Nuclear Science and Techniques **22** (2011) 277–281

Electron-beam induced degradation of bisphenol A

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Abstract E-beam degradation of bisphenol A (BPA) was carried out, under reductive condition of ethanol-water solution and oxidative condition of acetonitrile-water solution. The degradation efficiency is higher in oxidative condition than that in reductive condition, and increases with the dose but decreased with increasing initial concentration. The BPA radiolysis follows the pseudo-first-order kinetics. Adding H_2O_2, or neutral condition, does not benefit BPA degradation in oxidative conditions. Pulsed radiolysis was used to investigate mechanism of the BPA radiolysis. The rate constant for BPA reaction with $^{\cdot}OH$ (1.85×10^{10} L·mol^{-1}·s^{-1}) is about an order of magnitude higher than that with e^{-}_{aq} (1.80×10^{9} L·mol^{-1}·s^{-1}). The degradation products were analyzed by ion chromatograph. Smaller molecules such as formic acid and acetic acid were detected, indicating that $^{\cdot}OH$ attacks the BPA molecule. The work is of significance for the practical E-beam treatment of waste water containing BPA.

Key words Bisphenol A, E-beam irradiation, Degradation, Pulsed radiolysis

1 Introduction

Bisphenol A is an important industrial chemical, used widely in synthesis of polycarbonate plastic, phenol resins, and flame retardants[1]. As a highly toxic chemical of slow degradation, it can be enriched in aquatic animals, and come into human body finally. This biological amplification effect may cause endocrinopathy diseases, threatening especially the health of fetus and child. Cancer and obesity caused by metabolic disorder are considered relevant to BPA. Consequently, BPA is listed as one of the endocrine disruptors.

Discharge of industrial wastewater containing BPA into surface waters causes serious environmental pollution[2-4]. A considerable interest has been focused on BPA degradation using physicochemical[5-8] and biodegradable technologies[9,10]. The former is realized virtually with catalysts and oxidants, which adds to the cost and causes possible secondary pollution; while the latter needs large land area and long reaction time. Moreover, the biodegraded BPA metabolites at whiles can enhance estrogenicity or toxicity, and biodegrading or metabolizing BPA by micro-organisms does not mean that BPA has no estrogenic or toxic effect on organisms[11].

Radiation processing is advantageous in its complete degradation of pollutants without chemicals and secondary pollution[12]. It can be used as a pretreatment of biological treatment. Zhang *et al.* investigated kinetics and mechanisms of radiolytic degradation of nitrobenzene[13]. Al-sheikhly *et al.* did radiolytic detoxification of 2,6-dichlorobiphenyl under different conditions[14]. Hakoda T *et al*. decomposed Trichloroethylene was by irradiation[15]. But most of the BPA radiolysis researches were done with γ-rays.

In this paper, we report electron beam radiolysis of BPA in both reduction (ethanol-water solution) and oxidation system (acetonitrile-water solution). The radiolysis mechanism, i.e. effects of the free radicals on pollutants reaction kinetics, is studied by pulsed radiolysis. Effects of initial concentration, irradiation dose, pH and H_2O_2 on the BPA radiolysis

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Supported by National Natural Science Foundation of China (Nos.40973073, 40830744, 11025526, 11175112), National Key Technology R&D Program in the 11th Five-year Plan of China (No.2009BAA24B04) and Shanghai Leading Academic Discipline Project (No.S30109)

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Received date: 2011-04-06

are evaluated. The work provides technical support for E-beam treatment of BPA-containing wastewater.

2 Materials and methods

2.1 Reagents

BPA (>99%), ethanol and acetonitrile (HPLC grade) were purchased from Sigma Chemical Company, Perchloric acid (AR) and sodium hydroxide (AR), hydrogen peroxide (AR, 30%). *Tert*-butyl alcohol (*t*-BuOH) was redistilled.

2.2 Sample preparation

Throughout the experiments, all solutions were prepared with water in resistivity of > 18 MΩ·cm. BPA was dissolved in organic solution due to its low water-solubility. The initial concentrations of BPA for E-beam irradiation were 5, 10, 20, and 50 mg·L^{-1} in acetonitrile-water (*v*/*v*=1:9) or ethanol-water (*v*/*v*=1:9). For pulsed radiolysis, the BPA initial concentrations were 0.1–0.5 mmol·L^{-1}. Before irradiation, 4.9×10^{-6} and 4.9×10^{-5} mol·L^{-1}of H_2O_2 were added to the BPA solutions. The pH of solutions was adjusted with $HClO_4$ and NaOH. All solutions were bubbled with high purity N_2O (99.99%) or high purity N_2 (99.99%) in pulsed radiolysis experiments.

2.3 E-beam radiolysis and pulse radiolysis

The BOA solutions were irradiated to 5–50 kGy at Shanghai University by 1.8 MeV 1 mA E-beams. A solution sample, of 50 cm^2×0.2 cm, was placed at 30 cm from beam scan window.

The pulsed radiolysis was carried out on a 10-MeV 8-ns linac at Shanghai Institute of Applied Physics, Chinese Academy of Sciences. The pulse dose was determined by thiocyanate dosimeter containing 100 mmol·L^{-1} KSCN saturated with N_2O, taking $\varepsilon_{(SCN)2^-}$=7600 mol·L^{-1}·cm^{-1} at 480 nm. Analysis was performed with a xenon lamp (300 W), shining perpendicularly through a quartz cuvette having an optical path length of 10 mm. The transient signals acquired by oscilloscope were analyzed on a PC.

2.4 Analytical methods

The BPA concentrations was analyzed at 30°C by a high performance liquid chromatograph (HPLC, Aglient 1200, USA) coupled with an UV detector at 275 nm. HPLC separation was accomplished by a C_{18} column (150×4.6 mm^2). BPA of 10 μL was injected by an auto-sampler, and the mobile phase was a mixture of acetonitrile-water solution (*v*/*v*=40:60) at a flow rate of 1 mL·min^{-1}. The pH values were measured by PHS–3C meter (DAPU Instrument, Shanghai). Ion chromatograph (IC-Metrohm MIC advanced) consisting of a hydrophilic anion exchange column and an auto-sampler was used to determine the negative ions produced from radiolysis. A METROSEP A SUPP 5-250 (5 mm particle size, 250 mm–4 mm) column was employed and an eluent of Na_2CO_3 (3.2 mmol·L^{-1})/$NaHCO_3$ (1.0 mmol·L^{-1}) at a flow rate of 0.70 mL min^{-1} was used. The injection volume was 10 mL.

3 Results and discussion

3.1 Effect of BPA initial concentration and dose

Initial BPA concentration and dose delivered to the sample solutions are important parameters affecting the radiolytic degradation. Over 90% of the initial concentration of BPA in oxidative solutions could be removed by irradiating it to 30 kGy, where the degradation rates for BPA solutions of different initial concentrations began to vary little at the same dose.

In general, BPA degradation efficiency increased with the dose at the same initial concentration, and decreased with increasing initial concentration at the same dose. These can be explained as follows. A certain dose of E-beam irradiation induces certain amount of active radicals, and lower initial concentration means less number of BPA molecules, hence the more complete reaction with the solution of lower initial concentration than that of higher initial concentration. The dose effect is due to the increased amount of active radicals reacting with fixed number of BPA molecules.

A regressive analysis on BPA concentration and absorbed dose was performed, and it was found that the BPA degradation followed a pseudo-first-order kinetics,

$$-\mathrm{d}A/\mathrm{d}D = kA \qquad (1)$$

where, *A* is BPA initial concentration, *D* is irradiation dose, and *k* is kinetics parameters of BPA degradation. The *k* determined from the residual/initial concentration exhibited a significant correlations (R^2> 0.99), as shown in Table 1.

Table 1 First-order reaction parameters for E-beam degradation of BPA in an acetonitrile/water system

BPA concentration / mg·L^{-1}	Reaction constant / k·Gy^{-1}	R^2
5	0.1344 ± 0.0051	0.9985
10	0.1184 ± 0.0054	0.9969
20	0.0944 ± 0.0049	0.9947
50	0.0756 ± 0.0026	0.9977

3.2 Effect of the reductive and oxidative conditions

In diluted solution, E-beam irradiation of water results in the formation of some active specials, such as hydrated electrons (e^-_{aq}), hydroxyl radicals ($^{\cdot}OH$) and hydrogen atoms (H·), which can be described by Eq.(2). In oxidative conditions, as shown in Eq.(3), e^-_{aq} is scavenged by acetonitrile. Then, $^{\cdot}OH$ is the main reactive species. In Eq.(4) for reductive conditions, e^-_{aq} is the main reactive species, as ethanol can scavenge the $^{\cdot}OH$, forming relatively inert ethanol radicals. Therefore, the degradation efficiency was higher in oxidative conditions than that in reductive conditions at the same absorbed dose and the same initial concentration. For example, at 30 kGy and 10-mg·L^{-1} initial concentration, the BPA degradation efficiencies in oxidative and reductive conditions were 97% and 31%, respectively. The $^{\cdot}OH$ degrades BPA more effectively than e^-_{aq} does, because the phenolic compounds are readily oxidized by $^{\cdot}OH$ [6, 16–18].

$$H_2O \rightarrow (0.28)\cdot OH+(0.27)e^-_{aq}+(0.06)\cdot H+ (0.05)H_2+(0.07)H_2O_2+(0.27)H^+ \quad (2)$$

$$e^-_{aq}+CH_3CN \xrightarrow{H_2O} CH_3\cdot CHN(\text{or } CH_3C\cdot NH)+OH^- \quad (3)$$

$$CH_3CH_2OH+\cdot OH \rightarrow CH_3\cdot CHOH+H_2O \quad (4)$$

3.3 Effect of H_2O_2

A typical dose of BPA degradation under oxidative and reductive conditions was obtained by adding different amounts of H_2O_2 (Fig.1). At 30 kGy, the oxidative BPA degradation efficiency reduced from 97% without H_2O_2 to 76% with 4.9×10^{-5} mol·L^{-1} H_2O_2. Increasing the H_2O_2 concentration in reductive condition, however, could not improve the BPA degradation efficiency. As shown in Eq.(5), $^{\cdot}OH$, the main reactive species in oxidative condition, reacts with H_2O_2, hence the decrease of $^{\cdot}OH$ concentration, and degradation efficiency, with increasing concentration of H_2O_2. In Eq.(6) for reductive conditions, the main reactive species e^-_{aq} reacts with H_2O_2 to form $^{\cdot}OH$, which is scavenged by ethanol. Therefore, the $^{\cdot}OH$ concentrations changed little, so did the BPA degradation efficiency. This suggests also a significant role of $^{\cdot}OH$ in BPA degradation.

$$H_2O_2+\cdot OH \rightarrow H_2O+HO_2\cdot \quad (5)$$

$$H_2O_2+e^-_{aq} \rightarrow \cdot OH+OH^- \quad (6)$$

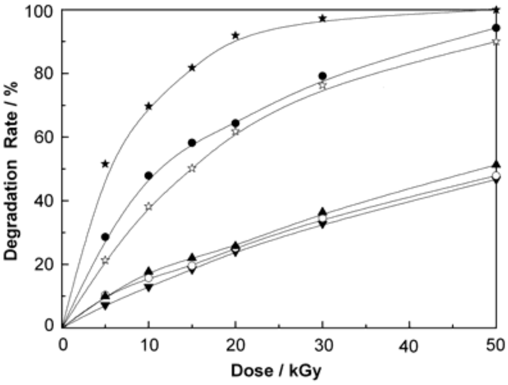


Fig.1 BPA degradation (10mg·L–1) in oxidative conditions with 0(★), 4.9×10^{-6}(●) and 4.9×10^{-5} mol·L–1 H_2O_2(☆); and in reductive conditions with 0(▼), 4.9×10^{-6} (○), and 4.9×10^{-5} mol·L–1 H_2O_2(▲).

3.4 Effect of initial pH values

The initial pH was an important parameter in radiolysis processes[19], and it is necessary to study the pH effect on BPA radiation. The initial pH of BPA solution was adjusted to 3, 5, 7, 9 and 11 by perchloric acid and sodium hydroxide, respectively. The BPA degradation efficiency *vs*. pH value is given in Fig.2.

The degradation of BPA was more effective under acidic or alkaline conditions than neutral conditions, and the lowest BPA degradation efficiency was at pH 9 in oxidation conditions, which is consistent with the results in Ref.[12], as phenolate anion was far less reactive than protonated phenol[20]. Conversely, alkali ethanol-water solutions were benefit to BPA degradation due to increasing e^-_{aq}[21]. In addition, the *G*-values of primary species generated from water radiolysis were altered under different pH values. Consequently, the BPA degradation efficiency was affected by pH of the initial BPA solutions.

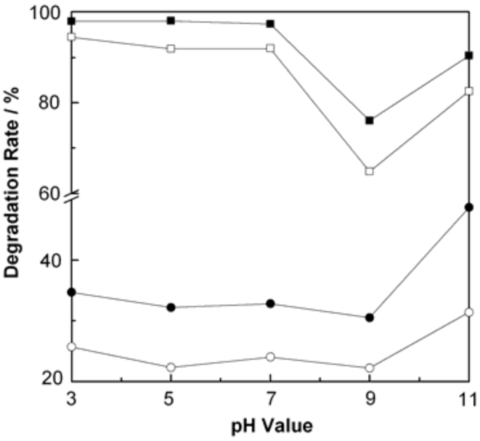


Fig.2 Effect of pH on BPA degradation (10 mg·L^{-1}). Oxidative conditions: (■) 30 kGy, (□) 20 kGy. Reductive conditions: (●) 30 kGy, (○) 20 kGy.

3.5 Degradation mechanism

The BPA pulsed radiolysis was performed so as to have a better understanding the property of intermediate radicals species produced in BPA radiolytic degradation, and for further identifying whether $^{\cdot}OH$ is more important than e^-_{aq} in BPA degradation. N_2O can quantitatively convert e^-_{aq} to $^{\cdot}OH$ *via* Reaction (7)[22], the reaction of $^{\cdot}OH$ with BPA was studied in BPA solutions (0.5 mmol·L^{-1}) saturated with N_2O at pH=7. The transient absorption spectra had a maximum absorption around 300 nm and a week peak at 340 nm (Fig.3). It was a faster decay occurred at 340 nm, and its half-life was just 5.5 μs, but no continuous transient product was formed. The transient lifetime and absorption maxima in 300–350 nm were characteristic of $^{\cdot}OH$ addition to the aromatic ring to form the corresponding hydroxyclohexadienyl radicals[23]. The reaction rate of the $^{\cdot}OH$ with BPA was measured from the transient species at the maximum absorption by changing the BPA concentrations, and the rate constant was 1.85×10^{10} L·mol^{-1}·s^{-1} according to a linear fit (insert of Fig.3).

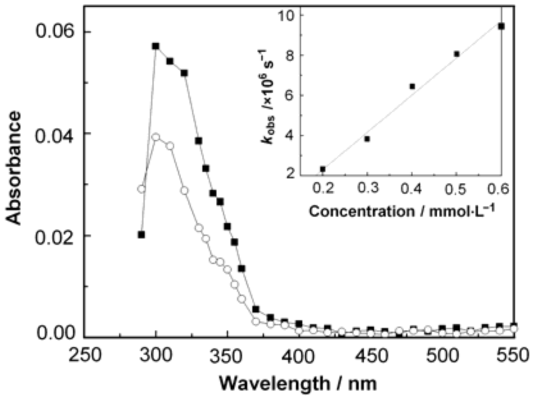
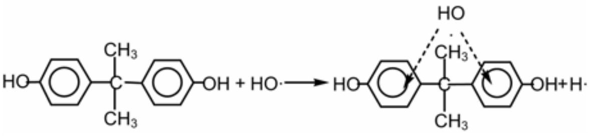


Fig.3 Transient absorption spectra of the saturated BPA neutral solution recorded in pulse radiolysis in N_2O, (■) 0.5 μs (○) 0.1 μs after the pulse. Insert: plot of k_{obs} *vs.* the BPA concentration.

Ion chromatograph (IC) analysis was used to determine the negative ions produced from radiolysis. Two kinds of organic acids, formic and acetic acids, were detected. This indicates that the hydroxyl radicals attacked BPA, and formed the small molecules products including formic and acetic acids. These corresponds with Eq. (8) reported in Ref.[24].

$$e^-_{aq}+N_2O+H_2O \rightarrow N_2+OH^- + \cdot OH \qquad (7)$$



(8)

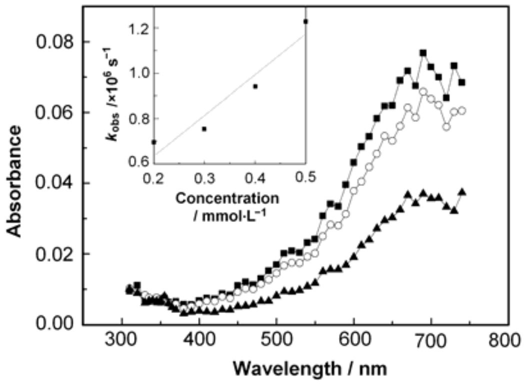


Fig.4 Transient absorption spectra obtained on pulse radiolysis of N_2 saturated BPA neutral aqueous solution of containing 100 mmol·L^{-1} *t*-BuOH at (■) 0.1 μs (○) 0.2 μs (▲) 0.5 μs after the pulse. Insert: plot of k_{obs} *vs.* the concentration of BPA.

To study reductive conditions, the reaction of e^-_{aq} with BPA was carried out in N_2 with saturated BPA neutral aqueous solution (0.5 mmol·L^{-1})

containing *t*-BuOH (100 mmol·L^{-1})[22], and its transient absorption spectra of e^-_{aq} with BPA had broad lengths from 500 to 740 nm, which belonged to e^-_{aq} and decayed fast in few microsecond (Fig.4). From plots of the decay kinetics values against BPA concentrations, the reaction rate constant of BPA with e^-_{aq} was 1.80×10^9 L·mol^{-1}·s^{-1} (insert of Fig.4).

$$\cdot OH + t\text{-BuOH} \rightarrow t\text{-BuO}\cdot + H_2O \qquad (9)$$

The rate constant of BPA reaction with $^{\cdot}OH$ is about ten times higher than that with e^-_{aq}, which further indicates that while both $^{\cdot}OH$ and e^-_{aq} can degrade BPA, $^{\cdot}OH$ plays a more important role than e^-_{aq} in BPA radiolytic degradation.

4 Conclusion

BPA degradation was investigated by E-beam irradiation and the results demonstrated that E-beam irradiation was a practicable method for the degradation of BPA. The rate of BPA radiolytic degradation was affected by initial BPA concentration, irradiation dose, pH, and the addition of H_2O_2. The BPA degradation efficiency increased with the decreasing initial concentration and increasing absorbed dose, and BPA degradation followed pseudo-first-order kinetics. It was favorable for acidic or basic condition to decompose BPA in oxidative conditions, and in alkali reductive conditions. The addition of H_2O_2 decreased the degradation rate of BPA in oxidation system, and there was no change in reductive system. The BPA degradation efficiency was much higher in oxidation system than that in reductive condition. The rate constants for BPA reaction with $^{\cdot}OH$ and e^-_{aq} determined by pulse radiolysis were 1.85×10^{10} L·mol^{-1}·s^{-1} and 1.80×10^9 L·mol^{-1}·s^{-1}, respectively. The results demonstrated that both $^{\cdot}OH$ and e^-_{aq} could degrade BPA, whereas $^{\cdot}OH$ played a more important part in degradation of BPA than e^-_{aq}. The products from BPA radiolysis based on the analytical results of IC analysis method contained formic acid, acetic acid, etc., which mean $^{\cdot}OH$ attacked the BPA molecule. Researching on radiolytic degradation of BPA has a guiding significance in actual industrial wastewater treatment.

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