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Comparison of EB-radiolysis and UV/H_2O_2-degradation of CBZ in pure water and solutions*

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It was learned that 99 % degradation rate of carbamazepine (CBZ) (75 mg/L) in solutions was got under 10 kGy by EB (electron beam) irradiation while 15.74% and 96.02% CBZ (2 mg/L) degradation rate was got by UV and UV/H_2O_2 process in 180 min. EB-radiolysis was thought to be an efficient and energy-saving method to decompose CBZ in comparison of energy consumption between EB irradiation and UV/H_2O_2. Alkali metal cations which existed in surface water have little inhibition on the degradation of CBZ under EB and UV/H_2O_2 process. The anions usually existed in surface water had little suppression on EB-radiolysis of CBZ, while have an inhibition on UV-photodegradation of CBZ. Fe^{3+} promoted the degradation under EB irradiation and UV (ultraviolet) irradiation because of being the OH· promoter. In addition, Fe^{2+} hugely enhanced the degradation of CBZ under UV irradiation. On the basis of the intermediates' appearance during the radiolysis, the main degradation pathway for the mineralization of CBZ was proposed under EB irradiation. It came to a conclusion that EB-radiolysis was an efficient and energy-saving method to completely mineralize CBZ.

Keywords: Carbamazepine, Electron beam radiolysis, UV-photodegradation, Ions, Intermediates

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I. INTRODUCTION

Carbamazepine (CBZ) was widely consumed psychotropic pharmaceutical, and is most commonly detected persistent pharmaceuticals in the environment [1]. It impacts not only the surface water but also the groundwater [2]. Its concentration can be up to 6.3 μg/L in wastewaters, 1.1 μg/L in surface waters and 30 ng/L in drinking water. [3] It was refractory to both conventional and advanced wastewater treatment processes. [4, 5] And it can affect organisms greatly [5].

Transformation of carbamazepine by different means has been reported, such as by biotechnology [5–10] and advanced oxidation processes (AOPs). However, the traditional oxidation processes are not always completely mineralized. Hu reported only 7% removal efficiency of CBZ by conventional wastewater treatment [11], and Tixier found only a slight elimination through phototransformation [12].

Electron beam (EB) treatment is an advanced oxidation processes [13], being efficient, safe, simple and completely mineralized for organic pollutants, especially for the thorough decomposition of biorefractory compounds [14–19]. In EB-radiolysis, water is degraded into hydroxyl radical (OH·), hydrogen radical (H·), and hydrated electron (e^-_{aq}) with different G-values (μmol/J), and OH· and e^-_{aq} are the main active species [20].

In this paper, EB-radiolysis and UV/H_2O_2 degradation of CBZ in pure-water are performed to compare their degradation efficiency and energy consumption. As various ions are generated in surface water, a study is needed on the effect on degradation of carbamazepine of EB and UV/H_2O_2 treatments. The transformation path of CBZ in EB irradiation of water is proposed. These shall be of help in finding the best method to dispose pharmaceutical and personal care products (PPCPs) in surface water.

II. MATERIALS AND METHODS

A. Materials

CBZ ($>$ 98%), methanol (HPLC grade), and acetonitrile (LCMS grade) were obtained from Sigma-Aldrich. Formic acid (HCOOH), acetic acid (CH_3COOH), oxalic acid ($H_2C_2O_4$), NaCl, Na_2SO_4, $NaHCO_3$, $CaCl_2$, $MgCl_2$, Fe_2SO_4, $Fe_2(SO_4)_3$, $FeCl_2$ and $FeCl_3$ were purchased from Shanghai Chemical Reagent Co., Ltd. All chemicals were of analytical grade unless otherwise stated. The pure water (resistance $>$ 18.2 MΩ) was prepared by filtering through a Millipore Milli-Q system. The surface water was collected from a local river and the 0.22 μm filters was used to filter the degradation water. All experiments were performed at temperature of 20 ± 2 °C.

B. Photo irradiation procedure

A merry-go-round photochemical reactor (Sidongke Electric Plant, Nanjing, China) coupled with a max of 12 quartz tubes containing the reaction solution was used for the photodegradation experiments. The total volume of the tube was 100 mL and the liquid layer thickness was 35 mm. UV (ultraviolet) light irradiation from a 300 W high-pressure mercury lamp with 254 nm wavelength immersed in the circulated-water cooled quartz well were employed in the photolysis

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experiments. The light intensity was 9 W and the cell path length was 2 cm. The temperature inside the reactor was kept at 20 ± 2 °C by a water-cooling jacket.

C. EB irradiation

The samples were irradiated to 0.5, 1, 2, 5, 10 and 20 kGy at ambient temperatures by 1.8 MeV electron beams of up to 10 mA from an electron accelerator. The samples were placed at 30 cm under the beam scanner.

D. Analytical methods

A high performance liquid chromatography (HPLC, Agilent 1200 series), consisted of C18 column (150 mm × 4.6 mm) and an auto-sampler with 10 µL 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/min.

Organic acids, nitrate and nitrite ammonium ions produced by EB-radiolysis were detected by ICS1100 (Dionex). A hydrophilic anion exchange column was IonPac As22 (analytical, 4 mm × 250 mm). The eluent mixed with 4.5 mM Na_2CO_3 and 1.4 mM $NaHCO_3$ at 1.20 mL/min flow rate and the injection volume was 25 µL. The suppressor was Anion Self-Regenerating Suppressor (ASRS 300 4 mm under AutoSuppression Recycle Mode at 31 mA. A hydrophilic cation exchange column was IonPac CS12A (analytical, 4 mm × 250 mm). The eluent was methanesulfonic acid (20 mM) at 1 mL/min flow and the injection volume was 25 µL. The suppressor was Cation Self-Regenerating Suppressor (CSRS ULTRA II, 4 mm) under Auto-Suppression Recycle Mode at 59 mA.

Other by-products of CBZ by EB-radiolysis were monitored by LC/MS/MS using an Agilent 1260LC chromatograph coupled to an Agilent 6460 mass spectrometer with electron spray ionization (ESI) interface and a heated nebulizer. A Porshell 120 100 mm × 3 mm EC-C18 end-capped column (2.7 µm particle size) was used at the flow rate of 0.4 mL/min. 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. For positive electron spray ionization, ESI (+), the operation conditions of the source were: capillary voltage, 4000 V; nebulizer pressure, 40 psi (0.28 MPa); drying gas flow, 8 L/min at 300 °C; and nozzle voltage, 0 V. For negative electron spray ionization, ESI (-), the operation conditions of the source were: capillary voltage, 3250 V; nebulizer pressure, 40 psi; drying gas flow, 7 L/min at 350 °C; and nozzle voltage, 500 V.

Total organic carbon (TOC) was determined using a TOC analyzer (multi C/N 2100, Analytik Jena AG).

III. RESULTS AND DISCUSSION

A. UV-photodegradation and EB-radiolysis of CBZ in pure-water

As shown in Fig. 1, only 15.74% CBZ (2 mg/L) was degraded after 180-min UV radiation; and 96%, under UV/H_2O_2; and 99.9% CBZ (75 mg/L), under 10-kGy EB irradiation. So, CBZ was refractory to degrade under UV irradiation only, and the existence of H_2O_2 in solution promoted the CBZ degradation; while EB-radiolysis is an efficient method to degrade CBZ, which was reported by Kwon *et al* [16], too.

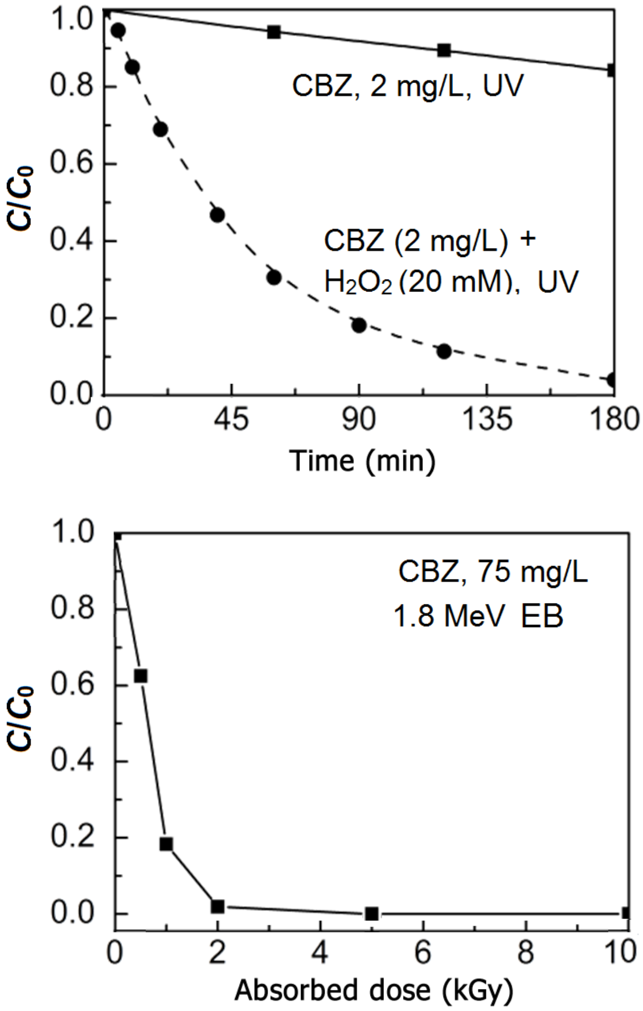


Fig. 1. Degradation of CBZ in pre-water by EB, UV and UV/H_2O_2 treatments (pH =6.3, no pH adjustment).

The EB-radiolysis enhancement is due to a large amount of free radicals of hydroxyl (H·) and hydrogen (OH·), and hydrated electrons (e^-_{aq}) generated during EB irradiation [20] at different G-values (µmol/J) (Reaction I). As well known, OH·, e^-_{aq} and H· are high reactive radicals to react with organic compounds and cause degradation. The OH· is an active particle with oxidation potential ($E_0 = 2.8\,\mathrm{V}$), with strong

TABLE 1. Pseudo first order reaction rate k, coefficient of determination R^2 and energy consumption per molar Q for EB radiation and UV/H_2O_2, at EB-radiolysis efficiency $D_{0.90}$, photolysis time $T_{0.90}$ (min)

CBZ/ mg L^{-1}	EB, pH = 6.3, 20 °C				UV/H_2O_2, [H_2O_2]=20 mM pH = 6.5, 20 °C			
	k_1/kGy^{-1}	R^2	$D_{0.90}$ /kGy	Q_1/J mol^{-1}	k_2/min^{-1}	R^2	$T_{0.90}$(min)	Q_2/J mol^{-1}
20.0	4.902	0.9941	0.470	110.9	1.20×10^{-3}	0.9945	1918	1.00×10^{10}
25.0	4.275	0.9978	0.539	127.2	5.64×10^{-4}	0.9956	4083	1.71×10^{10}

oxidative ability to oxidize organic compounds in aqueous solutions, while e^-_{aq} and H· are of strong reductive ability to deoxidize the targeted organic substance, with the e^-_{aq} having a strong reductive ability ($E_0 = -2.9$ V) to effectively dehalogen the halogenated organic compounds [14].

The photooxidation of organic substances was using the line source spherical emission model which was proposed by previous authors in similar studies [22]. Similar to the above, when 90 % CBZ was degraded, the consumption energy Q_2 (J/mol) could be calculated by following Eq. (1).

$$Q_2 = (T_{0.9} I_{(0,\lambda)} M)/(\Delta C L), \tag{1}$$

where $I_{0,\lambda}$ (Einstein/(L·s)) is the intensity of the incident light at 253.7: 9 w, $T_{0.9}$ is the time when 90% CBZ is degraded, M is molecular mass of carbamazepine (236.27 g/mol), ΔC is the concentration variation at 90 % CBZ degradation and L is the volume of CBZ solution (1.350 L).

The low percent of CBZ UV-photolysis in the UV treatment suggested that CBZ might degrade slowly. The numerous oxydic free radicals produced in the UV/H_2O_2 process (Reaction II– IV) react effectively with organic pollutants. [21] The results indicated that the removal of CBZ in UV/H_2O_2 system is probably controlled by the amount of hydroxyl radicals available. Therefore, EB irradiation and UV/H_2O_2 process are efficient methods to decompose the refractory pollutant organics, and EB irradiation is simple and convenient without adding any oxidizing agent.

$$H_2O \rightarrow (0.28)OH\cdot + (0.27)e^-_{aq} + (0.06)H\cdot + (0.05)H_2 + (0.07)H_2O_2 + (0.27)H^+ \tag{I}$$

$$H_2O_2 + h\nu \rightarrow 2OH\cdot \tag{II}$$

$$OH\cdot + OH\cdot \rightarrow H_2O_2 \tag{III}$$

$$H_2O_2 + OH\cdot \rightarrow HO_2\cdot + H_2O \tag{IV}$$

B. Comparison of EB-radiolysis and UV/H_2O_2 photodegradation efficiency on CBZ degradation

For understanding energy consumption of the EB radiation and UV/H_2O_2 treatments, CBZ initial concentrations of 20 mg/L and 25 mg/L were used, with the initial pH of the solutions being 6.3. Degradation of CBZ at different initial concentrations by EB and UV/H_2O_2 treatments follows well the pseudo-first-order kinetics

$$\ln(C/C_0) = -kx, \tag{2}$$

where, C and C_0 are the residual and initial concentrations of CBZ in mg/L, respectively; k is the pseudo-first order rate constant for overall degradation rate of CBZ; and x is the absorbed dose (kGy) of EB irradiation or time (min) of UV/H_2O_2 process. Table 1 shows the fitted k of initial concentrations.

Generally, the $D_{0.90}$ (kGy) was used to represent the needed absorbed dose that the degradation efficiency was 90 % in EB degradation. Then, we defined the Q_1 (J mol) which the consumption energy of 90% CBZ was degraded. The equation was represented at Eq. (3):

$$Q_1 = D_{0.90} M, \tag{3}$$

where $D_{0.90}$ (kGy) is the degradation efficiency at the dose point where 90% CBZ is degraded, and M is molecular mass of carbamazepine (236.27 g/mol).

As shown in Table 1, the EB process was more efficient than the UV/H_2O_2 process, the latter has a greater Q values than the former. A smaller Q means better efficiency and EB irradiation is an efficient method for CBZ degradation.

C. Effect of ions on CBZ degradation

1. *Effect of salts on CBZ EB-radiolysis*

CBZ (75 mg/L) was dissolved in solutions with different cations (NaCl, $CaCl_2$, $MgCl_2$ and $FeCl_3$, 5 mM each) or different anions (NaCl, Na_2SO_4 and $NaHCO_3$, 5 mM each), and was EB-irradiated to check their effects on CBZ degradation. The experiment was performed three times and the coefficient of variation was within 5%. As shown in Fig. 2, the Na^+, Mg^{2+} and Ca^{2+} cations, and Cl^-, SO_4^{2-} and HCO_3^-

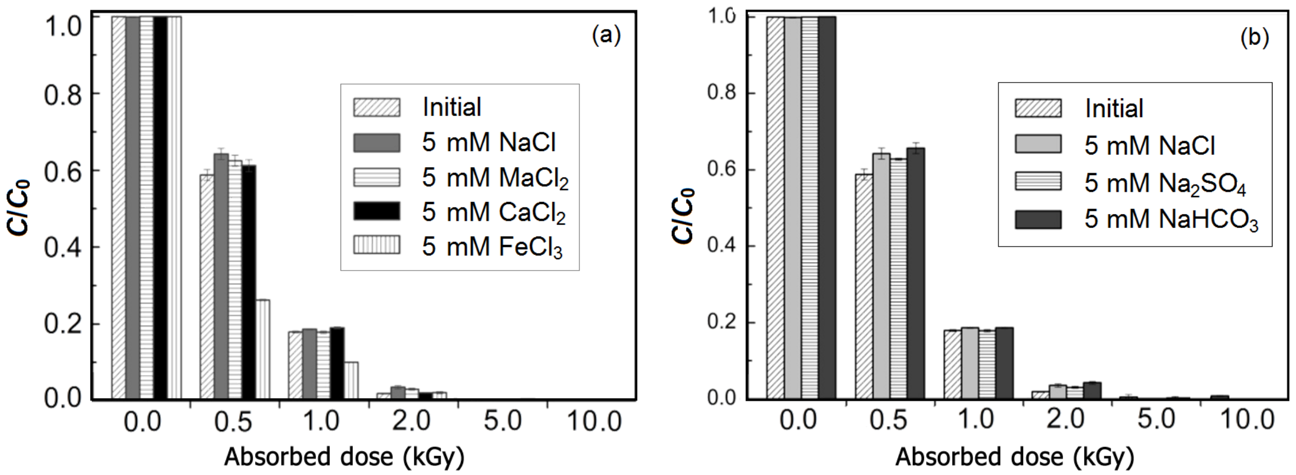


Fig. 2. Effect of cations (a) and anions (b) in salts on EB-degradation of CBZ ([CBZ] =75.0 mg/L; pH =6.3, no pH adjustment).

anions, had little impact on EB-radiolysis of CBZ, while Fe^{3+} promoted the degradation because of being as OH· promoter.

2. *Effect of salts on CBZ photodegradation*

CBZ (2 mg/L) was dissolved in salt solution of NaCl, $CaCl_2$, Na_2SO_4 and $NaHCO_3$ (10 mM each). The samples were added with 20 mM H_2O_2 and irradiated under a 300 W mercury lamp. The sampling intervals were 0, 5, 10, 20, 40, 60, 90 and 120 min. The experiment was carried out three times and the variation was within 2%.

As shown in Fig. 3, $NaHCO_3$ (32.93%) inhibited the CBZ degradation more than Cl^- (78.60%) at 120 min. It could be that HCO_3^- might react with OH· to produce $CO_3^{\cdot-}$, which is lower in activity than OH· [23, 24]. Being similar to HCO_3^-, NaCl and $CaCl_2$ had a little inhabitation on the CBZ degradation, because Cl^- could also eliminate OH· and competed with CBZ for OH·. [25]

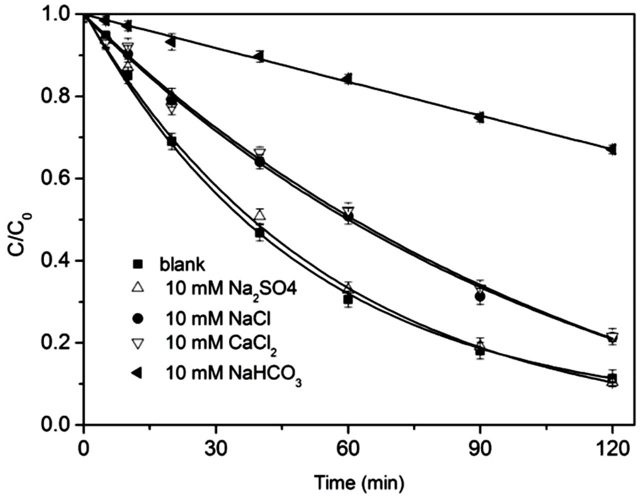


Fig. 3. Effect of salts on CBZ degradation in UV/[H_2O_2] process ([CBZ] =2.0 mg/L; [H_2O_2]=20 mM; pH =6.3, without pH adjustment).

3. *Effect of Fe^{2+} and Fe^{3+} on CBZ photodegradation*

The experiments were conducted by adding 2.0 mM Fe_2SO_4 and 1.0 mM $Fe_2(SO_4)_3$ into CBZ solution, respectively, and photodegraded under 300 W UV. Using an initial CBZ concentration of 2.0 mg L^{-1} at pH=3, experiments were carried out three times and the variation of coefficients was within 5%.

As shown in Fig. 4, the CBZ-removal efficiency increased greatly by adding Fe^{2+} and Fe^{3+}. Because the oxidation of Fe(II) to Fe(III) can produce H_2O_2 and OH· (Reaction V-VIII) in the presence of O_2. Fe(III) ions create hydroxyl radicals under UV irradiation (Reaction IX), and hydroxyl radicals react with organic substances and create organic radicals (Reaction X).

$$\mathrm{Fe}^{2+} + \mathrm{O}_2 + h\nu \rightarrow \mathrm{Fe}^{3+} + \mathrm{O}_2^{\cdot -} \tag{V}$$

$$\mathrm{Fe}^{2+} + \mathrm{O}_2^{\cdot -} + 2\mathrm{H}^+ \rightarrow \mathrm{Fe}^{3+} + \mathrm{H}_2\mathrm{O}_2 \tag{VI}$$

$$\mathrm{Fe}^{2+} + \mathrm{H}_2\mathrm{O}_2 \rightarrow \mathrm{Fe}^{3+} + \mathrm{OH}^- + \mathrm{OH}\cdot \tag{VII}$$

$$\mathrm{Fe}^{2+} + \mathrm{OH}\cdot \rightarrow \mathrm{Fe}^{3+} + \mathrm{OH}^- \tag{VIII}$$

$$\mathrm{Fe}^{3+} + \mathrm{H}_2\mathrm{O} + h\nu \rightarrow \mathrm{Fe}^{2+} + \mathrm{H}^+ + \mathrm{OH}\cdot \tag{IX}$$

$$\mathrm{OH}\cdot + \mathrm{RH} \rightarrow \mathrm{H}_2\mathrm{O} + \mathrm{R}\cdot \tag{X}$$

Therefore, the anions existed in natural water affected enormously UV-degradation of CBZ, while they had little effect on EB-radiolysis of CBZ. And the alkali metal cations had little influence on both UV- and EB-degradation of CBZ. The existence of Fe^{3+} could enhance the CBZ degradation. So, EB irradiation was a perfect method to degrade the contaminants in solution with various salts.

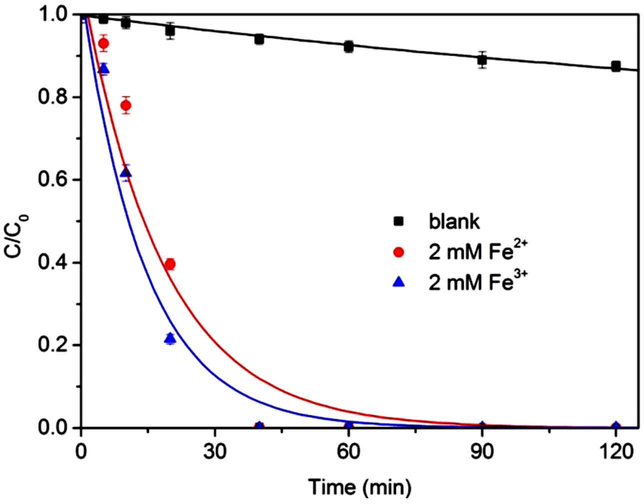


Fig. 4. (Color online) Effects of Fe^{2+} and Fe^{3+} on CBZ degradation in UV process ([CBZ]=2.0 mg L^{-1}; pH=3).

D. Degradation process of CBZ EB irradiation in solution with ions

The intermediates of CBZ dissolved in solution with all ions were detected by IC and LC/MS/MS. The organic acids were formic, acetic, oxalic, malonic and succinic acid, and the inorganic ions were nitrite and nitrate ions detected by IC under anion mode and the ammonium ion under the cation mode. Nitrite and nitrate ions were disappeared after 15 kGy, therefore the organic nitrogen was mainly transformed to ammonium ion (NH_4^+) or N_2. Other complex transformations were showed in Table 2.

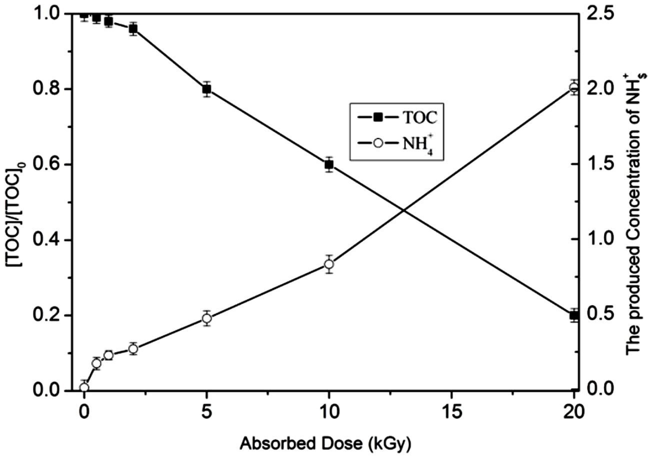


Fig. 5. The evolution of TOC and NH_4^+ concentration in EB-irradiation of CBZ (CBZ 25 mg/L;■, TOC in the left-Y-coordinate; ○, NH_4^+ in the right-Y-coordinate; [TOC], the residual TOC concentration; $[TOC]_0$, the initial TOC concentration).

Figure 5 shows the dose effects on the removal efficiency of TOC and the concentration evolution of NH_4^+ for CBZ solutions. At 20 kGy, the residual TOC was about 20%, and the NH_4^+ concentration was about 2.01 mg/L. The calculated total organic nitrogen was 3.81 mg/L, suggesting that 52.8% organic nitrogen might be changed into ammonia nitrogen and about 25% of it might be translated into N_2.

On basis of the intermediates' appearance detected by LC/MS/MS and the variation of ions detected by IC in the radiolysis, a main degradation pathway for the mineralization of CBZ was proposed, as shown in Fig. 6.

A 20 kGy EB-irradiation led to almost mineralized CBZ into CO_2, H_2O and mineral nitrogen, while it took a much longer time to mineralize CBZ by UV/H_2O_2-photodegradation than by the EB irradiation.

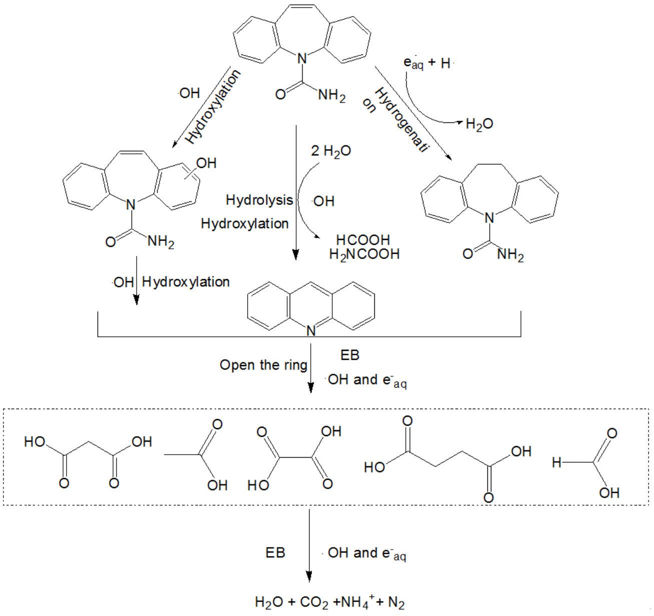


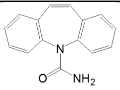
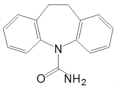
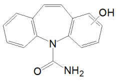
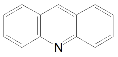
Fig. 6. Proposed radiolysis process of CBZ (25 mg/L) in ion water under EB irradiation.

IV. CONCLUSION

Comparison of EB-radiolysis and UV-photodegradation of CBZ in pure-water, we found that CBZ was easily degraded under EB irradiation while was refractory under UV irradiation. As the degradation rate was promoted markedly under UV/H_2O_2 process and OH· played a vital role in the degradation of CBZ, the solutions should be set in oxidation system when processed the wastewater. EB radiation was an efficient method when compared the energy consumption between EB irradiation and UV/H_2O_2 process.

The ions had little influence on the EB-radiolysis of CBZ, while an inhibition on CBZ's degradation under UV/H_2O_2 process. Fe^{2+} and Fe^{3+} could hugely enhance the CBZ UV photodegradation. Therefore, EB irradiation was inferred to be an efficient method to degrade the contaminants in surface water with various salts. Furthermore, the intermediates of CBZ by EB irradiation were detected by LC/MS/MS and IC, and CBZ could be completely mineralized into CO_2 detect-

TABLE 2. Intermediates and products detected by LC-MS/MS during EB-radiolysis of CBZ (25 mg/L)

Code	Structure	ESI(+) Precursor ion m/z[a]	[a]ESI(+) MS^2	Remarks
CBZ		237[M+H]$^+$, 259[M+Na]$^+$, 275[M+K]$^+$,	237, 220, 194[b]	Detected
I		239[M+H]$^+$, 261[M+Na]$^+$, 277[M+K]$^+$	239, 194[b]	Detected
II		253[M+H]$^+$, 275[M+Na]$^+$, 291[M+K]$^+$	253, 236, 210[b], 180	Detected
III		239[M+H]$^+$, 180[M+H]$^+$	180, 152[b]	Detected

[a] probable fragment ions from the precursor ions;

[b] the most abundant fragment ion.

ed by TOC analyzer, H_2O and mineral nitrogen. It is learned that electron beam is an efficient and energy-saving methods in decompose CBZ and could be applied in disposal of other persistent PPCPs.

[1] Loos R, Locoro G, Comero S, *et al.* Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water. Water Res, 2010, **44**: 4115–4126. DOI: 10.1016/j.watres.2010.05.032

[2] Zhou H, Wu C, Huang X, *et al.* Occurrence of selected pharmaceuticals and caffeine in sewage treatment plants and receiving rivers in Beijing, China. Water Environ Res, 2010, **82**: 2239–2248. DOI: 10.2175/106143010x12681059116653

[3] Kosjek T, Andersen H R, Kompare B, *et al.* Fate of carbamazepine during water treatment. Environ Sci Technol, 2009, **43**: 6256–6261. DOI: DOI: 10.1021/es900070h

[4] Xue W, Wu C, Xiao K, *et al.* Elimination and fate of selected micro–organic pollutants in a full–scale anaerobic/anoxic/aerobic process combined with membrane bioreactor for municipal wastewater reclamation. Water Res, 2010, **44**: 5999–6010. DOI: 10.1016/j.watres.2010.07.052

[5] Keen OS, Baik S, Linden K G, *et al.* Enhanced biodegradation of carbamazepine after UV/H_2O_2 advanced oxidation. Environ Sci Technol, 2012, **46**: 6222–6227. DOI: 10.1021/es300897u

[6] Golan–Rozen N, Chefetz B, Ben–Ari J, *et al.* Transformation of the recalcitrant pharmaceutical compound carbamazepine by Pleurotus ostreatus: role of cytochrome P450 monooxygenase and manganese peroxidase. Environ Sci Technol, 2011, **45**: 6800–6805. DOI: 10.1021/es200298t

[7] Rodriguez–Rodriguez C E, Marco–Urrea E and Caminal G. Degradation of naproxen and carbamazepine in spiked sludge by slurry and solid–phase Trametes versicolor systems. Bioresour Technol, 2010, **101**: 2259–2266. DOI: 10.1016/j.biortech.2009.11.089

[8] Kang S I, Kang S Y and Hur H G. Identification of fungal metabolites of anticonvulsant drug carbamazepine. Appl Microbiol Biotechnol, 2008, **79**: 663–669. DOI: 10.1007/s00253-008-1459-5

[9] Togunde O P, Oakes K D, Servos M R, *et al.* Determination of pharmaceutical residues in fish bile by solid–phase microextraction couple with liquid chromatography-tandem mass spectrometry (LC/MS/MS). Environ Sci Technol, 2012, **46**: 5302–5309. DOI: 10.1021/es203758n

[10] Marco–Urrea E, Radjenovic J, Caminal G, *et al.* Oxidation of atenolol, propranolol, carbamazepine and clofibric acid by a biological Fenton–like system mediated by the white–rot fungus Trametes versicolor. Water Res, 2010, **44**: 521-532. DOI: 10.1016/j.watres.2009.09.049

[11] Hu L, Martin H M, Arcs–Bulted O, *et al.* Oxidation of Carbamazepine by Mn(VII) and Fe(VI): Reaction kinetics and mechanism. Environ Sci Technol, 2009, **43**: 509-515. DOI: 10.1021/es8023513

[12] Tixier C, Singer H P, Oellers S, *et al.* Occurrence and fate of carbamazepine, clofibric acid, diclofenac, ibuprofen, ketoprofen, and naproxen in surface waters. Environ Sci Technol, 2003, **37**: 1061–1068. DOI: 10.1021/es025834r

[13] Xu G, Bu T, Wu M, *et al.* Electron beam induced degradation of clopyralid in aqueous solutions. J Radioanal Nucl Chem, 2011, **288**: 759–764. DOI: 10.1007/s10967-011-0986-1

[14] Unob F, Hagege A, Lakkis D, *et al.* Degradation of organolead species in aqueous solutions by electron beam irradiation. Water Res, 2003, **37**: 2113–2117. DOI: 10.1016/S0043-1354(02)00620-6

[15] Poster D L, Chaychian M, Neta P, *et al.* Degradation of PCBs in a marine sediment treated with ionizing and UV radiation. Environ Sci Technol, 2003, **37**: 3808–3815. DOI: 10.1021/es030363

[16] Kwon M, Yoon Y, Cho E, *et al.* Removal of iopromide and degradation characteristics in electron beam irradiation process. J Hazard Mater, 2012, **227-228**: 126–134. DOI: 10.1016/j.jhazmat.2012.05.022

[17] Sun W, Chen L, Tian J, *et al.* Degradation of a monoazo dye Alizarin Yellow GG in aqueous solutions by gamma irradiation: Decolorization and biodegradability enhancement. Radiat Phys Chem, 2013, **83**: 86–89. DOI: 10.1016/j.radphyschem.2012.10.014

[18] Ghanbari F, Ghoorchi T, Shawrang P, *et al.* Comparison of electron beam and gamma ray irradiations effects on ruminal crude protein and amino acid degradation kinetics, and in vitro digestibility of cottonseed meal. Radiat Phys Chem, 2012, **81**: 672–678. DOI: 10.1016/j.radphyschem.2012.02.014

[19] Taghinejad–Roudbaneh M, Ebrahimi S R, Azizi S, *et al*. Effects of electron beam irradiation on chemical composition, antinutritional factors, ruminal degradation and in vitro protein digestibility of canola meal. Radiat Phys Chem, 2010, **79**: 1264–1269. DOI: 10.1016/j.radphyschem.2010.07.007

[20] Buxton G V, Greenstock C L, Helman W P, *et al*. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (OH/O) in aqueous solution. Phys Chem Ref Data, 1988, **17**: 513–886.

[21] Zhang J D, Hu X Y, Yang J A, *et al*. UV/H_2O_2 degradation of 4–aminoantipyrine: A voltammetric study. Chem Eng J, 2010, **161**: 68–72. DOI: 10.1016/j.cej.2010.04.025

[22] Legrini O, Oliveros E and Braun AM. Photochemical processes for water treatment. Chem Rev, 1993, **93**: 671–698. DOI: 10.1021/cr00018a003

[23] Minero C, Pellizzari P, Maurino V, *et al*. Enhancement of dye sonochemical degradation by some inorganic anions present in natural waters. Appl Catal B-environ, 2008, **77**: 308–316. DOI: 10.1016/j.apcatb.2007.08.001

[24] Daneshvar N, Behnajady M A and Asghar Y Z. Photooxidative degradation of 4-nitrophenol (4–NP) in UV/H2O2 process: Influence of operational parameters and reaction mechanism. J Hazard Mater, 2007, **139**: 275–279. DOI: 10.1016/j.jhazmat.2006.06.045

[25] Ghodbane H and Hamdaoui O. Decolorization of antraquinonic dye, C.I. Acid Blue 25, in aqueous solution by direct UV irradiation, UV/H_2O_2 and UV/Fe(II) processes. Chem Eng J, 2010, **160**: 226–231. DOI: 10.1016/j.cej.2010.03.049