	253	137.0 (100)	[M−H] <sup>−</sup>	93.1 (100)	CO <sub>2</sub> loss [M−H−COO] <sup>−</sup>	
			196.6 (32)	[M+CH <sub>3</sub> COO] <sup>−</sup>			
			274.7 (28)	[2M−H] <sup>−</sup>			
I	10.9	290	123.1 (17)	See text	125 (100)	CO <sub>2</sub> loss	
			118.7 (100)				
			59.0 (80)				
II	11.7	265	154.9 (18)		151.0 (100) 169.0 (51)	Deshydration	
			169.1 (100)	[M−H] <sup>−</sup> HBA+2 OH			
			178.6 (23)	Acetic acid			
III	20.3	260	169.0 (100)	[M−H] <sup>−</sup> HBA+2 OH	151.0 (100) 125.1 (18)	Deshydration	
			118.7 (38)	Acetic acid			
			169 (100)	[M−H] <sup>−</sup> HBA+2 OH			
IV	21.3	255–315	59 (16)	Acetic acid	81(11) 109.1 (100) 109.1 (100)	CO <sub>2</sub> loss	
			118.7 (21)				
			338 (17)	[2M−H] <sup>−</sup>			
V	22.8	260–295	109.1 (9)	[M−H−COO] <sup>−</sup>	109.1 (100)	CO <sub>2</sub> loss	
			153.1 (100)	[M−H] <sup>−</sup> HBA+OH			
			306.7 (89)	Dimer			



**Fig. 3.** UV chromatogram of irradiated HBA solution (300 Gy).  $[HBA]_0 = 100 \mu\text{M}$ ;  $\text{pH} = 4.5$ . (Representation of the integration of UV absorbance from 210 to 600 nm).

still present on this by-product. Considering that the attack of the hydroxyl radical on the aromatic ring was favoured in the ortho- and para-position of the phenol, the proposed structure for the by-product V was the 3,4-dihydroxybenzoic acid (3,4-DHBA; also known as protocatechuic acid). This structure was confirmed by the analysis of a standard solution. Hence this result agrees with the UV spectra and the MS characterization made by Sun et al. (2007) for this molecule.

The compounds II, III, and IV presented a main peak at  $m/z$  169; this fragment corresponds to compounds resulting from a second hydroxylation of the aromatic ring. The  $\text{MS}^2$  spectra of these molecular ions showed the loss of  $\text{CO}_2$  neutral fragment ( $m/z$  125) or undergo a dehydration ( $m/z$  151). In accordance with the  $\text{MS}^2$  spectra of the molecular ion obtained by Sun et al. (2007), the compound II seems to be gallic acid (3,4,5-trihydroxybenzoic acid), this structure was confirmed by the study of Alkhouraiji (2013). Compounds III and IV have a similar behavior and are certainly the 2,4,5-trihydroxybenzoic and 2,3,4-trihydroxybenzoic acids formed from the hydroxylation of the activated sites of the ring (i.e. ortho and para position of the OH group). This result is in accordance with the results of Azrague et al. (2012) which detected these two compounds as by-products of 2,4-dihydroxybenzoic acid degradation by hydroxyl radical. They also found that the formation of 2,4,6-trihydroxybenzoic acid is not likely to occur. Finally, compound I was not detected by mass spectrometry under the conditions used in this study, as the main peak resulted in the dimerization of acetic acid present in the eluent ( $m/z = 118$ ). The minor peak observed at 123 was not attributed; however, some information can be obtained from the UV spectrum recorded by the diode array detector. The maximum of absorbance was plotted at 290 nm, corresponding to the maximum UV absorbance of hydroquinone. In order to confirm the chemical structure of compound I, an aqueous solution of hydroquinone was then analyzed under similar conditions resulting in identical retention time and UV spectra, and confirming the absence of detection by MS analysis.

### 3.3.2. In presence of persulfate

In presence of persulfate, the chromatogram and the mass spectra obtained were totally different from the experiment performed in absence of this reactant. In this case one major by-product with a retention time smaller than that of HBA was observed (Fig. 4). The compounds identified in the experiment performed in absence of persulfate were not present in the chromatograms, indicating that if they were formed (since in the presence of persulfate both  $\text{OH}^\bullet$  and  $\text{SO}_4^{\bullet-}$  radicals are produced in

irradiated solutions) they were transformed rapidly in the presence of this oxidant. The by-product which eluted at 17.8 min presented a large absorbance in the UV domain with a maximum at 244 nm. This product was hardly detected by MS analysis; like hydroquinone a peak at  $m/z = 123$  with a weak intensity was found. In comparison with the work of Deborde et al. (2008), we assigned this product to 1,4-benzoquinone. This chemical structure was confirmed by the analysis of a standard aqueous solution of this compound.

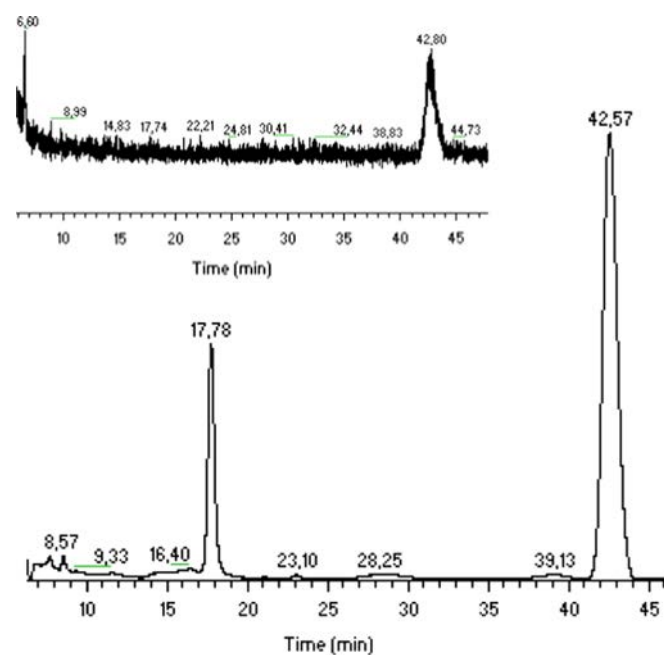
### 3.4. By-product quantification and reactivity

The quantification of the main product identified in presence and in absence of persulfate was performed. The variation of the concentration of these compounds is represented in Fig. 5 in parallel with the HBA degradation.

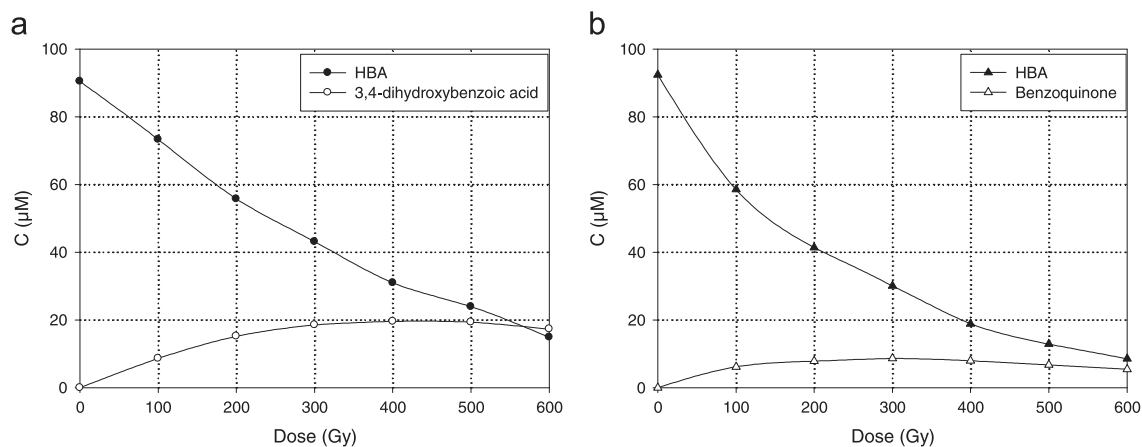
In absence of persulfate, the concentration of 3,4-dihydroxybenzoic acid reached a maximum of  $20 \mu\text{M}$ ; This by-product formation represented a maximum of 50% of the HBA degraded. The concentration of 3,4-DHBA in solution increased with the increase of the absorbed dose and decreased for doses above 500 Gy indicating the transformation of this product. Because of its high reactivity towards hydroxyl radical, the di-hydroxybenzoic acid was not found to accumulate in solution. The higher electron density of the aromatic ring promotes its further hydroxylation.

UV chromatograms of irradiated HBA solutions in presence of persulfate showed a small formation of benzoquinone; the maximum concentration reached was less than  $10 \mu\text{M}$ . Similar to the 3,4-DHBA evolution observed in absence of persulfate, the concentration of benzoquinone decreased for the highest doses of irradiation; this compound represented a maximum of 20% of the HBA degraded in the presence of persulfate.

Obviously, the by-products quantified did not represent all the compounds that were formed. According to the rate constants of reaction of hydroxyl and sulfate radical with some compounds that were expected (Table 3), many would have been easily degraded by these radicals.



**Fig. 4.** UV detection and mass spectra (inset) of by-products formed after irradiation of HBA solution (300 Gy) in presence of persulfate.  $[HBA]_0 = 100 \mu\text{M}$ ;  $[\text{S}_2\text{O}_8^{2-}]_0 = 2000 \mu\text{M}$ ;  $\text{pH} = 4.5$ . LC-UV (total scan 210–600 nm) and LC-MS (TIC 50–250  $\text{u}m\text{a}$ ).



**Fig. 5.** Degradation and by-product formation during irradiation of HBA solutions in presence and absence of persulfate. (a) Without persulfate:  $[HBA]_0=90 \mu\text{M}$ ;  $[O_2]=250 \mu\text{M}$ ;  $\text{pH}=4.4$ ; quantification of 3,4-dihydroxybenzoic acid. (b) With persulfate:  $[HBA]_0=92 \mu\text{M}$ ;  $[S_2O_8^{2-}]_0=2000 \mu\text{M}$ ;  $[O_2]=250 \mu\text{M}$ ;  $\text{pH}=3.9$ ; quantification of 1,4-benzoquinone.

**Table 3**

Rate constants of reaction of hydroxyl and sulfate radicals with HBA and some of its potential oxidation by-products.

Compounds	$k_{OH^\bullet}$ ( $M^{-1} s^{-1}$ ) <sup>a</sup>	Reference	$k_{SO_4^{\bullet-}}$ ( $M^{-1} s^{-1}$ )	Reference
<i>p</i> -Hydroxybenzoic acid (HBA)	$2.19 \times 10^9$	Beltran de Heredia et al. (2001)	$2.5 \times 10^9$	Neta et al. (1977)
<i>p</i> -Hydroxybenzoate	$6.7 \times 10^9$	Swoboda and Solar (1999)	$2.5 \times 10^9$	Neta et al. (1988)
3,4-Dihydroxybenzoic acid	$6.7 \times 10^8$ $2.2 \times 10^{10}$	Beltran de Heredia et al. (2001) Oturán and Pinson (1995)		
2,3,4-Trihydroxybenzoate	$1.9 \times 10^{10}$	Buxton et al. (1988)		
2,3,6-Trihydroxybenzoate	$4.8 \times 10^{10}$	Buxton et al. (1988)		
3,4,5-Trihydroxybenzoate	$1.0 \times 10^{10}$ $4.0 \times 10^{10}$	Buxton et al. (1988)	$2.9 \times 10^9$	Caregnato et al. (2008)
Gallic acid	$1.2 \times 10^{10}$	Melo et al. (2009)	$6.3 \times 10^8$	Caregnato et al. (2008)
Hydroquinone	$5.2 \times 10^9$ – $2 \times 10^{10}$	Buxton et al. (1988)		
1,4-Benzoquinone	$1.2 \times 10^9$	Buxton et al. (1988)	$1 \times 10^8$	Buxton et al. (1988)

<sup>a</sup> The second order rate constants above  $1 \times 10^{10} M^{-1} s^{-1}$  are subject to caution as above the theoretical limit of diffusion controlled rate constant.

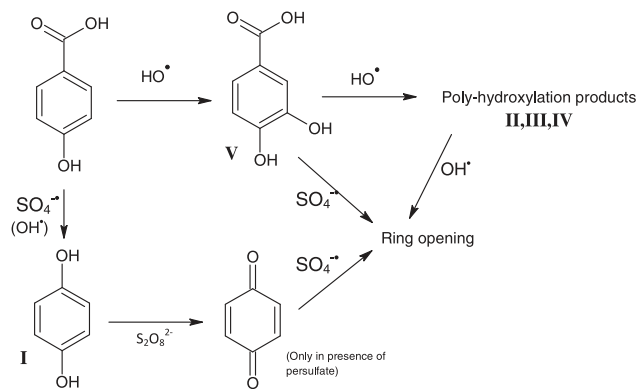
Except for benzoquinone, the rate constants of reaction of hydroxyl radical with the products are higher than with the parent compound, HBA. Thus the existing maximum concentrations of the by-products detected confirmed that these compounds were only intermediate compounds. Considering benzoquinone, this product could be formed by oxidation of hydroquinone in presence of persulfate in solution.

Based on the results obtained, a scheme of the degradation of HBA by the hydroxyl and sulfate radical could be proposed (Fig. 6).

In absence of persulfate, the hydroxyl radical induced the formation of poly-hydroxylated compounds, and in a smaller extent the formation of hydroquinone. These results are in accordance with the works previously published (Swoboda and Solar, 1999; Krimmel et al., 2010) where the formation of 3,4-DHBA as the major product was observed and the formation of hydroquinone during the  $\gamma$ -irradiation of HBA solution (3 times less than 3,4-DHBA) was also noticed.

The reaction of OH radicals with aromatic rings forming hydroxylated products has been well described in the literature (Mvula et al., 2001). This reaction occurs via different steps; i.e. (i) the formation of the hydroxycyclohexadienyl radical (here dihydroxyBA radical) from OH addition, (ii) the subsequent rapid reaction with oxygen leading to the formation of the corresponding peroxy radical, (iii)  $HO_2^\bullet$  elimination with formation of the stable hydroxylation product.

In presence of persulfate, the main by-product detected (i.e. benzoquinone) as well as the absence of hydroxylated-HBA gave



**Fig. 6.** Proposed reaction pathways for the degradation of *p*-hydroxybenzoic acid in absence and in presence of persulfate.

some information about the mechanism involved. The sulfate radical does not add to aromatic rings. It would react directly with HBA by electron transfer from the ring (Neta et al., 1977; Paul (Guin) et al., 2014) leading to the formation of an intermediate radical cation. The radical cation could hydroxylate with water or  $OH^-$  to form the carboxylated dihydroxycyclohexadienyl radical (Neta et al., 1977; Madhavan et al., 1978; Zemel and Fessenden, 1978) that would react as in the  $OH^\bullet$  radical mechanism. Zemel and Fessenden (1978) from the study of transient species, reported that the radical cation also deprotonates to form the carboxylated

phenoxy radical. However, the decarboxylation of the radical cation as suggested by these authors for benzoate seems to be more significant in our system regarding the reaction products observed. It would form the hydroxyphenyl radical that would result in the formation of hydroquinone after subsequent hydration and dihydroxycyclohexadienyl radical intermediate (Neta et al., 1977; Nicolaescu et al., 2003). Hydroquinone is easily oxidized, then in presence of persulfate, this compound is oxidized to benzoquinone. This is relevant to one of the main existing difference of reactivity between hydroxyl and sulfate radical. In fact, hydroxyl radical reacts with aliphatic carboxylic acids by H abstraction, and by OH addition on aromatic rings, both leading in the two cases to the hydroxylation of the molecule. In contrast, it has been shown that most carboxylic acids (aromatic and aliphatic) undergo efficient decarboxylation by sulfate radical (Madhavan et al., 1978; Criquet and Karpel Vel Leitner, 2009). Experiments on benzoate showed around 70% of decarboxylation of the molecule by reaction with the sulfate radical, the alternate reaction being hydroxylation of the benzenic ring (Madhavan et al., 1978; Zemel and Fessenden, 1978). Moreover a slightly higher decrease of the TOC in presence of persulfate was observed (data not presented) which supports the reaction of decarboxylation proposed in presence of persulfate. The concentrations of hydroxylated products in presence of persulfate are not significant; therefore, these compounds formed by the reaction of hydroxyl radical with HBA are certainly very reactive with sulfate radical. The reaction of sulfate radical certainly induced the formation of different by-products through the formation of decarboxylated compounds. However, it can be assumed that the transformation of other hydroxylated compounds into quinonic forms due to the presence of persulfate does not happen. Those compounds would have been easily detected in the UV chromatogram due to their high absorbance. In the same idea, it can be conclude that the dimer products are not present in a large extent. Analysis of small carboxylic acids as performed in a previous study (Criquet and Karpel Vel Leitner, 2009) showed numerous peaks corresponding to products formed by the ring opening. The overlapping of the abundant peaks limited the determination and quantification of the compounds. Among them, only formic acid had been identified with certainty.

#### 4. Conclusion

In this study, we investigated the degradation of *p*-hydroxybenzoic acid solution by electron beam irradiation. It was shown that this compound is rapidly degraded by the ionizing radiation process; however, further irradiation is needed to obtain mineralization. Despite the fact that the addition of persulfate does not contribute to a significant enhancement of the degradation of HBA in acidic media, it was shown that the addition of this reactant improved the degradation in basic solution. Moreover the reaction pathway involved in presence of persulfate is different. Many different by-products issued of the hydroxylation and polyhydroxylation of the benzenic ring were found in absence of persulfate. In contrast, those compounds were hardly detected in presence of persulfate showing their high reactivity towards sulfate radical; benzoquinone formed by decarboxylation of HBA was the main by-product detected in presence of persulfate.

Moreover, despite the difficulties due to the large number of possible compounds, a screening of the by-products resulting in the cleavage of the HBA ring should be considered when trying to determine the complete pathway of HBA degradation. Finally, the study of ionizing irradiation of real waters is under consideration, it will be accompanied of studies on the interest of persulfate addition for different types of toxic and/or refractory compounds.

Therefore the addition of persulfate could be studied in oxidation processes, for example, in the case of generation of toxic by-products by reaction of hydroxyl radical in order to change the reaction pathways and the nature of the by-products formed.

#### References

- Alkhouraji, T.S., 2013. Ionisation par faisceau d'électrons de solutions aqueuses de benzènesulfonate et naphthalènesulfonate et sous-produits. Thèse de l'Université de Poitiers.
- Azrague, K., Pradines, V., Bonnefille, E., Claparols, C., Maurette, M.T., Benoit-Marqué, F., 2012. Degradation of 2,4-dihydroxybenzoic acid by vacuum UV process in aqueous solution: kinetic, identification of intermediates and reaction pathway. *J. Hazard. Mater.* 237–238, 71–78.
- Basfar, A.A., Mohamed, K.A., Al-Abduly, A.J., Al-Shahrani, A.A., 2009. Radiolytic degradation of atrazine aqueous solution containing humic substances. *Ecotoxicol. Environ. Saf.* 72, 948–953.
- Beltran de Heredia, J., Torregrosa, J., Dominguez, J.R., Peres, J.A., 2001. Kinetic model for phenolic compounds oxidation by Fenton's reagent. *Chemosphere* 45, 85–90.
- Boukari, S.O.B., Pellizzari, F., Karpel Vel Leitner, N., 2011. Influence of persulfate ions on the removal of phenol in aqueous solution using electron beam irradiation. *J. Hazard. Mater.* 185 (2–3), 844–851.
- Buxton, G.V., Greenstock, C.L., Helman, W.P., Ross, A.B., 1988. Rate constants for reactions of radicals in aqueous solution. *J. Phys. Chem. Ref. Data* 17 (2), 513–886.
- Caregnato, P., David Gara, P.M., Bosio, G.N., Gonzalez, M.C., Russo, N., Micheline Mdel, C., Martire, D.O., 2008. Theoretical and experimental investigation on the oxidation of gallic acid by sulfate radical anions. *J. Phys. Chem. A* 112, 1188–1194.
- Creanga Manole, C., Julcour Lebigue, C., Wilhelm, A.M., Delmas, H., 2007. Catalytic oxidation of 4-hydroxybenzoic acid on activated carbon in batch autoclave and fixed-bed reactors. *Ind. Eng. Chem. Res.* 46, 8388–8396.
- Criquet, J., Karpel Vel Leitner, N., 2009. Degradation of acetic acid with sulfate radical generated by persulfate ions photolysis. *Chemosphere* 77, 194–200.
- Criquet, J., Karpel Vel Leitner, N., 2011a. Radiolysis of acetic acid aqueous solutions—effect of pH and persulfate addition. *Chem. Eng. J.* 174, 504–509.
- Criquet, J., Karpel Vel Leitner, N., 2011b. Electron beam irradiation of aqueous solution of persulfate ions. *Chem. Eng. J.* 169, 256–262.
- Criquet, J., Karpel Vel Leitner, N., 2012. Electron beam irradiation of citric acid aqueous solutions containing persulfate. *Sep. Purif. Technol.* 88, 168–173.
- Deborde, M., Rabouan, S., Mazellier, P., Duguet, J.P., Legube, B., 2008. Oxidation of bisphenol A by ozone in aqueous solution. *Water Res.* 42, 4299–4308.
- Follut, F., Karpel Vel Leitner, N., 2007. Radiolysis of aqueous 4-nitrophenol solution with Al<sub>2</sub>O<sub>3</sub> or TiO<sub>2</sub> nanoparticles. *Chemosphere* 66, 2114–2119.
- Follut, F., Legube, B., Karpel Vel Leitner, N., 2007. Modelling of phenol removal in aqueous solution depending on the electron beam energy. *Radiat. Phys. Chem.* 76, 827–833.
- Gonzalez, M.D., Moreno, E., Quevedo Sarmiento, J., Ramos Cormenzana, A., 1990. Studies on antibacterial activity of waste waters from olive oil mills (alpechin): inhibitory activity of phenolic and fatty acids. *Chemosphere* 20 (3–4), 423–432.
- Homlok, R., Takacs, E., Wojnarovits, L., 2011. Elimination of diclofenac from water using irradiation technology. *Chemosphere* 85, 603–608.
- Krimmel, B., Swoboda, F., Solar, S., Reznicek, G., 2010. OH-radical degradation of hydroxybenzoic and hydroxycinnamic acids and formation of aromatic products—a gamma radiolysis study. *Radiat. Phys. Chem.* 79, 1247–1254.
- Kwon, B.G., Kim, E., Lee, J.H., 2009. Pentachlorophenol decomposition by electron beam process enhanced in the presence of Fe(III)-EDTA. *Chemosphere* 74, 1335–1339.
- Liu, S.Y., Chen, Y.P., Yu, H.Q., Zhang, S.J., 2005. Kinetics and mechanisms of radiation-induced degradation of acetochlor. *Chemosphere* 59, 13–19.
- Madhavan, V., Levanon, H., Neta, P., 1978. Decarboxylation by SO<sub>4</sub><sup>•-</sup> radicals. *Radiat. Res.* 76, 15–22.
- Melo, R., Leal, J.P., Takacs, E., Wojnarovits, L., 2009. Radiolytic degradation of gallic acid and its derivatives in aqueous solution. *J. Hazard. Mater.* 172, 1185–1192.
- Mvula, E., Schuchmann, M.N., von Sonntag, C., 2001. Reactions of phenol-OH-adduct radicals. Phenoxyl radical formation by water elimination vs. oxidation by dioxygen. *J. Chem. Soc., Perkin Trans. 2*, 264–268.
- Neta, P., Madhavan, V., Zemel, H., Fessenden, R.W., 1977. Rate constants and mechanism of reaction of SO<sub>4</sub><sup>•-</sup> with aromatic compounds. *J. Am. Chem. Soc.* 99 (1), 163–164.
- Neta, P., Huie, R.E., Ross, A.B., 1988. Rate constants for reactions of inorganic radicals in aqueous solution. *J. Phys. Chem. Ref. Data* 17 (3), 1027–1247.
- Nicolaescu, A.R., Wiest, O., Kamat, P.V., 2003. Radical-induced oxidative transformation of quinoline. *J. Phys. Chem. A* 107, 427–433.
- Oturan, M.A., Pinson, J., 1995. Hydroxylation by electrochemically generated OH<sup>•</sup> radicals. Mono- and polyhydroxylation of benzoic acid: products and isomer distribution. *J. Phys. Chem.* 99, 13948–13954.
- Paul, J., Rawat, K.P., Sarma, K.S.S., Sabharwal, S., 2011. Decoloration and degradation of reactive red-120 by electron beam irradiation in aqueous solution. *Appl. Radiat. Isot.* 69, 982–987.



- Paul (Guin), J., Naik, D.B., Bhardwaj, Y.K., Varshney, L., 2014. Studies on oxidative radiolysis of ibuprofen in presence of potassium persulfate. *Radiat. Phys. Chem.* 100, 38–44.
- Poskrebyshev, G.A., Neta, P., Huie, R.E., 2002. Temperature dependence of the acid dissociation constant of the hydroxyl radical. *J. Phys. Chem. A* 106, 11488–11491.
- Quici, N., Litter, M.I., Braun, A.M., Oliveros, E., 2008. Vacuum-UV-photolysis of aqueous solutions of citric and gallic acids. *J. Photochem. Photobiol., A* 197, 306–312.
- Sanchez-Polo, M., Lopez Penalver, J., Prados Joya, G., Ferro Garcia, M.A., Rivera-Utrilla, J., 2009. Gamma irradiation of pharmaceutical compounds, nitroimidazoles, as a new alternative for water treatment. *Water Res.* 43, 4028–4036.
- Spinks, J., Woods, R., 1990. *An Introduction to Radiation Chemistry*, third ed. John Wiley & Sons Pub, New York.
- Stanbury, D.M., 1989. Reduction potentials involving inorganic free radicals in aqueous solution. *Adv. Inorg. Chem.* 33, 69–138.
- Sun, J., Liang, F., Bin, Y., Li, P., Duan, C., 2007. Screening non-colored phenolics in red wines using liquid chromatography/ultraviolet and mass spectrometry/mass spectrometry libraries. *Molecules* 12, 679–693.
- Swoboda, F., Solar, S., 1999. Comparative study on the radiolytic degradation of 4-hydroxybenzoate and 4-hydroxybenzoic ethyl ester. *Radiat. Phys. Chem.* 56, 291–301.
- Vahdat, A., Bahrami, S.H., Arami, M., Motahari, A., 2010. Decomposition and decoloration of a direct dye by electron beam radiation. *Radiat. Phys. Chem.* 79, 33–35.
- Villegas, E., Pomeranz, Y., Shellenberger, J.A., 1963. Colorimetric determination of persulfate with alcian blue. *Anal. Chim. Acta* 29, 145–148.
- Yu, H., Nie, E., Xu, J., Yan, S., Cooper, W.J., Song, W., 2013. Degradation of diclofenac by advanced oxidation and reduction processes: kinetic studies, degradation pathways and toxicity assessments. *Water Res.* 47, 1909–1918.
- Yu, S., Lee, B., Lee, M., Cho, I.H., Chang, S.W., 2008. Decomposition and mineralization of cefaclor by ionizing radiation: kinetics and effects of the radical scavengers. *Chemosphere* 71, 2106–2112.
- Zemel, H., Fessenden, R.W., 1978. The mechanism of reaction of  $\text{SO}_4^{\bullet-}$  with some derivatives of benzoic acid. *J. Phys. Chem.* 82 (25), 2670–2676.
- Zhang, S.J., Yu, H.Q., Li, Q.R., 2005. Radiolytic degradation of Acid Orange 7: a mechanistic study. *Chemosphere* 61, 1003–1011.
- Zhang, X.H., Cao, D.M., Zhao, P., Gong, D.Q., Hei, D.Q., Zhang, H.Q., 2011. Gamma radiolysis of ceftriaxone sodium for water treatment: assessment of the activity. *Water Sci. Technol.* 63, 2767–2774.