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Radiolytic degradation and mechanism study of electron beam-irradiated solutions of 4-tert-octylphenol

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Abstract In this study, we have investigated the degradation and primary radiolytic degradation mechanism of 4-tert-octylphenol (4-t-OP) by using of electron beam (EB) -irradiation. The results show that at an absorbed dose of 10 kGy and an initial concentration of 25 mg·L^{-1}, the degradation of 4-t-OP in a methanol/water reduction system is higher than in a acetonitrile/water oxidation system by 19.4% and higher than in an acetone/water system by 26.8%, which is due to both of ·OH and e_{aq}^- playing an important role in the decomposition of 4-t-OP, although the latter is more effective. The degradation rate of 4-t-OP will decrease with increment of absorbed dose in a methanol/water solution, and increase with decrement of initial concentration at a constant absorbed dose. The degradation efficiency will also decrease with the addition of anions and H_2O_2 into the solution. A system saturated with N_2 will make an increment in the degradation of 4-t-OP. The pH value of solution has been also found to affect the degradation efficiency, while the degradation is more efficient in alkaline conditions. Finally, the initial products involved in degradation reaction have been determined to be ethylbenzene, styrene, bicyclo[4.2.0]octa-1,3,5-triene, 2,2,4-trimethylpentane and p-tert-butyl-phenol, which may arise from e_{aq}^- attack at the position of the alkyl side chain of 4-t-OP molecule. The results have been revealed that EB irradiation is a promising method for degradation of 4-t-OP, and e_{aq}^- may be main reactive species to attack at the position of the alkyl side chain of 4-t-OP.

Key words 4-tert-octylphenol (4-*t*-OP), Endocrine disruptor, Degradation, Electron beam (EB) irradiation, Mechanism

1 Introduction

Over the last few decades, various organic chemicals in the environment have been reported to have an effect on estrogen levels. These compounds, which are known as endocrine disrupting chemicals, have received a great deal of attention due to their potential impact on the health of animals and humans. When compared with other endocrine disruptors, 4-tert-octylphenol (4-*t*-OP) has received more attention due to its widespread applications and ubiquity in the environment[1,2]. Octylphenol ethoxylates (OPEOs) are a group of non-ionic surfactants that have been widely used in domestic and industrial applications for over 40 years. 4-*t*-OP is used as a raw material to produce OPEOs, and conversely 4-*t*-OP is produced by the degradation of OPEOs[3]. 4-*t*-OP had been recognized to have carcinogenic genetic and reproductive toxicity[4,5], and it is more toxic and stable than its parent compounds in the environment[6]. It is widely distributed in rivers and lakes, as well as in aquatic wildlife in some regions[3,7-9]. Therefore, effective methods for the removal of 4-*t*-OP from the environment need to be developed.

A large number of studies have been carried out on the removal of 4-*t*-OP[10-13], most of which have focused on photodegradation processes. Those processes are often initiated by ·OH, which is generated during illumination with bandgap

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radiation[14]. An investigation into photocatalytic degradation of 4-*t*-OP by recirculation of an aqueous solution through a packed bed reactor with TiO_2 showed that 83.2% of 4-*t*-OP was degraded after illumination for 6 h at a flow rate of 28.5 $mL \cdot min^{-1}$[12]. Another study reported the probable mechanism of 4-*t*-OP photolysis. Degradation of 4-*t*-OP has been shown to be by ·OH attack of the alkyl side chain and benzene ring of 4-*t*-OP, although this does not directly lead to 4-*t*-OP ring cleavage[10]. Other photolysis studies have shown that ·OH plays an important role in the decomposition of contaminants. Adding TiO_2 can dramatically promote the degradation of contaminants due to it generating a large amount of ·OH in photodegradation processes[15,16]. Although photodegradation process is a useful method for the decomposition of contaminants, it has some obvious disadvantages, such as low efficiency and long decomposition time. Other physicochemical methods have also been reported for the degradation of 4-*t*-OP. For example, Zhou investigated the sorption and desorption process of 4-*t*-OP in aquatic systems[13]. However, physicochemical methods have obvious disadvantages; such as high cost and additional pollution.

Radiation processes are classified as advanced oxidation processes (AOPs) and are a promising alternative for organic pollutant destruction using electron beam (EB) or gamma radiation. EB radiation has advantages over other methods for the treatment of wastewater. For example, it can achieve the complete degradation of the pollutants without the need for chemicals and it is an environmentally friendly method for the treatment of water and soil contaminated by organic compounds[17]. However, compared with photodegradation, radiation processes produce more reactive species, such as ·OH, e_{aq}^- and ·H. The usefulness of gamma radiation for the efficient degradation of a large variety of organic compounds has been successfully demonstrated[18]. Zhang *et al.* reported the kinetics of radiolytic degradation of microcystin using different additives[19]. Yu et al. have investigated the kinetics and mechanisms of radiolytic degradation of p-nitrophenol[20]. However, to the best of our knowledge, no information is available for 4-*t*-OP degradation with EB radiation.

To investigate the reaction mechanism, radiation induced degradation of 4-*t*-OP under various conditions has been explored in this study. We have evaluated the degradation efficiency when varying the choice of the solvent, changing the initial concentration of 4-*t*-OP, adding anions and H_2O_2 to the solution, a catalyst is present, saturating with different gases, and adjusting the pH of the solution. In addition, the degradation products of 4-*t*-OP were analyzed using ion chromatography and GC-MS. A possible degradation mechanism for the radiolytic degradation of 4-*t*-OP is also proposed. The results provided here give an overview of the degradation of 4-*t*-OP and should have a direct impact on the management of 4-*t*-OP in wastewater treatment by EB radiation in the future.

2 Materials and methods

2.1 Chemicals and reagents

Zinc oxide (ZnO), 4-*t*-OP, and titanium dioxide (TiO_2) were purchased from Sigma Chemical Co. (St. Louis, MO, USA) (>98% purity). Potassium hydroxide (KOH), sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), sodium bisulfate ($NaHSO_4$), sodium sulfite (Na_2SO_3), sodium nitrate ($NaNO_3$) and sodium nitrite ($NaNO_2$) were obtained from Acros Organics (Geel, Belgium). HPLC grade methanol and acetonitrile were supplied by CNW (Düsseldorf, Germany). 30% H_2O_2 and perchloric acid ($HClO_4$) were obtained from Shanghai Chemical Reagent Co. Ltd in the highest purity commercially available. Distilled and deionized water were produced using a Milli-Q system (R>18.1 MΩ).

2.2 Sample preparation

4-*t*-OP was dissolved in an organic solution for investigating the reaction mechanism. Solutions with different concentrations of 4-*t*-OP were prepared by dissolving 4-*t*-OP in a solvent/water solution (30/70, v/v). Different additives were added to the methanol/water solutions to determine their effect on the degradation of 4-*t*-OP. Catalysts were added to the 4-*t*-OP solutions in a 50 mL beaker. The mixture was then stirred for about 2 h to achieve adsorption–desorption equilibrium for 4-*t*-OP. After reaching equilibrium, 1 mL of suspension was extracted in order to determine the initial concentration of 4-*t*-OP solution. The pH of the methanol/water solutions was adjusted by KOH and $HClO_4$. All investigations were performed at ambient temperature.

2.3 Irradiation experiments

All irradiation experiments were conducted using an electron accelerator (GJ-2-II accelerator, Xianfeng electrical plant) belonging to the Institute of Applied Radiation, Shanghai University, China. The EB energy was 1.8 MeV and the variable current power was in the range 0–10 mA. The solutions of 4-*t*-OP were irradiated by transmitting radiation at a distance of 30 cm from the source. The volume and thickness of the solutions of 4-*t*-OP in the film bag were 10 mL and 2 mm, respectively. The experiments were carried with an electron beam current of 1 mA. Samples were irradiated at absorbed doses ranging from 2 to 20 kGy. Before analysis, all samples were filtered through 0.45 μm syringe micro filters.

2.4 Products and analytical procedures

The samples of 4-*t*-OP irradiated by EB radiation were extracted three times with 50 ml of DCM and then three times with 50 ml of ethyl acetate, shaking for 30 min each time. The DCM and ethyl acetate layers were subsequently filtered and dehydrated through anhydrous Na_2SO_4. The extract was then concentrated to about 2 ml at 40 °C using a rotary vacuum evaporator and finally to near dryness under a nitrogen stream. The dried residue was dissolved in 1 ml of hexane for GC-MS analysis.

2.5 Analytical methods

A HPLC system (Agilent, USA, 1200 Series high-performance liquid chromatography) equipped with a XDB-C_{18} reverse phase column (150 mm×4.6 mm^2) was used for quantitative determination of 4-*t*-OP before and after EB irradiation. The injection volume was 10 μL. The mobile phase was a mixture of methanol and Milli-Q water (80/20, v/v), with a flow rate of 1.0 $mL\cdot min^{-1}$. The column temperature was maintained at 298 K, and the wavelength for UV detection was set at 220 nm.

The organic acids, the 4-*t*-OP decomposition products of the irradiated samples, were analyzed using an ion chromatograph (IC-Metrohm MIC advanced) with a METROSEP A SUPP 5-250 (5 mm particle size, 250 mm×4 mm) column. The eluent was 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ at a flow rate of 0.7 $mL\cdot min^{-1}$. The injection volume of the sample was 10 μL.

A GC 7890A gas chromatograph (Agilent, USA) coupled to a 5975C mass spectrometer (Agilent, USA) with a DB-5MS capillary column (length:30 m; i.d.: 0.25 mm; thickness: 0.25 μm) was used for analyzing the degradation products of 4-*t*-OP. Helium was used as the carrier gas and flowed through the column at a rate of 1.0 $mL\cdot min^{-1}$. The oven temperature program was set as follows: the initial temperature was held at 50°C for 2 min, increased at the rate of 10°C·min^{-1} to 200°C, increased at 15°C·min^{-1} to 260°C, increased at 5°C·min^{-1} to 300°C and finally maintained at 300°C for 5 min. The MS was by electron impact ionization at 70 eV and operated in full-scan mode from m/z 35–300 for qualitative analysis. The inlet and MS transfer line temperatures were maintained at 300°C, and the ion source temperature was 230°C. The sample injection was operated in splitless mode at a temperature of 280°C and 1 μl sample volumes were used.

3 Results and discussion

3.1 Irradiation of 4-*t*-OP in different solutions

During EB irradiation, water radiolysis happened within a short time. The radiation technology used very reactive species such as $H^\bullet$, e_{aq}^- and ·OH as well as less reactive species, such as H_2O_2, H_2 and H_3O^+, produced by water radiolysis (Eq.(1)) for the decomposition of the toxic or refractory organic compounds[21].

$$\begin{aligned}H_2O \rightarrow (2.7)\cdot OH + (2.6)e_{aq}^- + (0.55)H^+ +\\ (0.45)H_2 + (0.7)H_2O_2 + (2.6)H_3O^+\end{aligned} \quad (1)$$

In methanol/water solution, ·OH is easily scavenged by methanol and eaq- is the main reactive species:

$$CH_3OH + \cdot OH \rightarrow \cdot CH_2OH + H_2O \quad (2)$$

In acetonitrile/water solution, acetonitrile scavenges a large amount of e_{aq}^- and ·OH is the main reactive species:

$$e_{aq}^- + CH_3CN \rightarrow CH_3CHN\cdot(\text{or } \cdot CH3CNH) + \cdot OH^- \quad (3)$$

The effect of different solutions on the degradation of 4-*t*-OP by EB irradiation is shown in Fig.1. The degradation rate in the reducing methanol/water solution is higher than that in the oxidizing acetonitrile/water and acetone/water solutions at the same absorbed dose. For example, at an absorbed dose of 10 kGy and an initial concentration of 25 mg·L^{-1}, the degradation efficiency of 4-*t*-OP was 62.3% in the methanol/water solution, but only 42.9% and 35.5% in acetonitrile/water and acetone/water solutions, respectively. Furthermore, it was removed more rapidly by EB radiation as the absorbed dose increased in methanol/water solution than in acetonitrile/water and acetone/water solutions. These results indicate that both ·OH and e_{aq}^- play an important role in the decomposition of 4-*t*-OP, but that e_{aq}^- is more effective. Because of the higher degradation rate in the methanol/water solution, we used it for further investigations.

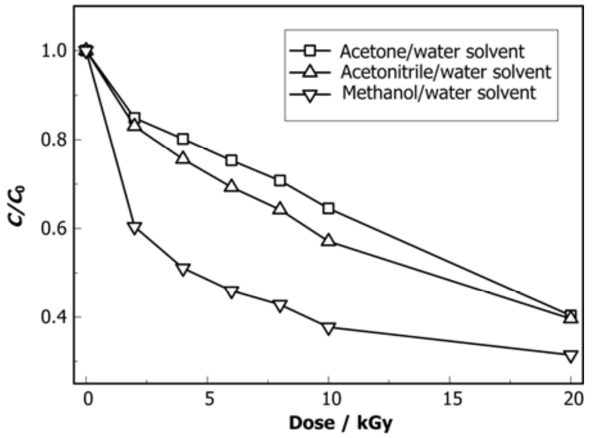


Fig.1 Radiolysis of 4-*t*-OP (25 mg·L^{-1}) in different solutions.

The decomposition efficiency depends on the unit dose and can be expressed by the specific reduction efficiency (*G*), which was defined by Mohamed *et al*[18] as:

$$G = \frac{\Delta R N_A}{D(6.24\times10^{17})} \quad (4)$$

where ΔR is the change in 4-*t*-OP concentration (mol·L^{-1}) at a given absorbed dose, *D* is the absorbed dose in kGy, 6.24×10^{17} is the conversion constant from kGy to 100 eVL^{-1}, and N_A is Avogadro's constant (6.02×10^{23}).

According to Eq.(4), the *G* values of 4-*t*-OP in methanol /water solution are shown in Fig.2. The results show that the *G* values decrease with increment of absorbed dose, which is due to the relative concentration of active species being lower at higher absorbed doses[22].

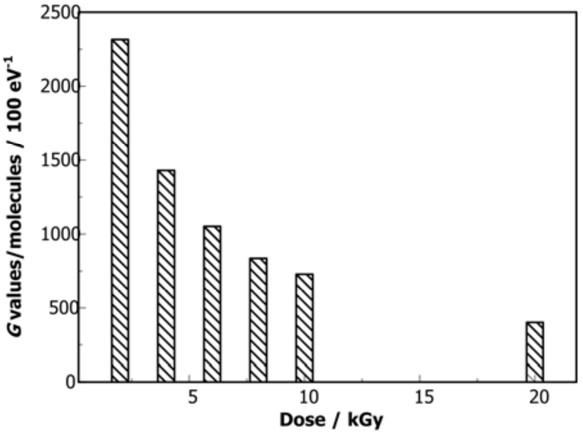


Fig.2 Relationship between specific reduction efficiency (G) and dose of EB radiation for 4-*t*-OP in a methanol /water solution.

3.2 Effect of initial concentration and absorbed dose in methanol/water solution

Both initial concentration and absorbed dose of 4-*t*-OP are important parameters that effect the radiolytic degradation of 4-*t*-OP. Methanol /water solutions having initial concentrations of 10, 15, 20, 25, 30 mg·L^{-1} were irradiated by 2, 4, 6, 8, 10, 20 kGy EB radiation at room temperature. The influence of these two factors on 4-*t*-OP degradation is shown in Fig.3a. It shows that 4-*t*-OP in methanol /water solution can be efficiently decomposed by EB irradiation. The required absorbed doses to remove greater than 70% of 4-*t*-OP were 10, 20 and 20 kGy at the initial concentration of 10, 15 and 20 mg·L^{-1}, respectively. Even at the higher concentrations of 25 and 30 mg·L^{-1}, the concentration of 4-*t*-OP decreased by more than 60% when 20 kGy was applied. The results indicate degradation depends on the initial concentration of 4-*t*-OP, and better decomposition can be achieved with low initial concentrations and high applied absorbed doses. At higher concentration of 4-*t*-OP, degradation was somewhat slower, although the total degradation of 4-*t*-OP was higher. Furthermore, with decrement of

4-*t*-OP concentration, the absorbed dose needed for complete degradation decreased.

The absorbed dose required for the decomposition of 4-*t*-OP to 50% of its initial concentration ($D_{1/2}$) was investigated by varying the initial concentration of 4-*t*-OP and the absorbed dose of EB radiation (Fig.3b). The absorbed dose was found to have a linear relationship with initial concentration ($r > 0.99$). An increment of initial concentration leads to an increment of $D_{1/2}$, and the values of $D_{1/2}$ are lower than 10 kGy. Thus, EB irradiation is feasible method for removing 4-*t*-OP in methanol /water solution.

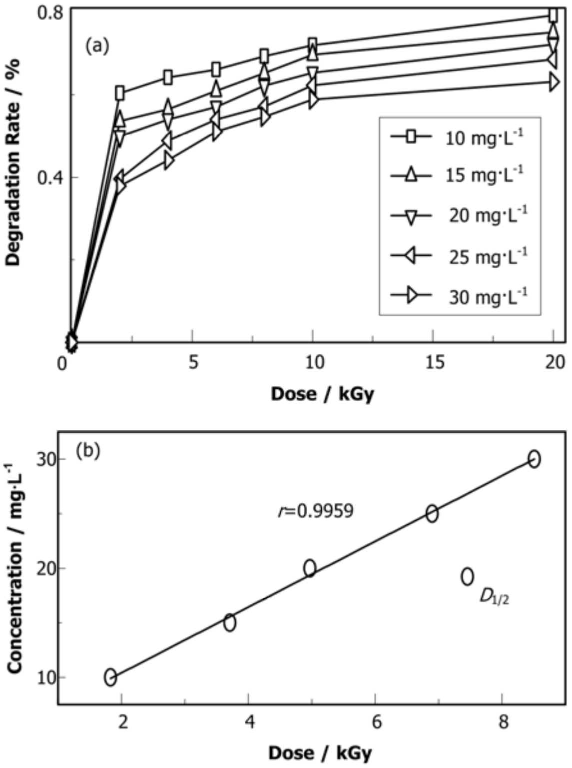


Fig.3 Degradation of 4-*t*-OP for different initial concentrations: (a) relationship between degradation rate and absorbed dose and (b) relationship between initial concentration and absorbed dose.

3.3 Effect of anions on radiolytic decomposition of 4-*t*-OP

It is well known that the presence of anions affect the degradation of organic pollutants in the environment. Natural ground water contains many potential anions, such as HSO_4^-, SO_3^{2-}, NO_3^- and NO_2^-. The same concentrations (10 mg·L^{-1}) of $NaHSO_4$, Na_2SO_3, $NaNO_3$, $NaNO_2$ were added to the methanol/water solution. The degradation efficiency of 4-*t*-OP in the presence of these anions improved with increment of absorbed dose (Fig.4). However, the degradation efficiency of 4-*t*-OP decreased with the addition of anion compared with the solution without the additive. This can be attributed to e_{aq}^- being removed by the HSO_4^-, SO_3^{2-}, NO_3^- and NO_2^- anions[19,23,24], further indicating that e_{aq}^- have a significant role in the decomposition of 4-*t*-OP.

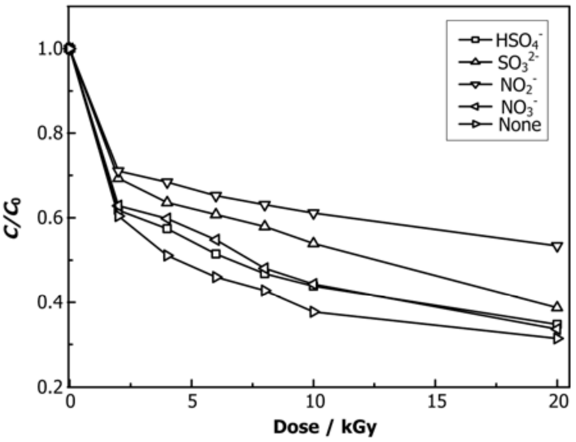


Fig.4 Degradation efficiency of 4-*t*-OP in the presence of different anions.

3.4 Effect of H_2O_2 on the degradation of 4-*t*-OP References

H_2O_2 is an oxidation agent that is widely used in wastewater treatment. As shown in Fig.5, removal of 4-*t*-OP was less effective in the presence of H_2O_2 than in pure solvent.

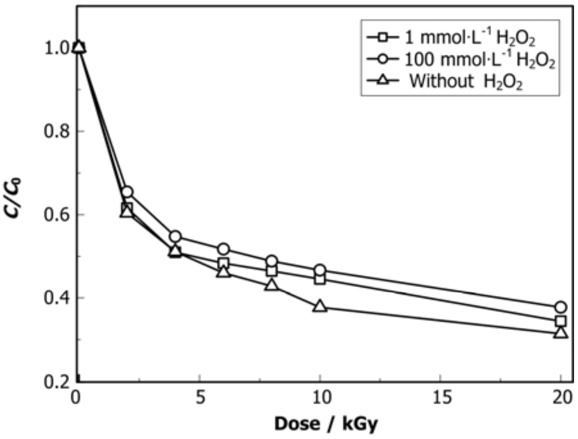


Fig.5 Effect of H_2O_2 on 4-*t*-OP degradation in methanol /water solution.

The degradation efficiency of 4-*t*-OP at an absorbed dose of 10 kGy was 62.3%, 53.4% and 55.5% for H_2O_2 concentrations of 0, 10 and 100 mmol·L^{-1}, respectively. This can be attributed to H_2O_2 reacting with e_{aq}^- by the equation[25,26]:

$$H_2O_2 + e_{aq}^- \rightarrow \cdot OH + OH^- \quad (5)$$

In reducing conditions, e_{aq}^- is the main reactive species that degrades 4-*t*-OP, e_{aq}^- is scavenged by H_2O_2 and the ·OH produced (Eq.(5) are scavenged by methanol (Eq.(2)). As a result, the amount of e_{aq}^- is reduced during EB irradiation in the presence of H_2O_2.

3.5 Effect of saturation with different gases on the decomposition of 4-*t*-OP

Decomposition curves of 4-*t*-OP by EB irradiation under N_2, O_2 and air -saturated conditions are shown in Fig.6. From the results, the degradation efficiency of 4-*t*-OP is in the order N_2 > Air > O_2. The highest degradation efficiency of 4-*t*-OP is in a N_2-saturated system. The concentration of 4-*t*-OP in N_2-saturated solutions decreases by more than 50% when 4 kGy is applied and in air-saturated solutions when 6 kGy is applied. In the O_2-saturated system, the degradation efficiency of 4-*t*-OP was low. However, it still degraded more than 50% of the 4-*t*-OP even at a relatively low absorbed dose of 10 kGy. In the presence of O_2, e_{aq}^- is converted into the oxidative species $O_2^{-\cdot}$[27-29], so the amount of e_{aq}^- is less in the presence of O_2. In summary, the N_2-saturated system leads to an increment of 4-*t*-OP degradation and 4-*t*-OP degradation efficiency is dependent on the concentration of e_{aq}^- in the methanol/water solution.

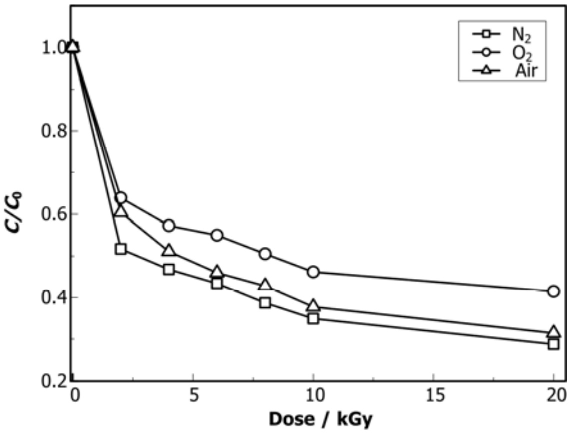


Fig.6 Degradation efficiencies of 4-*t*-OP saturated with different gases.

3.6 Effect of catalyst on decomposition of 4-t-OP

Although EB irradiation has been demonstrated to be effective for the degradation of numerous organic pollutants, improvement of the efficiency is still necessary for commercial use. As with photocatalysis, it has been reported that the addition of catalysts to the solution before photodegradation enhances the degradation of pollutants[30,31]. According to the literature, catalysts might accelerate the reactions induced by EB radiation[32,33]. The effect of the catalysts TiO_2 and ZnO on the decomposition of 4-*t*-OP are shown in Fig.7.

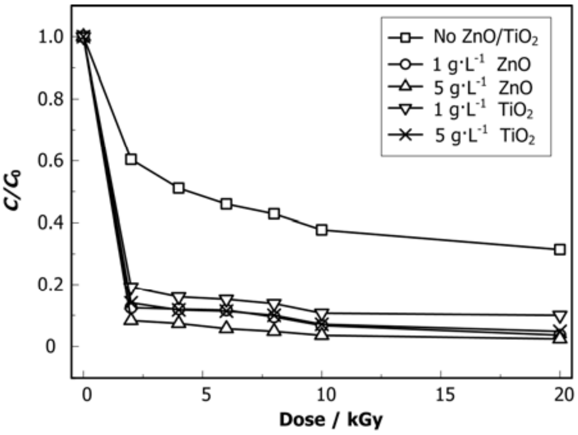


Fig.7 Effect of ZnO and TiO2 catalysts on the decomposition of 4-*t*-OP with EB radiation in a methanol/water solution.

As shown in Fig.7, the amount of 4-*t*-OP decreased and finally disappeared by increment of the amount of TiO_2 or ZnO from 0 to 5 $g\cdot L^{-1}$. This is in marked contrast to the removal of 4-*t*-OP without catalyst. The concentration of 4-*t*-OP decreased rapidly when increasing the absorbed dose from 0 to 20 kGy in the presence of the catalysts. The degradation rate of 4-*t*-OP was in the order: ZnO (5 $g\cdot L^{-1}$) > ZnO (1 $g\cdot L^{-1}$) > TiO_2 (5 $g\cdot L^{-1}$) > TiO_2 (1 $g\cdot L^{-1}$) > No catalyst. This indicates that the catalytic efficiency of ZnO is much higher than TiO_2 for degrading 4-*t*-OP under EB irradiation. The results indicate that the presence of both TiO_2 and ZnO promote the decomposition of 4-*t*-OP under EB irradiation.

3.7 Effect of initial pH values on 4-*t*-OP degradation

The initial pH value is an important parameter that might affect the decomposition efficiency of 4-*t*-OP during radiolysis[34]. The initial pH values of the 4-*t*-OP solutions were adjusted to 3, 5.9 and 11 by

$HClO_4$ and KOH. The 4-*t*-OP degradation efficiency by EB irradiation with different initial pH values are shown in Fig.8a. Removal of 4-*t*-OP was generally more effective under alkaline conditions than under acidic and neutral conditions. For example, the degradation efficiency at pH 11 is 70.7% at 10 kGy, while at the same absorbed dose the degradation efficiency at pH 5.9 and 3 are 62.3% and 67.2%, respectively. The highest 4-*t*-OP degradation efficiency was at pH 11, which is consistent with the results reported by Zhang[14]. As we knew, in alkaline condition, H· would be inverted into e_{aq}^- by the equation[35,36]:

$$H\cdot + OH^- \rightarrow H_2O + e_{aq}^- \tag{6}$$

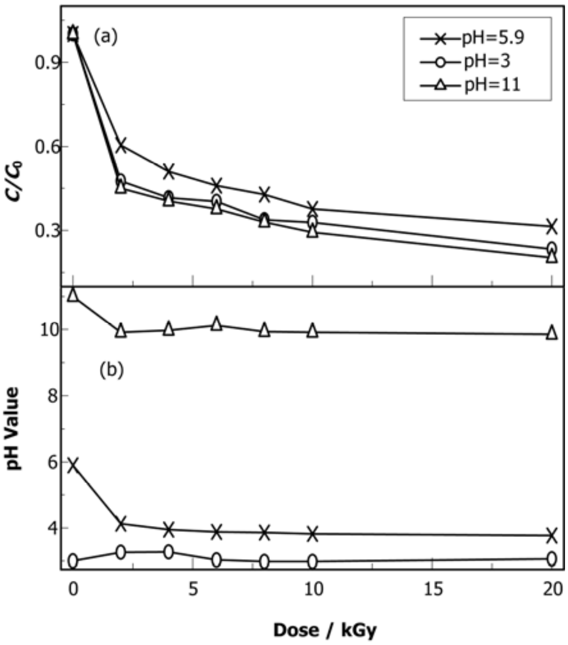


Fig.8 (a) Decomposition of 4-t-OP in different pH solutions and (b) Variation of pH with EB radiation dose.

As one of the main reactive species to degrade 4-*t*-OP, more e_{aq}^- existed under alkaline condition from the Eq.(6). In addition, e_{aq}^- played a crucial role in the decomposition of 4-*t*-OP in the reducing methanol/water solution. As a result, the relative concentration of e_{aq}^- was higher in alkaline condition and change of pH value could accelerate e_{aq}^- reacting with 4-*t*-OP. Therefore, the degradation efficiency of 4-*t*-OP is dependent on the initial pH value of the solution.

3.8 Change of pH value

Figure 8b shows the effect of EB irradiation on the pH value of methanol /water solution. In Fig.8b, the pH values were in the range 2.98 to 3.27 for an initial pH of 3. In contrast, the pH value significantly changed between 9.85 and 10.12 for an initial pH of 11. The results show that the pH value decreases smoothly with increment of absorbed dose due to H_3O^+ being produced by the irradiation process (Eq.(1)).

3.9 Analysis of the organic products of the 4-t-OP degradation process

When a new treatment process is being considered, not only is the removal of the target compounds of interest but also the reaction products. In our investigation, the organic acids produced by the degradation of 4-*t*-OP were identified using ion chromatography. Fig.9 shows the continuous accumulation of short-chain organic acids by the degradation process of 4-*t*-OP.

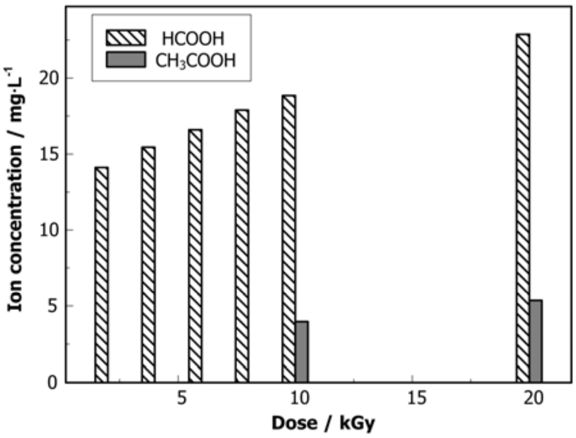


Fig.9 Concentrations of organic acids at different absorbed doses.

Ion chromatography analysis (Fig.9) shows that the main degradation product of 4-*t*-OP was HCOOH, which was produced immediately after the irradiation and increased with the increment of the absorbed dose. In addition, trace levels of CH_3COOH were also detected at the high absorbed doses. In the degradation process of 4-*t*-OP, the concentration of HCOOH was as high as 22.87 mg·L^{-1} when 20 kGy was applied. In contrast, CH_3COOH appeared at the high absorbed dose and maintained a steady value of about 4 mg·L^{-1}.

3.10 Reaction mechanism

When a radiation process is applied for treating various organic pollutants, not only are the degradation products of interest but also is the primary radiolytic degradation mechanism. Characterization of the 4-*t*-OP degradation products was helpful in determining the pathways for the degradation of the compound. HPLC shows the existence of intermediate compounds in the reaction mechanism, and analysis and identification of these compounds was done by GC–MS.

The decomposition intermediates of 4-*t*-OP were studied by GC–MS, and the total ion chromatograph is shown in Fig.10. Five 4-t-OP degradation products by radiolysis were identified, and are listed in Table 1. Based on the identification of the intermediate products, the corresponding degradation pathway of 4-*t*-OP by EB irradiation is proposed in Fig.11. This degradation pathway of other compounds arising by e_{aq}^- attacking was suggested by the literature[37,38].

The mechanism of radiolytic decomposition of 4-*t*-OP is initiated by e_{aq}^- attack of the alkyl side chain of 4-*t*-OP. When e_{aq}^- attack occurs, path A shows that 4-*t*-OP is decomposed to phenol and 2, 2, 4-trimethylpentane. Phenol is a very stable intermediate. In addition, 4-*t*-OP is also attacked by e_{aq}^- to produce p-tert-butyl-phenol (path B), p-tert-butyl-phenol is further attacked by e_{aq}^- and decomposed to ethylbenzene, styrene and bicyclo[4.2.0]octa-1,3,5-triene, which are all very stable. The pathway illustrates the important role played by e_{aq}^- in the decomposition of 4-*t*-OP.

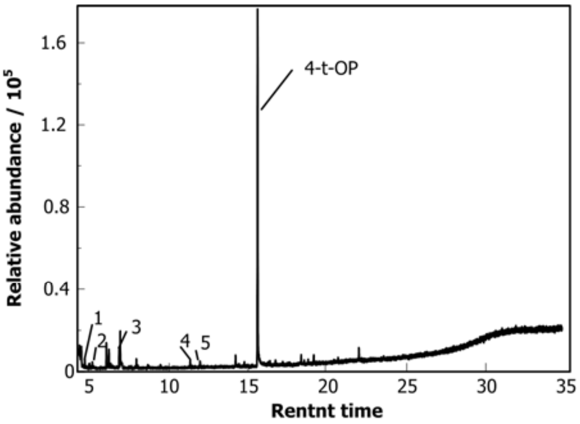


Fig.10 Total ion chromatogram of products extracted from irradiated solution of 4-*t*-OP. after 70% decomposition under EB irradiation (20 kGy).

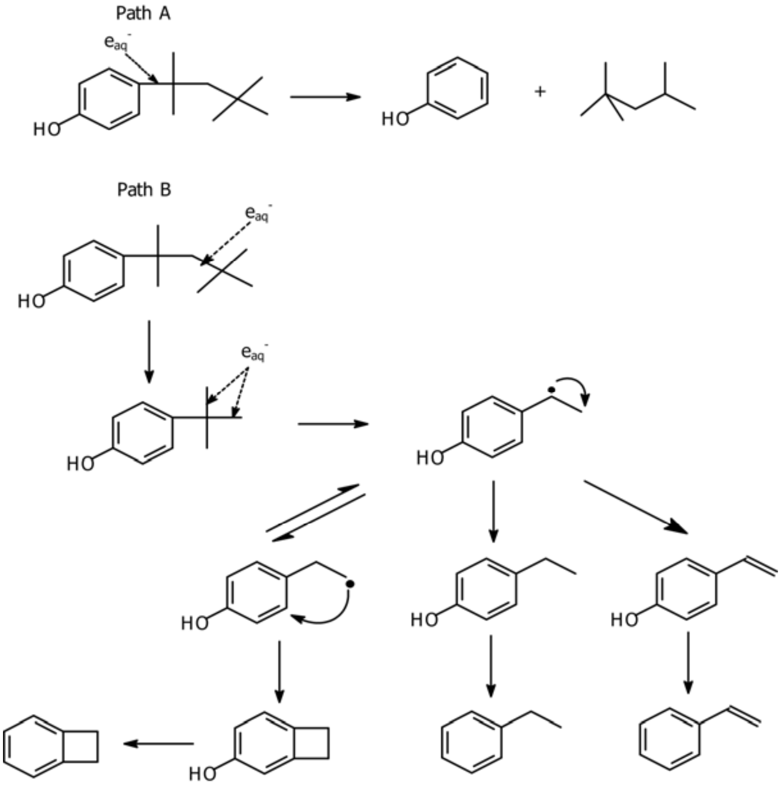
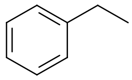
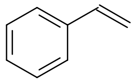
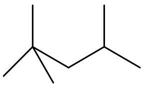
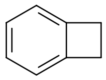
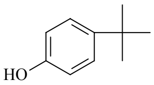


Fig.11 Schematic of initial degradation pathway of 4-*t*-OP.

Table 1 Retention time and m/z values of the 4-*t*-OP degradation products from GC–MS qualitative analysis.

Peak in Fig.10	Parent products	Retention time(min)	Structure	Fragment(relative abundance)
1	Ethylbenzene	4.92, 4.98		51.1, 65.1, 78, 85, 91, 106
2	Styrene	5.42, 5.45		78.0, 89.1, 103.9
3	2,2,4-trimethylpentane	7.08, 7.14		44, 57.1, 71, 85, 98.9, 111.9
4	Bicyclo[4.2.0]octa-1,3,5-triene	11.55, 11.65		27, 39, 51, 63, 78, 89, 104
5	P-tert-butyl-phenol	11.75, 11.85		64.8, 77, 95, 107, 118.9, 135, 150.1

4 Conclusion

Electron beam irradiation effectively degrades 4-*t*-OP. At an absorbed dose of 10 kGy, the degradation efficiency of 4-*t*-OP in methanol/water solution was 62%, while degradation efficiency of 43% and 36% were achieved in acetonitrile/water and acetone/water solutions, respectively. It indicated that both ·OH and e_{aq}^- played an important role in the decomposition of 4-*t*-OP, although e_{aq}^- was more effective. The degradation rate of 4-*t*-OP decreased with increment of absorbed dose in the methanol/water solution, which was illustrated by changes in the specific reduction efficiency (*G*). In methanol/water solution (30/70, v/v), the degradation rate of 4-*t*-OP increases with decreasing initial concentration and increasing absorbed dose. The *G* value decreased with the increment of absorbed dose.

The addition of HSO_4^-, SO_3^{2-}, NO_3^- and NO_2^- reduced the degradation efficiency, as did the addition of H_2O_2. A N_2-saturated system led to a relative increment of 4-*t*-OP degradation compared with O_2 saturation and in air. All systems indicated that e_{aq}^- played a crucial role in the decomposition of 4-*t*-OP. The degradation of 4-*t*-OP was dramatically increased by the addition of a catalyst (TiO_2 or ZnO) in methanol/water solution. The initial pH value was also found to have an effect on the decomposition efficiency. Furthermore, degradation rate increased in alkaline condition compared with neutral and acidic solutions. A preliminary investigation of the reaction mechanism suggested that the initial products of the reaction were ethylbenzene, styrene, bicyclo[4.2.0]octa-1,3,5-triene, 2,2,4-trimethylpentane and p-tert-butyl-phenol by e_{aq}^- attack at the alkyl side chain of 4-*t*-OP.

Based on these results, EB irradiation is a promising method for the degradation of 4-*t*-OP by e_{aq}^- attack at the alkyl side chains of 4-*t*-OP. The results support the idea of using EB irradiation to degrade pollutants in aquatic environments. Furthermore, EB irradiation could be used in combination with more traditional methods for the treatment of water and wastewater.

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