Effect of persulfate on the oxidation of benzotriazole and humic acid by e-beam irradiation

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ABSTRACT

These days, the use of persulfate in advanced oxidation processes (AOPs) has gained more attention as an emerging clean and efficient technology to degrade the organic pollutants. The objective of this study was to investigate the effect of the addition of persulfate on the oxidation of benzotriazole (BT) and humic acids (HAs) by irradiation. The degradation of BT ($3.7\,\mu$M) was followed under the influence of persulfate addition (200–$500\,\mu$M) in combination with a fixed radiation dose ($15\,$Gy) in the absence and presence of HA (5 and $20\,$mg/L) in deionized water. The main results obtained in this study on the degradation of BT in the presence of HA showed a different effect of $S_2O_8^{2-}$ addition during irradiation, depending on whether HA are oxidized or not-oxidized. (1) An inhibitory effect of $S_2O_8^{2-}$ was observed in the presence of non-oxidized HA. (2) The removal of BT was generally more important during irradiation in the presence of $S_2O_8^{2-}$ when HA is pre-oxidized. This could be explained by the different structures of humic acids. These differences of structures of HA were identified by physico-chemical parameters such as the absorbance in the UV ($254\,$nm), the fluorescence and the SUVA measurement.

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1. Introduction

Benzotriazole ($C_6H_5N_3$) is used in various industries and is characterized by a high water solubility ($28\,$g/L), a low octanol water distribution coefficient (log Kow: 1.23) and a low vapor pressure and is a weakly basic compound ($pK_{a1} = 0.4$; $pK_{a2} = 8.2$–8.8) [1,2]. These properties make BT very mobile in the aquatic environment. In recent years, many studies have been reported on the presence of benzotriazole (BT) in surface waters. BT was found at a concentration of 2.7–$3.69\,\mu$g/L in surface waters due to incomplete removal during the wastewater treatment operations [3,4]. The advanced oxidation processes (AOPs) are alternative methods for the elimination of micropollutants and many other organics in wastewaters and effluents. Among AOPs the efficiency of the e-beam irradiation for water treatment was tentatively improved by the addition of oxidants or catalysts [5,6]. Persulfate has been recently used alone or in combination with other processes to enhance their performance for the removal of organic contaminants [7–11]. Persulfate, known also as peroxydisulfate or peroxodisulfate, is a sulfate peroxide with the chemical structure $[O_3S-O-O-SO_3]^{2-}$. High aqueous solubility, high stability in the subsurface, relatively

low cost and benign end products make persulfate oxidation a promising choice among the advanced oxidation processes (AOPs) for treating organic compounds [9,12]. Persulfate salts are dissociated in water to the persulfate anion ($S_2O_8^{2-}$), that has a strong oxidation potential ($E^o = 2.01\,$V). However, the latter reacts only slowly with many organic compounds. Studies indicated that persulfate anions can be activated to generate the sulfate radicals ($SO_4^{\bullet-}$), which are stronger oxidants ($E^o = 2.6\,$V) compared to the persulfate anion [9,13,14]. Many methods have been widely used for the activation of persulfate, e.g. heat [15–27], UV [11], transition metals [7,8,18,19] or heterogeneous systems such as TiO_2 photocatalysis [20,21]. The sulfate radicals, like the hydroxyl radicals, are powerful oxidants and oxidize organic contaminants following three mechanisms: (1) hydrogen abstraction; (2) addition and substitution reactions with alkenes and aromatic compounds; and (3) electron transfer from carboxylate groups [22,23]. Studies performed by Neta et al. [24] indicate that $SO_4^{\bullet-}$ reacts with many organic compounds as an oxidant more effective than $OH^\bullet$. The reason would be that $SO_4^{\bullet-}$ is more selective to oxidation while $OH^\bullet$ would react quickly by hydrogen abstraction or addition [25].

Natural organic matter (NOM) is ubiquitously present in drinking water sources and plays a significant role during drinking water treatment processes. NOM is a group of various organic macromolecules causing wide-ranging problems in water treatment processes, e.g. the formation of disinfection by-products (DBPs) [26] and membrane fouling [27,28]. Furthermore, it con-

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sumes partly the chemicals added for the treatments and hence increases the cost. The effect of humic substances has gained a significant role in water treatment since they may interact with the chemicals through catalytic reactions, sorption, solubilization, photosensitizing, quenching and competition with target trace compounds [29]. Humic substances represent almost a fraction of 50% of the natural organic matter in water. In this study Aldrich humic acid was used to simulate the natural organic matter. This humic acid (HA) has a complex chemical structure and is polymeric and multifunctional, with a dominant acidic character [30]. For the removal of BT in water by the irradiation process, the understanding of the effect of HA on the micropollutant degradation is important for an effective treatment. In the present research, we wanted to promote the degradation of benzotriazole (3.7 μM) by adding persulfate (200–500 μM) in deionized water during electron beam irradiation. The experiments were conducted in the presence of non-oxidized HA and pre-oxidized HA.

2. Materials and methods

2.1. Electron beam irradiation

The irradiation experiments were carried out with a vertical electron beam from a Van de Graaff accelerator (Vivirad S.A.) set up at the Laboratory of Water Chemistry and Microbiology of the University of Poitiers (France). The electron energy was 2.5 MeV and the maximum beam current was 500 μA. In the bench scale device, solutions were exposed to the vertically scanned beam in a continuous flow reactor. Two types of reactors were used depending on the dose (for low doses, depth: 1 cm, width: 1.5 cm, volume under the beam: 3.75 cm^3 and for high doses, depth: 1.5 cm, width: 3 cm, volume under the beam: 45 cm^3) [31]. The doses were obtained by fixing the flow rate in the range 120–1200 L h^{-1}. All the experiments were carried out at uncontrolled temperature in the range of 18–25 °C. In order to modify the structure of HA, some of the solutions containing HA (5 mg/L) were previously oxidized by irradiation at 1.5 and 3 kGy under oxygen bubbling.

2.2. Solution and chemicals

The solutions used for the irradiation experiments were prepared from deionized water (resistivity = 4.4 MΩ cm, TOC = 0.1 mg/L). All the chemicals used were analytical grade reagents: acetic acid (99%, Riedel-de Haën), salicylic acid (99%, Sigma–Aldrich), oxalic acid (99%, Sigma–Aldrich), methanol (99%, CARLO ERBA), sodium persulfate (98%, Sigma–Aldrich), Alcian blue (Acros), benzotriazole and diuron (99%, Sigma–Aldrich). A stock solution of humic acid (Aldrich) was prepared by dissolving a known weight (1 g) in an appropriate volume (20 L) of deionized water at pH 8.5 (adjusted with NaOH). It was checked that a magnetic stirring for 48 h at room temperature was necessary for complete solubilization. This terrestrial peat humic acid has been well characterized in the literature [32]. Its chemical composition in %-mass is as follows: C, 39.03; H, 4.6; N, 0.61; S, 0.957; Na, 8.7; Ca, 1.4; Fe, 0.557; Si, 0.803.

2.3. Analytical methods

Benzotriazole was analyzed in the concentrated samples after solid-phase extraction with 60 mg hydrophilic–lipophilic balance (HLB) cartridges from *WATERS Oasis®*. Diuron (DI) used as the internal standard was added to each sample at a concentration of 0.5 μM before extraction. After extraction, BT as well as DI was analyzed with a Waters Alliance 2695 separation module equipped with a 2487 Dual λ absorbance detector and a C8 column Supelco (5 μm 250 mm × 4.6 mm). The detection was performed

for BT and DI at 275 and 250 nm, respectively. The mobile phase was a methanol/water mixture (acidified with acetic acid 0.1%). Depending on the compounds and experiments, isocratic or gradient elutions were used with a varying eluent ratio. The elution flow rate was 1 mL min^{-1} and the injection volume was 100 μL. Persulfate was determined by using the Alcian blue colorimetric method developed by Villegas et al. [33].
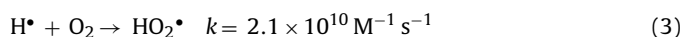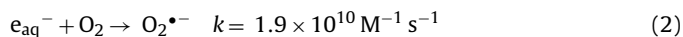
Humic acid was characterized from measurements of UV absorbance, fluorescence, DOC and HPSEC/UV. The UV absorbance at 254 nm was measured with a spectrophotometer SAFAS UV-Visible 320. The excitation–emission matrix (EEM) fluorescence spectra were obtained by using a Jobin Yvon Spex FluoroMax-3 scanning fluorometer equipped with a xenon lamp as an excitation source. Excitation and emission slit widths of 4 nm were used. 3D-EEM spectra were obtained by measuring the emission spectra in the range from 300 to 600 nm repeatedly, at the excitation wavelengths from 200 to 450 nm, spaced by 10 nm intervals in the excitation domain. Dissolved organic carbon (DOC) was analyzed using a Shimadzu TOC 5000A analyzer. The analyses by high-pressure size exclusion chromatography with UV detection (HPSEC/UV) were performed on BioSep SEC-S 2000 column (300 mm × 7.8 mm) coupled with a UV-visible detector WATERS 2487 at 254 nm (flow rate: 1 mL min^{-1}, mobile phase: 10 mM CH$_3$COONa, adjusted to pH 7 with acetic acid, ionic strength 0.1 M).

3. Results and discussion

Irradiation of pure water by ionizing radiations results in the formation of various species according to the following Eq. (1) [34]:
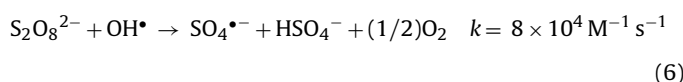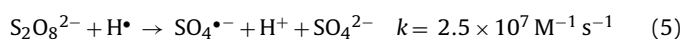
$$H_2O \rightsquigarrow (0.27)OH^\bullet + (0.27)e_{aq}^- + (0.06)H^\bullet + (0.27)H^+$$
$$+ (0.045)H_2 + (0.07)H_2O_2 \tag{1}$$
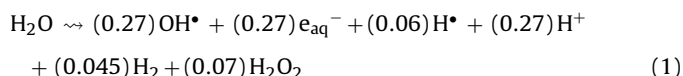
The values in brackets (G) are the number of moles of molecules or radicals produced per J absorbed energy (in μmol/J) and represent the efficiency of the conversion of the high energy electron radiation to a chemical process. Among the chemical species formed during the radiolysis of water, the hydroxyl radical (OH$^\bullet$), hydrated electron (e_{aq}^-) and hydrogen atom (H$^\bullet$) are the most reactive species with organic compounds. In aerated solution, the dissolved oxygen concentration is approximately 3×10^{-4} M (9.4 mg/L). In this case, solvated electrons (e_{aq}^-) and hydrogen atoms (H$^\bullet$) are practically scavenged by oxygen and rapidly converted into O$_2^{\bullet-}$ and HO$_2^\bullet$, respectively [35], which are very poor reacting species compared to the hydroxyl radical (Eqs. (2) and (3)) [36].

$$e_{aq}^- + O_2 \rightarrow O_2^{\bullet-} \quad k = 1.9 \times 10^{10} \, M^{-1} \, s^{-1} \tag{2}$$

$$H^\bullet + O_2 \rightarrow HO_2^\bullet \quad k = 2.1 \times 10^{10} \, M^{-1} \, s^{-1} \tag{3}$$

The irradiation of aqueous solutions of persulfate leads to the formation of sulfate radicals from the reaction with the solvated electrons Eq. (4) produced by the radiolysis of water [24,37].

$$S_2O_8^{2-} + e_{aq}^- \rightarrow SO_4^{\bullet-} + SO_4^{2-} \quad k = 1.1 \times 10^{10} \, M^{-1} \, s^{-1} \tag{4}$$
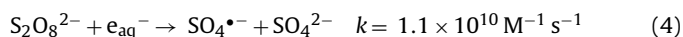
The sulfate radical is also formed by the reaction of persulfate with the H radical (Eq. (5)) or the OH$^\bullet$-radical (Eq. (6)). The kinetic of these reactions is much slower [38].

$$S_2O_8^{2-} + H^\bullet \rightarrow SO_4^{\bullet-} + H^+ + SO_4^{2-} \quad k = 2.5 \times 10^7 \, M^{-1} \, s^{-1} \tag{5}$$

$$S_2O_8^{2-} + OH^\bullet \rightarrow SO_4^{\bullet-} + HSO_4^- + (1/2)O_2 \quad k = 8 \times 10^4 \, M^{-1} \, s^{-1}$$
$$\tag{6}$$

In aqueous solution the water molecules and the hydroxide ions (OH$^-$) can consume the sulfate radical. Under these conditions the

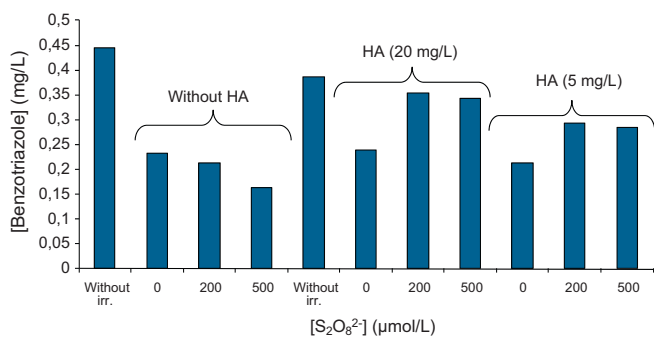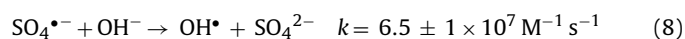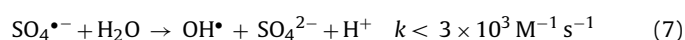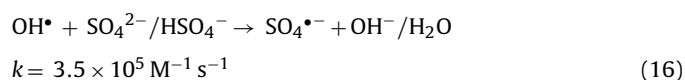**Fig. 1.** Degradation of BT at 15 Gy in deionized water in the absence and presence of HA (20 and 5 mg/L) and in the absence and presence of $S_2O_8^{2-}$ (200–500 μM), pH = 7.2.

sulfate radicals are converted to hydroxyl radicals (OH•) according to Eqs. (7) and (8) [39].

$$SO_4^{\bullet-} + H_2O \rightarrow OH^{\bullet} + SO_4^{2-} + H^+ \quad k < 3 \times 10^3 \, M^{-1} \, s^{-1} \tag{7}$$

$$SO_4^{\bullet-} + OH^- \rightarrow OH^{\bullet} + SO_4^{2-} \quad k = 6.5 \pm 1 \times 10^7 \, M^{-1} \, s^{-1} \tag{8}$$

The following Eqs. (9)–(16) represent the main reactions that occur immediately after the formation of $SO_4^{\bullet-}$ by either one of Eqs. (4)–(6) [31,37,38].

$$SO_4^{\bullet-} + OH^{\bullet} \rightarrow HSO_4^- + (1/2)O_2 \quad k = 1 \times 10^9 \, to \, 1 \times 10^{10} \, M^{-1} \, s^{-1} \tag{9}$$

$$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet-} \quad k = 6 \times 10^4 \, M^{-1} \, s^{-1} \tag{10}$$
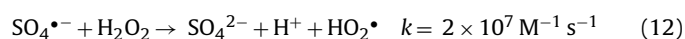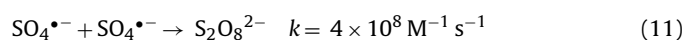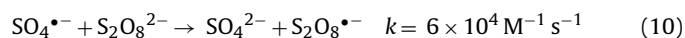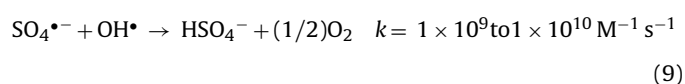
$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \quad k = 4 \times 10^8 \, M^{-1} \, s^{-1} \tag{11}$$

$$SO_4^{\bullet-} + H_2O_2 \rightarrow SO_4^{2-} + H^+ + HO_2^{\bullet} \quad k = 2 \times 10^7 \, M^{-1} \, s^{-1} \tag{12}$$

$$SO_4^{\bullet-} + HO_2^{\bullet} \rightarrow SO_4^{2-} + H^+ + O_2 \quad k = 3.5 \times 10^9 \, M^{-1} \, s^{-1} \tag{13}$$

$$SO_4^{\bullet-} + H^{\bullet} \rightarrow SO_4^{2-} + H^+ \quad k = 1 \times 10^{10} \, M^{-1} \, s^{-1} \tag{14}$$

$$SO_4^{\bullet-} + e^- \rightarrow SO_4^{2-} \quad k < 1 \times 10^6 \, M^{-1} \, s^{-1} \tag{15}$$

$$OH^{\bullet} + SO_4^{2-}/HSO_4^- \rightarrow SO_4^{\bullet-} + OH^-/H_2O$$
$$k = 3.5 \times 10^5 \, M^{-1} \, s^{-1} \tag{16}$$
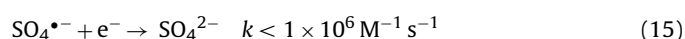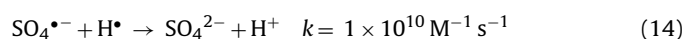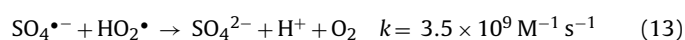
The sulfate radical is one of the strongest oxidizing species with a redox potential estimated to be 2.6 V, similar to that of the hydroxyl radical (2.7 V). It leads to the degradation of many organic and inorganic compounds. In the oxidation processes, the sulfate ions will be generated as the end-product, leading to an increase in salt content in the effluent. The SO_4^{2-} ion is practically inert and is not considered to be a pollutant; the USEPA has listed it under the secondary drinking water standards with a maximum concentration of 250 mg/L, based on aesthetic reasons.

3.1. Effect of persulfate on the degradation of BT in deionized water in the presence and absence of humic acid

The degradation of BT in deionized water was studied and the effect of persulfate addition was examined. Three series of irradiation experiments were performed at a fixed dose (15 Gy) for the elimination of BT in the absence and presence of HA (5 and 20 mg/L) with different concentrations of $S_2O_8^{2-}$ (200–500 μM). As shown previously [31], in the absence of HA, the presence of persulfate allows a significant increase of the removal of BT (Fig. 1). However in deionized water containing humic acid the presence of persulfate inhibits the degradation of BT. Indeed, while the concentration of HA increases, the degradation of BT is more inhibited. This was
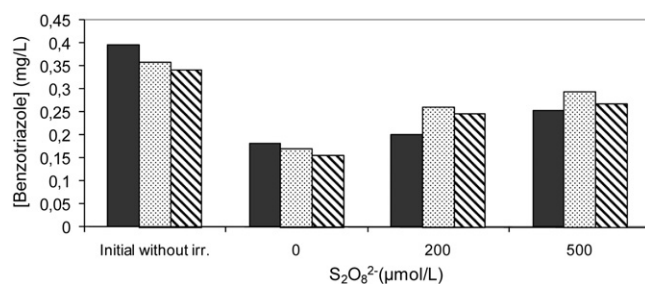
observed only in the presence of persulfate. The repeatability of BT degradation at 15 Gy was conducted in deionized water in the presence of HA (5 mg/L) and persulfate (200–500 μM). The results presented in Fig. 2 show that the three experiments are very close despite the step of solid phase extraction of BT. Fig. 2 shows a good repeatability and reproducibility of the experiments.

3.2. Degradation of BT in the presence of HA and pre-oxidized HA

In order to understand the results obtained (Figs. 1 and 2) and given the complexity of the humic acid structures, the system was studied in the presence of HA with characteristics modified by irradiation. After pre-oxidation of HA solutions at doses of 1.5 and 3 kGy, the BT was introduced into the solution to be irradiated at 15 Gy in the absence and presence of persulfate. Data in Fig. 3 show that the degradation of BT is more effective when HA is pre-oxidized. The presence of persulfate also plays an important role in the degradation of BT. The addition of persulfate (500 μM) to the solutions of HA pre-oxidized at 1.5 and 3 kGy increases the degradation of BT by 72% and 30%, respectively compared to the results without persulfate addition. On the contrary, in the presence of non-oxidized HA, without persulfate addition the removal of BT was 54% and the addition of persulfate (500 μM) led to a decrease of the efficiency of BT removal. Without irradiation and in the presence of pre-oxidized HA (5 mg/L) and persulfate (500 μM), the abatement of BT was lower than 12% after 160 min contact time (not presented).

4. Modification of humic acid by irradiation

4.1. UV spectroscopy of non-oxidized and oxidized humic acid

The change in the UV spectra of non-oxidized HA and HA oxidized at 1.5 kGy was examined in the range of wavelengths of 200–600 nm. The absorption spectra of non-oxidized and oxidized

Fig. 2. Reproducibility of BT degradation at 15 Gy in deionized water in the presence of HA (5 mg/L) and in the absence and presence of $S_2O_8^{2-}$ (200–500 μM), pH = 7.2.
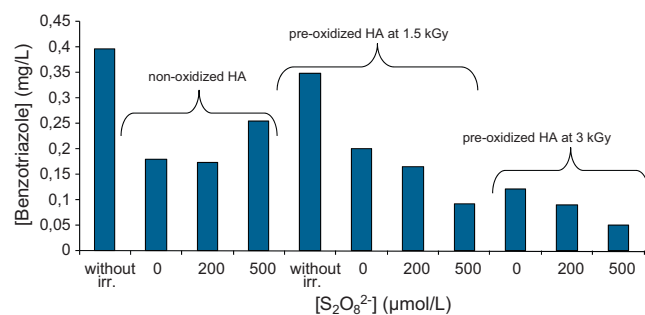

Fig. 3. Degradation of BT at 15 Gy in deionized water in the presence of non-oxidized and oxidized HA (5 mg/L) in the absence and presence of $S_2O_8^{2-}$ (200–500 μM), pH = 7.2.
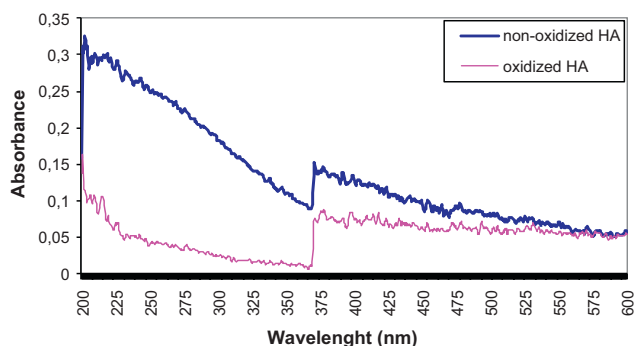
Fig. 4. The absorption spectra of non-oxidized and oxidized (1.5 kGy) humic acid ([HA] = 5 mg/L).

humic acid are shown in Fig. 4. The unsaturated bonds (double bonds and aromatic cycles) in the natural organic matter generate a characteristic UV spectrum [40]. A major difference between non-oxidized and oxidized HA was observed in the range of UV absorbance from 200 to 375 nm. Fig. 4 shows that the non-oxidized HA absorbs more UV photons. When the solution of HA was irradiated at a high dose (1.5 kGy), the absorbance of oxidized HA strongly drops. The decrease of the absorbance values is characteristic of compounds with small size and low molecular weight, resulting from oxidation [41,42]. Then, the analysis by HPSEC/UV was performed.

4.2. The impact of oxidation on the size distribution of humic acid

The separation mode is based on the method described by Vartiainen et al. [43]. The retention time is inversely proportional to the size of the components. The analysis by HPSEC/UV was carried out for two solutions containing HA, i.e. non-oxidized and oxidized at the dose of 1.5 kGy. Fig. 5 presents the HPSEC/UV chromatograms. The chromatogram of the non-oxidized HA exhibits a very intense peak at t_R = 9 min, corresponding to the presence of the chromophoric fractions of humic acid characterized by a high molecular weight generally assigned to aromatic components with functional groups absorbing the UV light at 254 nm. The chromatogram of the oxidized HA shows a reduction of the peak height at t_R = 9 min as a result of the breaking of the high molecular weight compounds with formation of smaller molecules (shift of the peak towards 10 min). Similarly, at t_R = 11 min a decrease of the peak height is observed and a small peak appears at t_R = 12 min in the oxidized HA sample. This peak corresponds to a low molecular weight, indicating again a decomposition or a transformation into molecules with a lower weight.
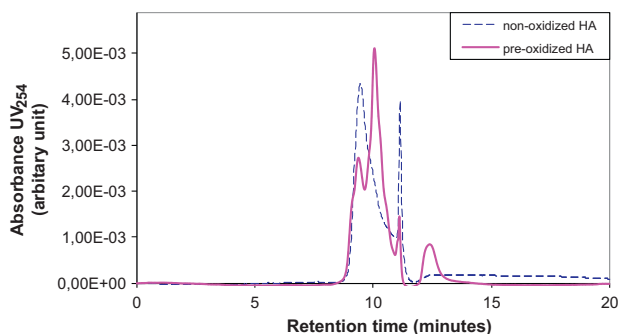

Fig. 5. HPSEC/UV chromatograms of the solutions of non-oxidized HA (5 mg/L) and oxidized HA at 1.5 kGy.

4.3. Fluorescence spectroscopy of non-oxidized and oxidized humic acid

Over the past few decades fluorescence spectroscopy has been widely used mainly to characterize and/or discriminate humic substances of different origins and naturally occurring organic matter [44]. The fluorescence spectra of HA non-oxidized and oxidized at 1.5 kGy are illustrated in Fig. 6a and b, respectively. As shown in Fig. 6a a large region of fluorescence intensity of the humic acid can be distinguished. This region is centered on excitation and emission wavelengths of about Ex/Em = 260/510 nm and corresponds to the UV hydrophobic humic-like fluorophores [44]. As shown in Fig. 6b, the intensity of this region decreased significantly after the oxidation of HA. The results obtained are in agreement with the HPSEC/UV analyses indicating a decomposition or transformation of the original structures of the humic acid by the e-beam irradiation.

4.4. The influence of persulfate on the transformation of HA by irradiation

Specific UV absorbance at 254 nm (i.e. SUVA that corresponds to the UV_{254} to DOC ratio expressed in $m\,L\,mg^{-1}$) is commonly used as a surrogate parameter for the aromatic content of NOM and can be used to describe the hydrophobic or hydrophilic nature of organic matter. Therefore, high SUVA values generally indicate the hydrophobic properties of high molecular weight aromatic compounds such as humic substances. The hydrophilic fractions generally have a lower specific UV absorbance than the hydrophobic fractions. According to Edzwald and Tobiason [45] SUVA values of 4 and higher indicate a relatively high content of hydrophobic, aromatic, and high molecular weight, humic acid fractions. For SUVA ratios in the range of 2–4, NOM is normally dominated by a mixture of hydrophobic and hydrophilic fractions of different molecular weights. For raw waters with SUVA below 2, NOM is mostly dominated by non-humic substances with low molecular weight and weakly hydrophobic. The results obtained for low and high radiation doses (15 Gy and 1.5–3.0 kGy, respectively) are presented in Table 1. As expected, the SUVA values of the initial samples range between 5.6 and 8.1 in agreement with the high aromatic content and the hydrophobic fractions of the humic acid.

The small radiation dose of 15 Gy that eliminates the BT has no effect on the humic acid transformation as presented in Table 1. Contrary, higher doses (1.5 and 3 kGy) in the absence of persulfate cause a low abatement of DOC (0.1–0.5 mg/L) and an important reduction of UV_{254} absorbance (60–70%). Consequently, an important abatement of SUVA was observed for the high doses. The SUVA values after irradiation at 1.5 and 3 kGy were decreased to 3.3 and 2.8 (corresponding to hydrophilic properties) from the initial values of 8.1 and 5.6, respectively. The decrease of the UV absorbance and the SUVA testifies the structure change of HA, namely the transformation of aromatic groups to aliphatic groups, which absorb very little at 254 nm wavelength. As shown in Table 1, similar changes are observed in the presence of persulfate. The presence of persulfate seems to have no influence on the transformation of HA for low and high doses.

5. Degradation of BT in the presence of model molecules

The characterization of HA by UV, HPSEC and SUVA indicated that the oxidation by e-beam irradiation tends to transform the aromatic structures of HA into aliphatic groups. The changes of the HA properties could be responsible for the differences of the removal of BT in the presence of persulfate depending on whether HA are oxidized or not. To verify this hypothesis, salicylic acid was selected
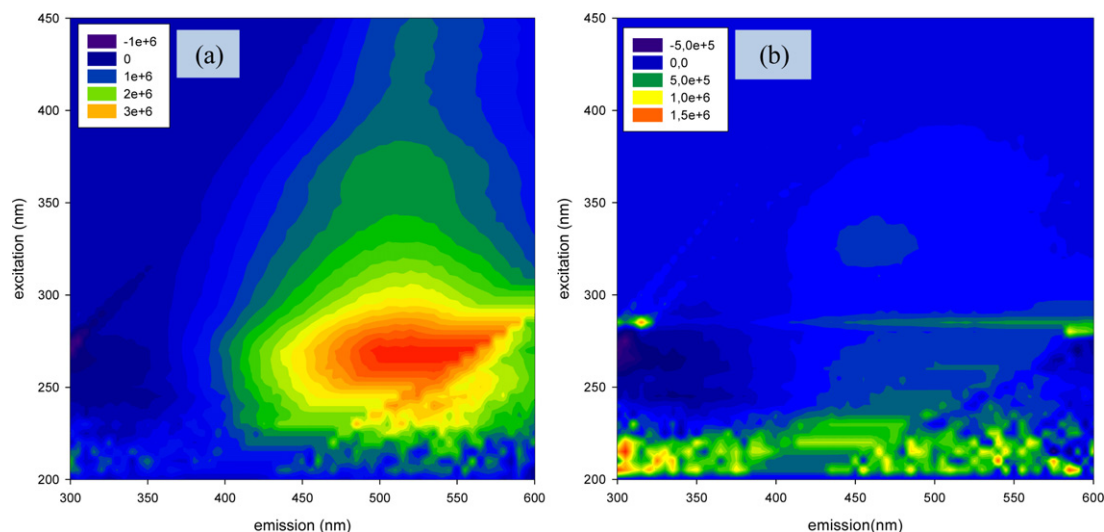
Fig. 6. (a) and (b) The fluorescence spectra of non-oxidized HA and oxidized at 1.5 kGy.

Table 1
The influence of irradiation on parameters of UV$_{254\,nm}$ absorbance of filtered and unfiltered samples, dissolved organic carbon (mg/L) and SUVA (L/mg m).

S$_2$O$_8$$^{2-}$	Initial				15 Gy			
	DOC	UVf	UVw/of	SUVA	DOC	UVf	UVw/of	SUVA
0 µM	1.72	0.14	0.16	8.14	2.35	0.14	0.15	6
	2.2	0.12	0.14	5.6	2	0.12	0.14	6.4
200 µM	2.12	0.16	0.16	7.5	1.95	0.13	0.15	6.7
	2	0.12	0.14	6.4	1.43	0.12	0.14	8.3
500 µM	2.25	0.14	0.16	6.4	2	0.12	0.15	6.2

S$_2$O$_8$$^{2-}$	1.5 kGy				3 kGy			
	DOC	UVf	UVw/of	SUVA	DOC	UVf	UVw/of	SUVA
0 µM	1.62	0.05	0.08	3.3	–	–	–	–
	–	–	–	–	1.74	0.05	0.08	2.8
200 µM	2.67	0.05	0.07	1.9	–	–	–	–
	–	–	–	–	1.99	0.05	0.07	2.6
500 µM	1.78	0.04	0.08	2.6	–	–	–	–

UVf: UV 254 nm after filtration (0.45 µM).
UVw/of: UV 254 nm without filtration (in cm^{-1}).

as a model to represent the aromatic group of the non-oxidized HA. Acetic and oxalic acids were chosen to simulate the aliphatic groups of the oxidized HA. Each of these model molecules was introduced separately to constitute the carbon source in the deionized water instead of HA. Their concentration ([salicylic acid] = 0.05 mM; [oxalic acid] = 0.2 mM or [acetic acid] = 0.2 mM) corresponded to the carbon brought by HA (4.2–4.8 mgC/L), that was added in all the previous experiments. The results obtained under these conditions are presented in Fig. 7. For the salicylic acid concentration of 0.05 mM, a very low elimination of BT was observed, in the presence or in the absence of persulfate. In fact, the rate constant of salicylic acid with hydroxyl radical (k_{OH}/salicylic = 1.6 × 10^{10} M^{-1} s^{-1} [37]) is very high compared to the rate constant of acetic acid and oxalic acid (k_{OH}/acetic = 8.5 × 10^7 M^{-1} s^{-1}, k_{OH}/oxalic = 7.7 × 10^6 M^{-1} s^{-1} [37]). As a consequence, it is probable that the OH$^\bullet$ radicals formed (but also the SO$_4$$^{\bullet-}$ radicals) will react preferably with salicylic acid instead of reacting with BT. Even in the presence of a lower concentration of salicylic acid (0.001 mM) that does not provoke a total scavenging effect (Fig. 7), the addition of S$_2$O$_8$$^{2-}$ ions in the presence of this model compound did not increase significantly the efficiency of BT removal. This behavior is close to the results observed with non-oxidized HA. In the presence of acetic or oxalic acid, the persulfate addition improves the degradation of BT. The

inhibitory effect of S$_2$O$_8$$^{2-}$ ions was not observed in the presence of these aliphatic structures. It appears that acetic and oxalic acids have the same behavior as oxidized HA.

An explanation can be found taking into consideration the species present in the system. The reactivity of the active species (the OH-radicals and the solvated electrons) generated from the
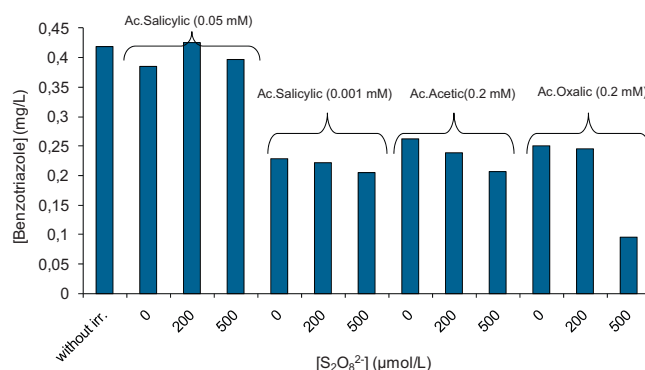

Fig. 7. Degradation of BT at 15 Gy in deionized water in the presence of model molecules, pH = 7.6.

water radiolysis depends on the structure of the molecules and functional groups. The reactivity of the solvated electrons is generally more important towards the aromatic compounds than the aliphatic compounds. Therefore, competition reactions may occur between the aromatic structures of HA and the persulfate ions towards the solvated electrons leading to a low production of sulfate radicals. It would result in an inhibition of the positive effect of the addition of the $S_2O_8^{2-}$ ions. In the presence of pre-oxidized HA, the lower reactivity of the aliphatic groups towards the solvated electrons would decrease the competition phenomenon, resulting to a higher production of sulfate radicals and hence a better degradation of BT.

6. Conclusions

In the e-beam irradiation process, the addition of $S_2O_8^{2-}$ ions can advantageously promote the removal of pollutants in aqueous solutions as a result of the production of the $SO_4^{\bullet-}$ radicals from the reactions with the solvated electrons. This was observed from the study of the removal of BT in pure water and in the presence of oxalic, acetic acids or pre-oxidized HA. However, in the presence of aromatic structures like salicylic acid or HA, the positive effect of the $S_2O_8^{2-}$ ions does not occur. The knowledge of the structures and physico-chemical properties of the organic components that act as competitors in the reaction system is essential to the estimation of the interest of $S_2O_8^{2-}$ addition and the generation of the $SO_4^{\bullet-}$ radicals for the removal of the target pollutants.

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