

# EB-radiolysis of carbamazepine: in pure-water with different ions and in surface water

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**Abstract** The electron beam (EB) radiolysis characteristics of carbamazepine (CBZ) in pure-water with different ions and that in surface water were studied in this paper. It suggested that the  $\cdot\text{OH}$ ,  $\cdot\text{H}$  and  $e_{\text{aq}}^-$  all played roles on CBZ EB degradation, and the  $\cdot\text{OH}$  played the vital role. Acidic solution was favorable for CBZ degradation, while alkaline environment inhibited it.  $\text{HSO}_4^-$  and  $\text{SO}_3^{2-}$  enhanced the CBZ degradation, but  $\text{CO}_3^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{Cl}^-$  inhibited. In surface water, the EB-radiolysis was an effective way to degrade CBZ; and CBZ might evolve in three different ways during EB radiation: reduction by  $e_{\text{aq}}^-$  and  $\cdot\text{H}$  (intermediate 10,11-dihydrocarbamazepine (I)), oxidation by  $\cdot\text{OH}$  (intermediates 10,11-dihydro-10-11-epoxycarbamazepine (II) and 2(3)-hydroxycarbamazepine (III)) and hydration into 10,11-dihydro-10-hydroxycarbamazepine (IV) and finally the intermediates were all mineralized into  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$  and  $\text{NH}_4^+$ . All the results contribute to study the EB-radiolysis of pharmaceuticals in surface water.

**Keywords** Carbamazepine (CBZ) · Electron beam radiolysis · Ions · Surface water

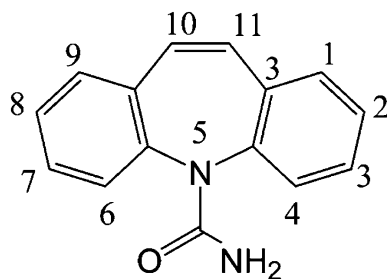
## Introduction

Carbamazepine (CBZ), the structure was shown in Fig. 1, a widely consumed psychotropic pharmaceutical, was one of the most commonly detected persistent pharmaceuticals in the environment [1]. It could widely impact the surface water and groundwater because of its widespread detection in wastewaters (up to  $6.3 \mu\text{g L}^{-1}$ ), surface waters (up to  $1.1 \mu\text{g L}^{-1}$ ), and drinking water ( $30 \text{ ng L}^{-1}$ ) [2, 3]. It is refractory to both conventional and advanced wastewater treatment processes [4, 5]. In fact, CBZ led a great impact on organisms, for instance, plants causing bioaccumulation in aquatic organisms and inhibiting the growth and morphology of human embryonic cells mixed with other pharmaceuticals. In addition, it could also restrain predator avoidance of fish when it caused synergy with antidepressants [5].

Transformation of CBZ by different methods have been reported, such as biotechnology [6–9] and oxidation technique (ozonation [10], direct photolysis [11],  $\text{TiO}_2$  caused photocatalytic degradation [12], UV treatment [13] and  $\text{UV}/\text{H}_2\text{O}_2$  degradation [14]). However, the removal efficiency of CBZ was very low by biotechnology [15, 16] or abundant transformation products (TPs) (i.e. hydroxycarbamazepone, acridine, acridone, aminobenzoic) were produced from above biochemistry treatment. Even resorting to the collaboration of them such as enhanced biodegradation of carbamazepine after  $\text{UV}/\text{H}_2\text{O}_2$  advanced oxidation [5], the operations were multi-step and cumbersome. The electron beam (EB) radiation technology, one of the AOPs [17], is an efficient, safe, simple and completely mineralized method and has showed great promise during the last three decades for efficient treatment of organic pollutants, especially for the thorough decomposition of biorefractory compounds [18–23].

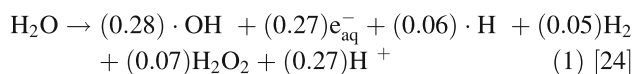
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**Fig. 1** Molecular structure of 5H-dibenzo[b, f]azepine-5-carboxamide (Carbamazepine)

As shown in reaction (1), water is degraded into hydroxyl free radical ( $\cdot\text{OH}$ ), hydrogen free radical ( $\cdot\text{H}$ ), and hydrated electron ( $e_{\text{aq}}^-$ ) with different G-values ( $\mu\text{mol J}^{-1}$ ) under EB irradiation. The radicals can react with the pollutants and caused its degradation [17, 20]. The  $\cdot\text{OH}$  has a strong oxidative ability with oxidation potential ( $E_0 = 2.8 \text{ V}$ ), and it can efficiently oxidize the organic compounds in aqueous solutions, while  $e_{\text{aq}}^-$  and  $\cdot\text{H}$  can reduce the targeted organic and  $e_{\text{aq}}^-$  has a strong reductive ability ( $E_0 = -2.9 \text{ V}$ ) [17].



The surface water contained a variety of constituents, such as ions, dissolved organic matter (DOM) and suspended solids (SS); therefore, it is necessary to study the effects of these different constituents on CBZ degradation during EB radiation. Thus, the influence of different ions, such as  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{HSO}_4^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  on CBZ EB radiolytic degradation were investigated in this paper. Then, the degradation characteristics of CBZ in surface water were studied. Finally, a probable degradation pathway of CBZ EB-radiolysis was proposed. This study (such as the function of hydroxyl radicals) gave some assistance to the investigation on disposal of other pharmaceuticals in surface water, even photocatalysis of drugs in water, generally  $\cdot\text{OH}$  played a vital role in the degradation.

## Materials and methods

### Materials

CBZ (>98 %), methanol (HPLC grade), and acetonitrile (LCMS grade) were obtained from Sigma-Aldrich. Formic acid ( $\text{HCOOH}$ ), acetic acid ( $\text{CH}_3\text{COOH}$ ), oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ), malonic acid ( $\text{COOHCH}_2\text{COOH}$ ), succinic acid ( $\text{COOH}(\text{CH}_2)_2\text{COOH}$ ),  $\text{NaCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,

$\text{Na}_2\text{SO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaHSO}_4$ ,  $\text{NaNO}_2$ , and  $\text{NaNO}_3$  were all purchased from Shanghai Chemical Reagent Co. Ltd. All chemicals were of analytical grade unless otherwise stated. The pure-water used in the experiments was prepared by filtering through a Millipore Milli-Q system (resistance >18.2 M $\Omega$ ). The surface water was collected from a local river and the 0.45  $\mu\text{m}$  filters were used to filter the surface water. All experiments were performed at room temperature.  $\text{NaCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaHSO}_4$ ,  $\text{NaNO}_2$ , and  $\text{NaNO}_3$  all were dissolved into 5 mM.

All samples were pouched in high density polyethylene (HDPE) bags. They were saturated with  $\text{N}_2$  to expel air firstly and then sealed after exhausting  $\text{N}_2$ . Before the experiment we had used IC and LC/MS/MS to determine whether any intermediates were produced from HDPE bags which contained pure-water when they were irradiated under different doses (from 0.5 to 20 kGy). The results showed there were no transformation products. Therefore, HDPE could be used to pack sample solutions.

### Irradiation conditions

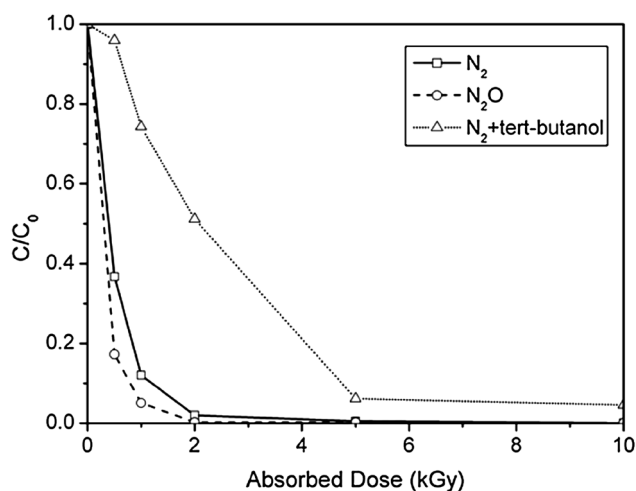
The samples were irradiated at ambient temperatures by 1.8 MeV and variable current (0–10 mA) EB from GJ-2-II electron accelerator (Shanghai Xianfeng electrical plant, China). The samples were placed in radiation field about 30 cm away from the radiation source, and the absorbed doses were at 0.5, 1, 2, 3, 5, 10 or 20 kGy.

### Analytical methods

A high performance liquid chromatography (HPLC, Agilent 1200 series), consisted of C18 column (150  $\times$  4.6 mm) and an auto-sampler with 10  $\mu\text{L}$  volume injection, was used to detect CBZ concentration at 230 nm by a VWD detector. The mobile phase was a mixture of methanol and water (55:45, v:v) at rate of 1.0 mL  $\text{min}^{-1}$ .

Organic acids, nitrate ion ( $\text{NO}_3^-$ ) and nitrite ion ( $\text{NO}_2^-$ ) produced from CBZ EB-radiolysis were detected by ICS1100 (Dionex). A hydrophilic anion exchange column was IonPac As22 (analytical, 4  $\times$  250 mm). The eluent was mixed with 4.5 mM  $\text{Na}_2\text{CO}_3$  and 1.4 mM  $\text{NaHCO}_3$  at 1.20 mL  $\text{min}^{-1}$  flow rate and the injection volume was 25  $\mu\text{L}$ . The suppressor was Anion Self-Regenerating Suppressor (ASRS 300 4 mm) under AutoSuppression Recycle Mode and its applied Current was 31 mA.

The other by-products of CBZ were monitored by LC/MS/MS using an Agilent 1260 LC chromatograph coupled to an Agilent 6460 mass spectrometer with electron spray ionization (ESI) interface and a heated nebulizer. A Porshell 120 100  $\times$  3 mm EC-C18 end-capped column (2.7  $\mu\text{m}$  particle size) was used, at the flow rate of



**Fig. 2** Effect of  $N_2$ -saturated,  $N_2O$ -saturated and  $N_2$ -saturated with tert-butanol conditions on the degradation of CBZ (75 mg/L) Where C is the residual concentration of CBZ in mg/L,  $C_0$  (mg/L) is the initial concentration of CBZ before EB radiation

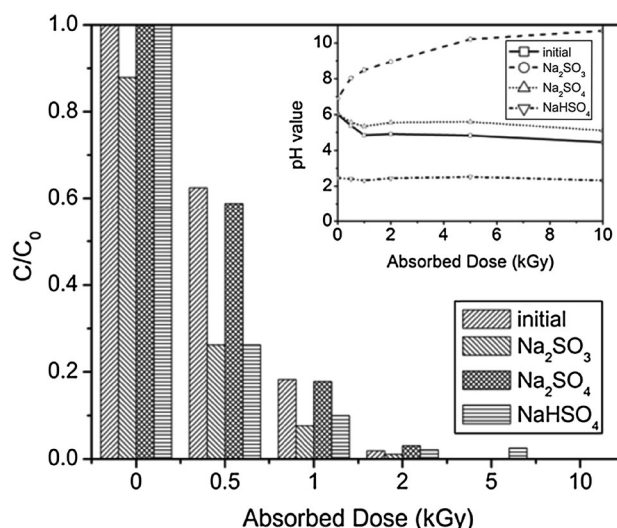
0.4 mL min<sup>-1</sup>. The injection volume was 10 μL. The mobile phase was a mixture of acetonitrile (A) and 0.1 % HCOOH in water (B); the gradient was operated from 5 to 95 % A for 8 min, from 95 to 100 % A for 2 min, held at 100 % for 2 min, and back to the initial conditions in 3.5 min. Mass spectrometry full scanning analysis was performed in the range of 50–500 m/z. The positive electron spray ionization (ESI (+)) operating conditions of the source were as follows: capillary voltage, 4000 V; nebulizer pressure, 40 psi; drying gas flow, 8 L min<sup>-1</sup> at a temperature of 300 °C; nozzle voltage, 0 V. The negative electron spray ionization ESI (-) operating conditions of the source were as follow: capillary voltage, 3250 V; nebulizer pressure, 40 psi; drying gas flow, 7 L min<sup>-1</sup> at a temperature of 350 °C; nozzle voltage, 500 V.

## Results and discussion

### Effect of radical scavengers on CBZ degradation

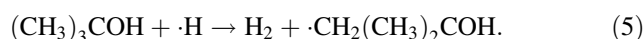
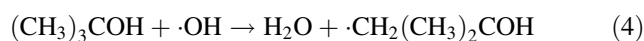
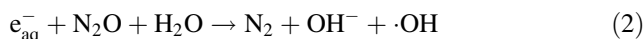
When aqueous solution was irradiated by high-energy electrons, the main active species products,  $\cdot OH$ ,  $e_{aq}^-$  and  $\cdot H$  were generated [6].

In order to investigate which active species played the leading role in the degradation of CBZ, the solution was saturated by  $N_2$ ,  $N_2O$  and 0.317 mol/L tert-butanol with  $N_2$ . As shown in Fig. 2, the higher degradation rate was achieved in  $N_2O$  situated solution, the lower degradation rate happened in  $N_2$  saturated solution containing 0.317 mol/L tert-butanol. When the solution was saturated with  $N_2O$ , the reaction of  $e_{aq}^-$  and  $\cdot H$  with  $N_2O$  forms  $\cdot OH$  active species (reaction (2) and (3)). In  $N_2$  saturated



**Fig. 3** Effect  $Na_2SO_3$ ,  $Na_2SO_4$  and  $NaHSO_4$  on CBZ (75 mg/L) removal and their corresponding evolution of pH with dose in pure-water

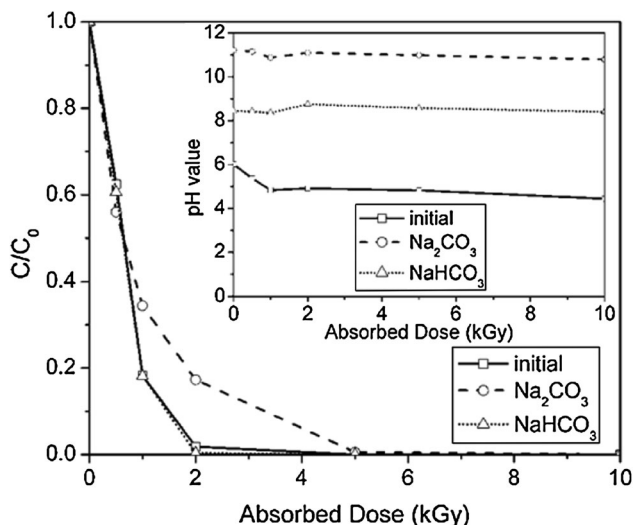
solution,  $\cdot OH$ ,  $e_{aq}^-$  and  $\cdot H$  were all existed and should be considered in the reactions process [17], while in  $N_2$  saturated solution containing 0.317 mol/L tert-butanol,  $e_{aq}^-$  was the main reactive species in the CBZ solutions because in the tert-butanol solution  $\cdot OH$  and  $\cdot H$  are scavenged by tert-butanol (reaction (4) and (5)). It came to the conclusion that  $\cdot OH$ ,  $\cdot H$  and  $e_{aq}^-$  played roles in the CBZ degradation process, and  $\cdot OH$  played the vital role.



### Effect $Na_2SO_3$ , $Na_2SO_4$ and $NaHSO_4$ on CBZ degradation

As shown in Fig. 3, the addition of  $Na_2SO_3$  and  $NaHSO_4$  enhanced the CBZ degradation, while  $Na_2SO_4$  had no effect on the CBZ degradation. In the inset of Fig. 3, the pH value increased in  $Na_2SO_3$  solution, decreased in the initial and  $Na_2SO_4$  solutions and had little change in  $NaHSO_4$  solution during EB radiation.

Generally, sulfite ion ( $SO_3^{2-}$ ) quickly reacts with  $\cdot OH$  ( $k_{SO_3^{2-}/\cdot OH} = 5.5 \times 10^9 M^{-1} s^{-1}$ ) (reaction (6)); therefore,  $SO_3^{2-}$  was recommended as a  $\cdot OH$  scavenger in the EB process [25]. As shown in Fig. 3, when  $SO_3^{2-}$  was added before EB irradiation, the CBZ concentration decreased to 85.4 %. It showed that CBZ could react with  $SO_3^{2-}$  directly before EB irradiation. During EB irradiation, CBZ degraded quickly in  $Na_2SO_3$  solution and the pH value gradually rose to 10.67. Sulfite radical ( $\cdot SO_3^-$ ) is produced (reaction (6)). The  $\cdot OH$  and  $\cdot H$  are decreased while the  $e_{aq}^-$  increases

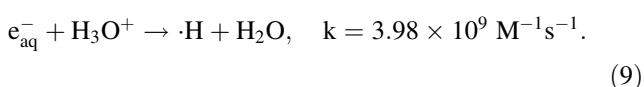
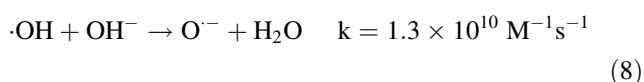
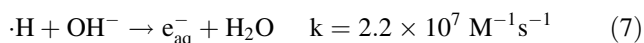
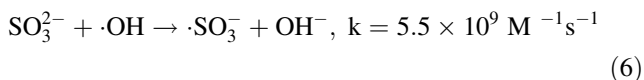


**Fig. 4** Effect of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  on CBZ (75 mg/L) removal and their corresponding evolution of pH with dose in pure-water

(reaction (7)) and the  $\text{O}^-$  occurs (reaction (8)), because of the increase of pH level. Therefore,  $\cdot\text{SO}_3^-$ ,  $e_{\text{aq}}^-$  and  $\text{O}^-$  played roles in decomposition of CBZ in  $\text{Na}_2\text{SO}_3$  solution.

Recently, sulfate radical ( $\cdot\text{SO}_4^-$ ) had received attention because of its high reactivity with organic pollutants such as pharmaceuticals [26–28], but the  $\cdot\text{SO}_4^-$  almost had no effect on CBZ degradation during EB irradiation from Fig. 3.

The enhancement of degradation in  $\text{NaHSO}_4$  solution (pH 2.45 before irradiation) illustrated that the degradation of CBZ was enhanced in acidic solution. Because the  $e_{\text{aq}}^-$  can immediately react with  $\text{H}^+$  to form  $\cdot\text{H}$  (reaction (9)) during EB radiation; therefore,  $\cdot\text{H}$  played a more important role on CBZ degradation than  $e_{\text{aq}}^-$ .



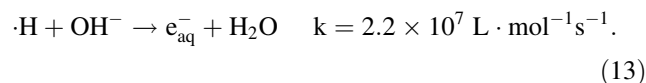
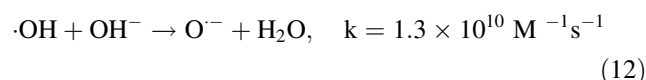
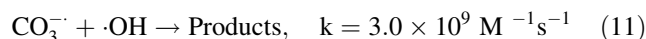
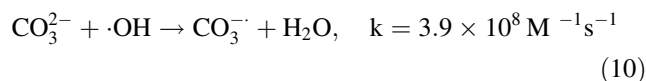
#### Effect of $\text{Na}_2\text{CO}_3$ , $\text{NaHCO}_3$ on CBZ degradation

The experiment about EB-radiolysis of CBZ in solutions with 5 mM  $\text{Na}_2\text{CO}_3$  and 5 mM  $\text{NaHCO}_3$  was performed. As shown in Fig. 4, the curves of initial and  $\text{NaHCO}_3$  almost overlapped, while the lower degradation rate happened in  $\text{Na}_2\text{CO}_3$  solution.

Due to the bicarbonate ion ( $\text{HCO}_3^-$ ) slowly reaction with  $e_{\text{aq}}^-$  ( $k_{\text{HCO}_3^-/e_{\text{aq}}^-} = 1.0 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ ), and  $\cdot\text{OH}$  ( $k_{\text{HCO}_3^-/\cdot\text{OH}} = 8.5 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ ) [29],  $\text{HCO}_3^-$  had a bit effect on CBZ

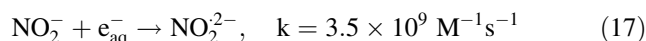
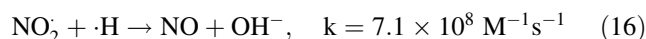
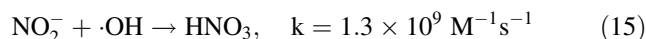
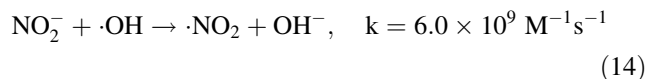
degradation [20]. However, the carbonate ion ( $\text{CO}_3^{2-}$ ) had a large suppression on CBZ degradation, as it slowly reacts with  $e_{\text{aq}}^-$  ( $k_{\text{CO}_3^{2-}/e_{\text{aq}}^-} = 3.9 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ ), whereas quickly reacts with  $\cdot\text{OH}$  (reaction (10), (11)) [24]. Therefore,  $\text{CO}_3^{2-}$  was regarded as a suitable  $\cdot\text{OH}$  scavenger in the EB irradiation process [30] and It was further demonstrated that  $\cdot\text{OH}$  was very important on CBZ degradation.

In the inset of Fig. 4, the initial pH value of  $\text{NaHCO}_3$  solution was 8.43 and the initial pH value of  $\text{Na}_2\text{CO}_3$  was 11.21. Both of them had little decrease during EB radiation. The inhibition in  $\text{Na}_2\text{CO}_3$  alkaline solution might be also partly due to the elimination of  $\cdot\text{OH}$  and  $\cdot\text{H}$  by  $\text{OH}^-$  (reaction (12) and (13)) [24]. This result further illustrated that  $\cdot\text{OH}$  and  $\cdot\text{H}$  played an important role on CBZ degradation and the degradation rate of CBZ was inhibited in alkaline solution.



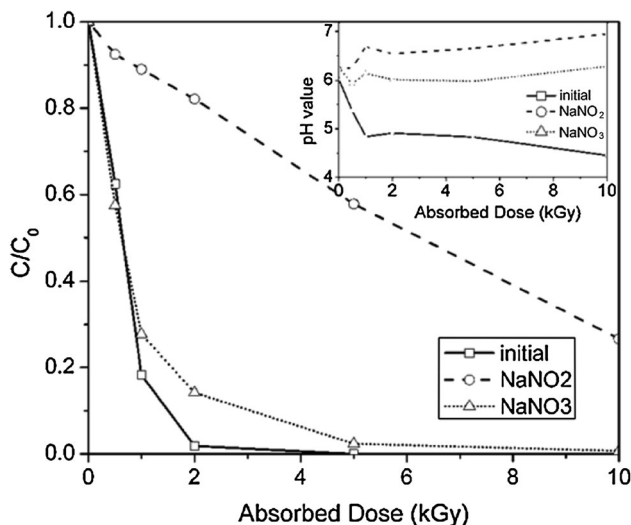
#### Effect of $\text{NaNO}_2$ , $\text{NaNO}_3$ on CBZ Degradation

As shown in Fig. 5, it caused a huge depression on CBZ degradation in  $\text{NaNO}_2$  solution. It could be attributed to the decrease of  $\cdot\text{OH}$ ,  $\cdot\text{H}$  and  $e_{\text{aq}}^-$  by  $\text{NO}_2^-$ , as shown in reaction (14)–(17) [31] in EB-radiolysis process.



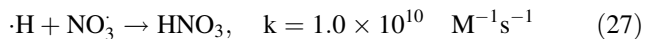
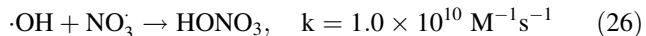
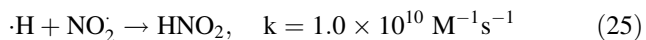
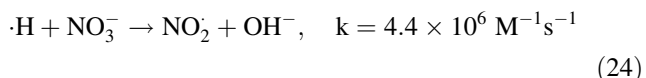
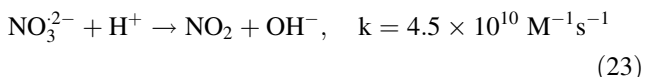
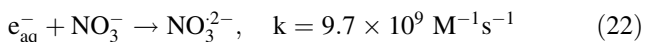
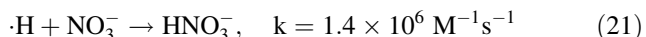
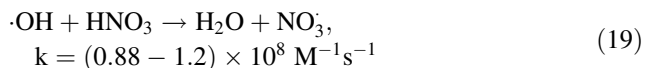
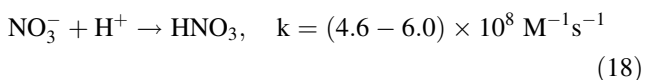
The degradation rate of CBZ in  $\text{NaNO}_3$  solution was decreased during EB radiation, because  $\text{NO}_3^-$  ion acts as a scavenger of  $\cdot\text{OH}$ ,  $\cdot\text{H}$  and  $e_{\text{aq}}^-$  radicals (reactions (18)–(27)) [31] which played roles in CBZ degradation rate. Although the rate constant is lower with  $\text{HO}\cdot$  radical  $k = (0.88 - 1.2) \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ ,  $\text{NO}_3^-$  could inhibit the CBZ degradation when  $\text{NO}_3^-$  concentrations was high, just as Velo et al. and Ocampo-Pérez et al. illustrated the decrease of diatrizoate and cytarabine degradation rates occurred when high  $\text{NO}_3^-$  concentrations (about 5 mM) were added [31, 32].

The effect of  $\text{NO}_2^-$  on the CBZ degradation constant was more marked in comparison to the  $\text{NO}_3^-$ , because the



**Fig. 5** Effect of NaNO<sub>2</sub> and NaNO<sub>3</sub> on CBZ (75 mg/L) removal and their corresponding evolution of pH with dose in pure-water

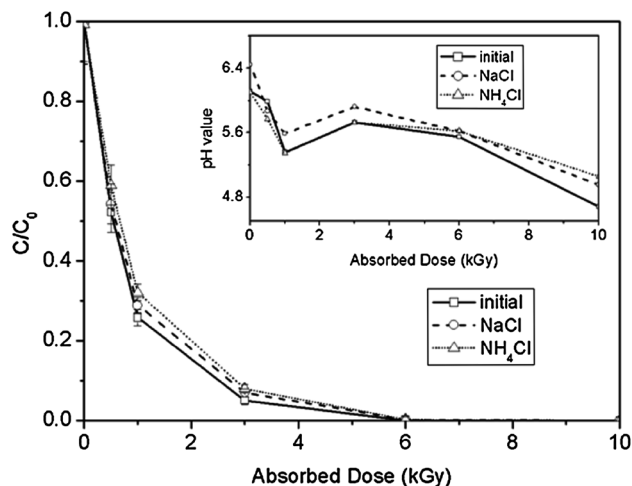
rate constant is of a higher order of magnitude for the ·OH than for NO<sub>3</sub><sup>-</sup>,  $k = 6.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$



As showed the inset of Fig. 4, pH value had a little increase (to 6.95) in both NaNO<sub>2</sub> and NaNO<sub>3</sub> solutions. It was explained that the H<sup>+</sup> (reaction (1)) from the irradiation of H<sub>2</sub>O is eliminated by OH<sup>-</sup> (reactions (14), (16)) in NaNO<sub>2</sub> solution and reactions (18), (23) and (24) in NaNO<sub>3</sub> solution.

**Effect of NaCl & NH<sub>4</sub>Cl on CBZ degradation**

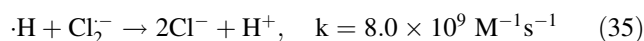
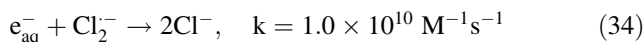
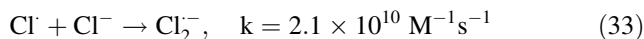
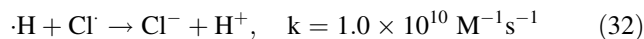
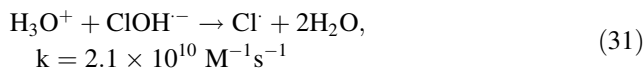
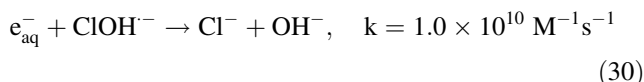
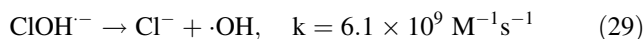
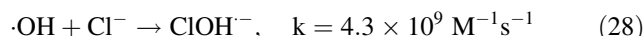
As shown in Fig. 6, sodium ion (Na<sup>+</sup>) didn't impact on the decrease of CBZ within 10 kGy, while chloride ion (Cl<sup>-</sup>) and ammonium ion (NH<sub>4</sub><sup>+</sup>) had a little inhibition on CBZ



**Fig. 6** Effect of NaCl and NH<sub>4</sub>Cl on CBZ (75 mg/L) removal and their corresponding evolution of pH with dose in pure-water

degradation. As the study of Ocampo-Pérez et al. [1] showed, Cl<sup>-</sup> can eliminate ·OH (reaction (28)) while the radical formed (ClOH·<sup>-</sup>) may again form the ·OH radical (reaction (29), and may react with e<sub>aq</sub><sup>-</sup> or H<sub>3</sub>O<sup>+</sup>, forming the Cl· (reactions (30) and (31)), which contributed to remove H· and e<sub>aq</sub><sup>-</sup> from the medium (reactions (32)–(35)). Therefore, the slight inhibition could be explained that the reaction with HO· is a reversible reaction and the Cl<sup>-</sup> removes H· and e<sub>aq</sub><sup>-</sup> from the medium. Apart from the effect of Cl<sup>-</sup>, the existence of NH<sub>4</sub><sup>+</sup> in solution might also inhibit the degradation of CBZ because NH<sub>4</sub><sup>+</sup> could produce from CBZ degradation under EB irradiation which would be illustrated below.

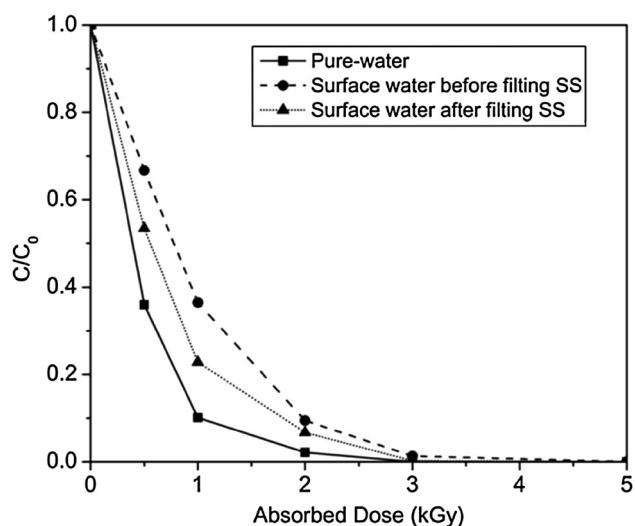
As shown in the inset of Fig. 6, the pH values of initial, NaCl and NH<sub>4</sub>Cl had little difference.



**CBZ degradation in surface water**

As shown in Fig. 7, more than 99 % of CBZ was removed from the surface water with or without the suspended solids (SS) at the absorbed dose of 5 kGy. However, the





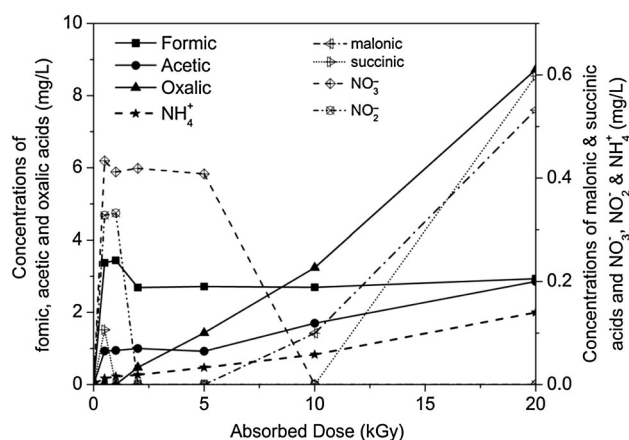
**Fig. 7** Degradation of CBZ (50 mg/L) in pure-water and surface water

degradation rate of CBZ radiolysis was still lower in surface water than that in pure water. Additionally, the SS in surface water inhibited the degradation of CBZ.

Different water sources could make the results of CBZ degradation different on account of various components in water (ions, dissolved organic matters (DOM) and SS) [33]. Ions, DOM and SS in surface water, which had side effects, could affect the degradation rate of CBZ. As Figs. 7, 8 showed, they all depressed the degradation of CBZ, because some ions, DOM and SS in surface water could compete with the CBZ for active radicals ( $\cdot\text{OH}$ ,  $e_{\text{aq}}^-$  and  $\cdot\text{H}$  during EB irradiation). This result strongly suggested that a higher absorbed dose was needed for the CBZ contaminated surface water treatment.

#### Radiolysis process of CBZ in surface water

The intermediates of CBZ in surface water were detected by IC and LC/MS/MS. As showed in Table 1, the determined organic acids were formic, acetic, oxalic, malonic, and succinic acid and the inorganic ions were  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  using IC. The concentration change of several short-chain carboxylic acids showed in Fig. 7. Malonic, and succinic acid were detected in the experiment suggested that the benzene ring was attacked and then opened. Previous study reported that the organic nitrogen might be transformed into nitrogen ( $\text{N}_2$ ),  $\text{NH}_4^+$  and  $\text{NO}_3^-$  during the oxidative degradation of CBZ [14]. Fig. 7 depicted that the concentration of  $\text{NO}_2^-$  and  $\text{NO}_3^-$  generated from CBZ EB degradation was very little and finally disappeared after 15 kGy and the production of  $\text{NH}_4^+$  increased as the increase of EB absorbed dose. There was a difference between the calculated values and the measured values of



**Fig. 8** The formation of organic acids and inorganic ions during the degradation of CBZ (50 mg/L) in surface water: The *left-top* legend belongs to the left Y-coordinate and the *right-top* legend to the right Y-coordinate

**Table 1** Structures and IC data for organic acids and inorganic ions during carbamazepine (CBZ) EB irradiation in surface water

Product Name	Structure of Molecules or Ions	Retention time (min) using anion exchange column
Formic acid		3.67
Acetic acid		3.35
Oxalic acid		15.21
Malonic acid		12.97
Succinic acid		14.30
Nitrite ion	$\text{NO}_2^-$	5.42
Nitrate ion	$\text{NO}_3^-$	7.26

total nitrogen ( $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$ ). Therefore, it was deduced that the organic nitrogen was mainly transformed to  $\text{NH}_4^+$  and  $\text{N}_2$ . It was consistent with the inhibition of  $\text{NH}_4^+$  on CBZ EB degradation was due to the production of  $\text{NH}_4^+$  from CBZ EB-radiolysis, as showed in Fig. 6.

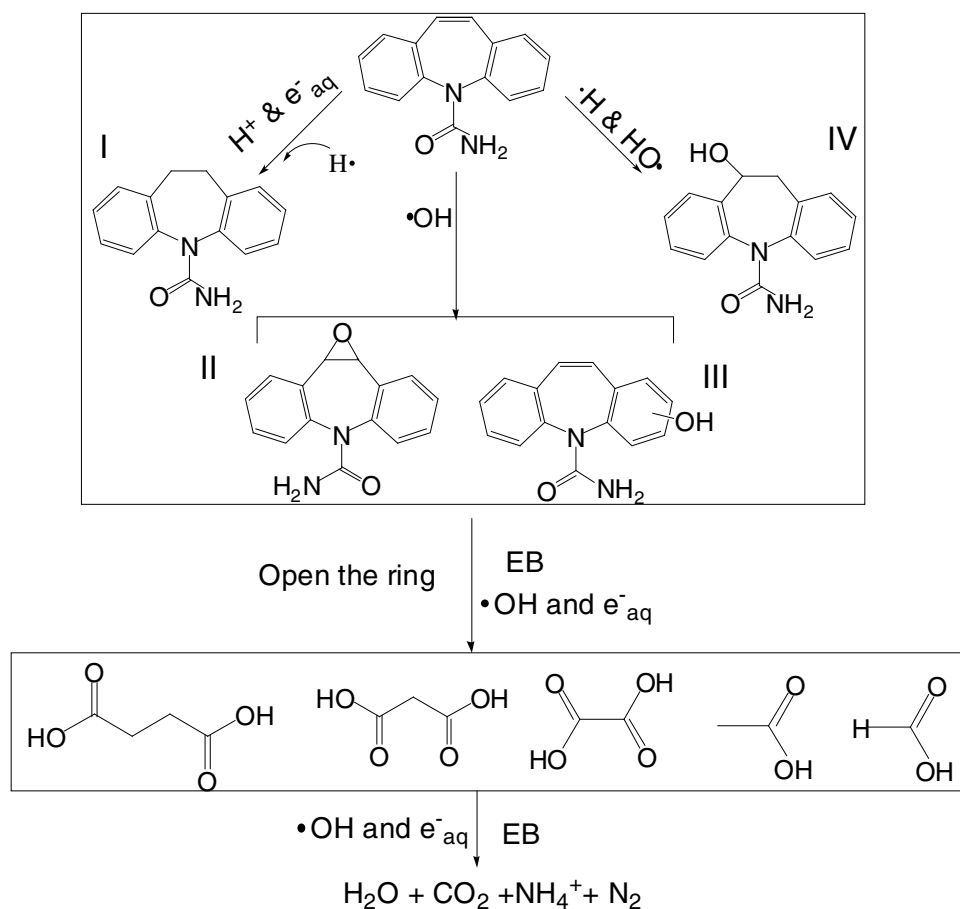
Other complex intermediates of CBZ radiolysis were detected by LC/MS/MS, and the determined products were listed in Table 2. CBZ, occurred redox reaction with  $\text{HO}\cdot$ ,  $\text{H}\cdot$  and  $e_{\text{aq}}^-$  during EB-radiolysis, and oxidation reaction usually acted the vital role. The olefinic double bond on the central heterocyclic ring of CBZ molecule was usually reactive [34].

**Table 2** Structures and LC/MS/MS data for carbamazepine (CBZ) and its detected EB-intermediates in surface water

Product ID	Structure	Retention time (min)	ESI(+) precursor ion m/z <sup>a</sup>	ESI(+) MS <sup>2</sup> main fragment ions <sup>a</sup>	Remarks
CBZ		6.041	237[M + H] <sup>+</sup> , 259[M + Na] <sup>+</sup> , 275[M + K] <sup>+</sup>	<b>237</b> , 220, 194*	Detected
I		6.106	239[M + H] <sup>+</sup> , 261[M + Na] <sup>+</sup> , 277[M + K] <sup>+</sup>	<b>239</b> , 194*	Detected
II		5.143	253[M + H] <sup>+</sup> , 275[M + Na] <sup>+</sup> , 291[M + K] <sup>+</sup>	<b>253</b> , 236, 180*	Detected
III		5.363 and 5.546		<b>253</b> , 236, 210*, 180	Detected
IV		4.932	255[M + H] <sup>+</sup> , 277[M + Na] <sup>+</sup> , 293[M + K] <sup>+</sup>	<b>255</b> , 240, 237*, 224, 222, 219, 211, 208, 195	Detected

<sup>a</sup> shown are the probable fragment ions from the precursor ions; \* shown are probable the most abundant fragment ion

**Fig. 9** Proposed radiolysis process of CBZ (50 mg/L) in surface water



On the central heterocyclic ring, CBZ could be hydrogenated to 10,11-dihydrocarbamazepine (I) by  $\cdot\text{H}$  [35] and hydrated to 10,11-dihydro-10-hydroxycarbamazepine (IV) by  $\cdot\text{OH}$  and  $\cdot\text{H}$  [11]. The epoxidation of CBZ to form epoxide 10,11-dihydro-10-11-epoxycarbamazepine (II) was also found in our study, which was generally mentioned in many other studies [34, 36–38]. Additionally,  $\cdot\text{OH}$  could attack on the two outside aromatic rings of CBZ to form 2(3)-hydroxycarbamazepine (III) [36]. As EB dose increased, the center heterocyclic and benzene rings were splintered into some short-chain acids which detected by IC and were finally mineralized into  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_4^+$  and  $\text{N}_2$ .

On the basis of the intermediates detected by LC/MS/MS and the various ions detected by IC during irradiation, a possible EB radiolytic degradation of CBZ was proposed as shown in Fig. 9.

## Conclusions

CBZ degradation by EB radiolysis had been demonstrated to be an effective way in water. The results showed that  $\cdot\text{OH}$  provided a powerful impact on CBZ degradation compared to  $e_{\text{aq}}^-$ . CBZ degradation in acidic solutions was better than that in alkaline solution except the  $\text{Na}_2\text{SO}_3$  solution.  $\text{SO}_3^{2-}$  should be avoided in surface water, because the synthesis reaction of  $\text{SO}_3^{2-}$  and CBZ hindered the mineralization, though a positive action was on the degradation of CBZ. Similarly,  $\text{NO}_3^-$  should also be precautionary in surface water, because  $\text{NO}_3^-$  had a suppression on CBZ degradation at high dose ( $>0.5$  kGy).  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$  and  $\text{Na}^+$  had a little effect on CBZ EB degradation. The degradation rate of CBZ in surface water was lower than that in pure water because of the existence of ions, DOM and SS in surface water. In addition, some intermediates of CBZ in surface water were detected using IC and LC/MS/MS and then the probable degradation pathway for the mineralization of CBZ was proposed. As result of the ubiquitous presence of inorganic salt ions, DOM and SS in surface water, all of above result gave assistance to the study of the EB-radiolysis of other pharmaceuticals in surface water.

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