Effect of electron beam irradiation on the degradation of monochlorophenols in aqueous solution

ADELEKE Olukunle Francis[1,*] , ZHOU Rui-min[2] , Zu Jian-hua[2] , Ekoko Bakambo Gracien[1]

(1.School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200072, China. E-mail: kadeleke@yahoo.com; 2. Shanghai Applied Radiation Institute, Shanghai University, Shanghai 201800, China)

Abstract: Electron beam was successfully used for the degradation of 2-chlorophenol(2-CP) and 4-chlorophenol(4-CP) in aqueous solutions in this research. The effect of radiation dose on substrate degradation and dechlorination of solutions with concentration of 50 mg/L was investigated. The effect of initial concentration, pH and presence of oxygen was also investigated. The concentration of 2-CP and 4-CP remaining in solution after irradiation were measured by HPLC. The results showed that increased radiation dose led to increased degradation of the chlorophenols and increased Cl^- yield. Deaeration was also found to significantly increase the rate of degradation of chlorophenols in water while degradation and dechlorination under alkaline condition was lower than at low to neutral pH.

Keywords: electron beam; monochlorophenols; degradation; deaeration

Introduction

The effectiveness of the degradation of toxic organic pollutants in water by advanced oxidation processes(AOPs) especially the use of ionizing radiation in form of γ-irradiation and electron beam irradiation has been demonstrated by several researchers. The studies have also shown that electron beam irradiations are efficient in the destruction of several classes of hazardous organic compounds (Cooper, 1992; Nickelsen, 1992; Getoff, 1996; Schmid, 1997; Sampa, 1998; Gehringer, 1998; Zele, 1998; Song, 2002).

Phenolic compounds, especially chlorophenols, are one of the most common anthropogenic pollutants found in natural water and wastes, as they are used in the production of biocides, dyes and drugs, and they are formed during paper production and water disinfection by chlorine or chlorine dioxide (Trojanowicz, 2002). 2-CP and 2, 4-DCP are included in the USEPA list of priority pollutants and 2-CP, 4-CP and 2,4-DCP are all listed in the European Community (EC) directive 76/464/EEC concerning dangerous substances discharged into the aquatic environment (Jáuregui, 2001). The Integrated Water Discharge Standard of China (GB 8978—1996) also listed 2,4-DCP among the some priority organic pollutants whose maximum discharge concentration should be regulated(Zhang, 1994).

Some papers have been published on the radiolytic degradation of monochlorophenols (Schmid, 1997; Zona, 1999) and 2, 4-DCP (Zona, 1999; Trojanowicz, 2002). However all these irradiation were carried out using γ-irradiation sources. Up till now, there are very few research on the irradiation of aqueous solutions of chlorophenols using electron beam (EB) from high energy electron accelerators except for Song et al .(Song, 2001).

The goals of this study were to investigate the effect of electron beam irradiation dose on the destruction of 2-

chlorophenol(2-CP) and 4-chlorophenol(4-CP) at different initial concentrations; the inorganic chloride produced; and the effect of initial pH and oxygen on the rate of degradation.
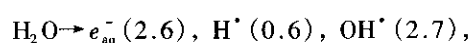
1   Materials and methods

Chemically pure phenol, 2-chlorophenol(2-CP) and 4-chlorophenol(4-CP) were used without further purification. Solutions were made in deionized water. Eluents for HPLC were water (twice distilled), methanol (HPLC-grade) and acetonitrile(HPLC-grade). H_2SO_4 and NaOH were used to adjust the initial pH of the solutions. N_2 gas was used to remove oxygen in the deaerated solution experiments.
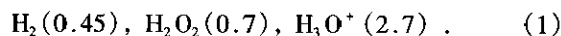
Electron beam irradiations using a 2 MeV electron beam accelerator were carried out at Shanghai Applied Radiation Institute, Jiading Campus, Shanghai University, China. The electron beam scans an area of 120 cm length and 7 cm width.

The determination of substrate degradation was performed by HPLC(Agilent 1100 Series, Zorbax SB-C18(5 μm) column; flow rate: 1 ml/min, isocratic elution(water: methanol: acetonitrile = 40:30:30). It was equipped with a multiple wavelength UV-VIS detector with diode array; the adsorption was measured at 225 nm and 280 nm for all compounds. Chloride ion measurement was done using Hach DR/2010 Spectrophotometer (Mercury (II) thiocyanate method), pH measurements were done with the pH electrode and dissolved oxygen(DO) measurements were determined by YSI 5095 BOD probe and YSI 58 dissolved oxygen meter.

2   Results and discussion

The irradiation of water produces hydrogen atoms, $H^\bullet$; solvated electrons, e_{aq}^- ; hydroxyl radicals, $OH^\bullet$; H_2 ; H_2O_2 , H_3O^+ and OH^- (Equation (1)).

$$H_2O \rightarrow e_{aq}^- (2.6), \ H^\bullet (0.6), \ OH^\bullet (2.7),$$

$$H_2(0.45), \ H_2O_2(0.7), \ H_3O^+(2.7) \ . \qquad (1)$$

While OH$^\bullet$ is a powerful oxidizing agent, e_{aq}^- and H$^\bullet$ are strong reducing agents. These three species are the most important in the destruction of toxic pollutants in water(Lin, 1995). The values in parentheses represent the G values. G is the number of reactive species formed or destroyed per 100 eV of absorbed energy. The absorbed dose is the energy transferred from the incident radiation to the material being irradiated. It is responsible for producing ions and excited species in the irradiated material which then induce radiation-induced chemical changes in the material(J/kg, Gy).

In the presence of air, H$^\bullet$ and e_{aq}^- are scavenged by oxygen, forming HO$_2^\bullet$ and O$_2^{\bullet-}$ (Getoff, 1996).

$$H + O_2 \rightarrow HO_2^\bullet \ , \qquad (2)$$

$$e_{aq}^- + O_2 \rightarrow O_2^{\bullet-} \ . \qquad (3)$$

However, the superoxide radicals HO$_2^\bullet$ and O$_2^{\bullet-}$ have been shown to contribute insignificantly to the degradation of chlorophenols. Thus in aerated solutions, the decomposition of chlorophenols are essentially due to OH$^\bullet$ radical attacks (Zona, 1999). The reaction radiolytic reactions of 4-CP in the presence of oxygen are given in Equations (4) to (7).

(4)

(5)

(6)

(7)
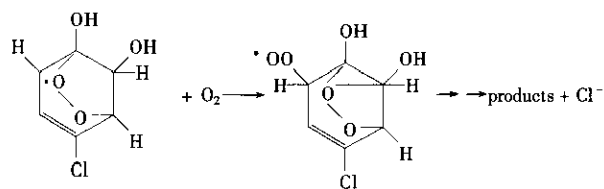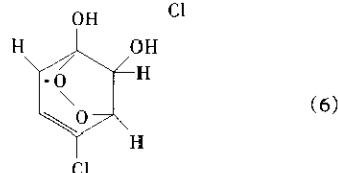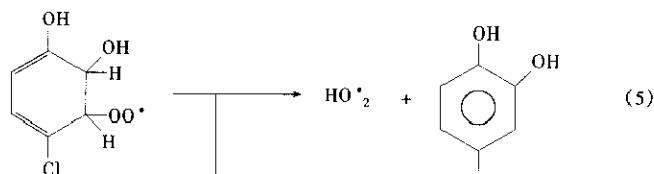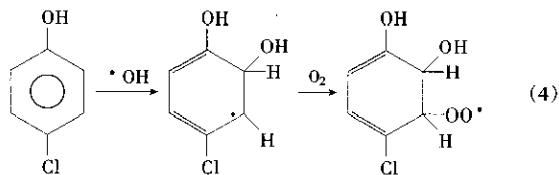
2.1 Effect of radiation dose on degradation of chlorophenols

Fig. 1 shows the HPLC chromatogram of 50 mg/L 4-CP at irradiation doses of 0 kGy(non-irradiated) and 4 kGy. It can be seen that not only has the concentration(area under the graph) of the substrate decreased after irradiation, but several reaction intermediates have also been formed at a dose of 4 kGy.

Fig. 2 shows the degradation of 50 mg/L 2-CP and 4-CP in aqueous solution at different irradiation doses. The result showed that the concentration of the original substrate decreases with increasing irradiation dose, it implies increasing degradation. At radiation doses of 4 kGy and 8 kGy, the concentration of 2-CP left in solution was 12.3 mg/L(75.4% degradation) and 9.4 mg/L(81.2% degradation) respectively, while that of 4-CP was 7.2 mg/L (81.4% degradation) and 4.0 mg/L(91.9% degradation). It is also obvious from the graph that at all the studied doses the rate of degradation of 4-chlorophenol was higher than 2-chlorophenol, which is in agreement with the studies on 5 × 10^{-4} mol/L γ-irradiated solutions of monochlorophenols (Zona, 1999). This means that the position of the chlorine on the phenol ring may have an effect on the rate of degradation. For both 2-CP and 4-CP, it can be seen from the slopes of the curves that the initial rate of degradation was higher at lower doses and falls with increasing dose. This is due to the competition with intermediate products formed for the OH$^\bullet$ radicals at increasing doses(Zona, 1999).

2.2 Effect of initial concentration on rate of degradation

To further examine the effect of initial concentration on the radiolytic degradation of the chlorophenols, 150 mg/L
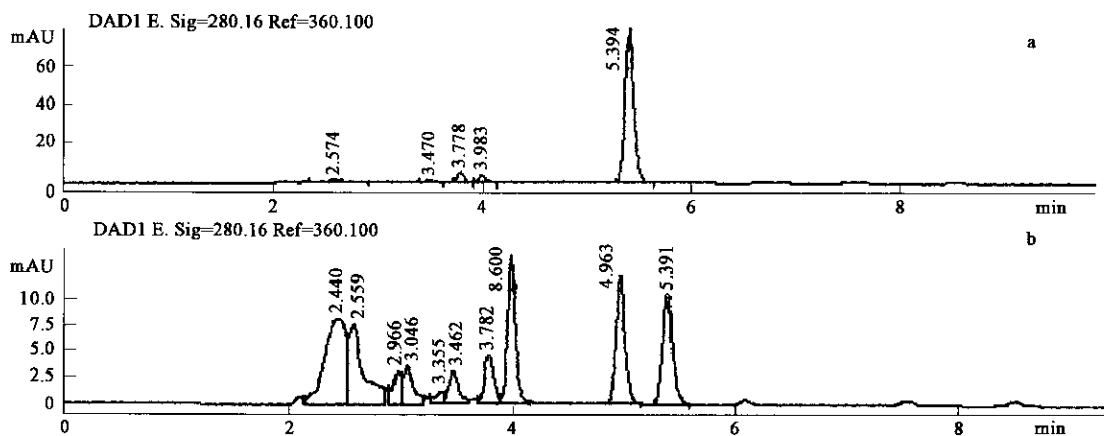
Fig. 1 HPLC chromatogram of 4-CP(50 mg/L) for (a) non irradiated solution and (b) after an irradiation dose of 4 kGy. The retention times of 5.394 (a) and 5.391 (b) represents 4-CP
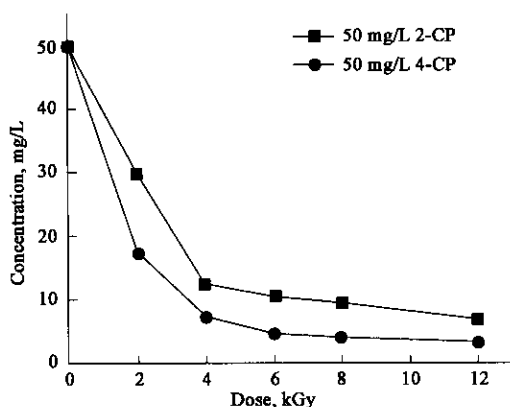
Fig. 2　Removal of 50 mg/L 2-CP and 4-CP in water by electron beam irradiation

2-CP and 200 mg/L 4-CP solutions were irradiated at doses of 4, 8 and 18 kGy as shown in Fig. 3. For the 2-CP solution, 51.7% degradation and 68.7% degradation were observed at doses of 4 kGy and 8 kGy respectively as compared to 75.4% and 81.2% in the 50 mg/L solution earlier discussed. For the 4-CP solution, degradation of 46.5% and 70.4% were observed for the 200 mg/L solutions at doses of 4 kGy and 8 kGy respectively compared to 81.4% and 91.9% in the 50 mg/L solutions. At a dose of 18 kGy, 86.1% degradation was achieved for 150 mg/L 2-CP and 89.5% for 200 mg/L 4-CP. These results showed clearly that the rate of degradation reduces with increasing initial concentration of the solute. The curves were generally in accordance with a first order exponential decay.
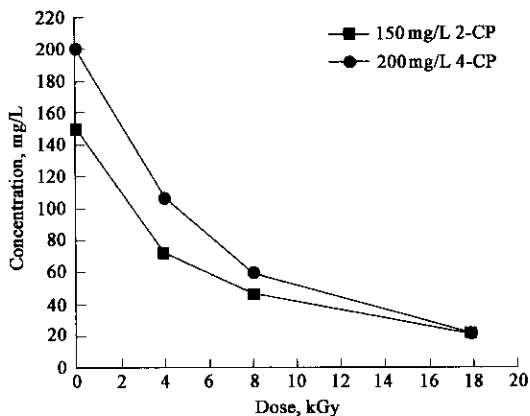

Fig. 3　Degradation of 200 mg/L 4-CP and 150 mg/L 2-CP in water by electron beam irradiation

2.3　Effect of irradiation on formation of inorganic chloride

During the irradiation of chlorine-containing organic compounds, the decomposition of the parent compound leads to inorganic chloride formation. Thus, chloride ion is one of the by-products of irradiation of chlorophenols (Equation (7)), and its formation increases with increasing radiation dose shown in Fig. 4 and Fig. 5. The yield of inorganic chloride from the decomposition of 2-CP at irradiation dose of

8 kGy is 62.3% (50 mg/L) and 17.6% (150 mg/L); while for 4-CP, the chloride yield is 68.8% (50 mg/L) and 20.1% (200 mg/L). These results showed that the rate of dehalogenation or chloride formation is much lower than that of decomposition of the original compound. This may be due to the formation of other organochlorides as intermediate products. Also, the dose rate required for dechlorination increases with increasing initial concentration of the substrate.
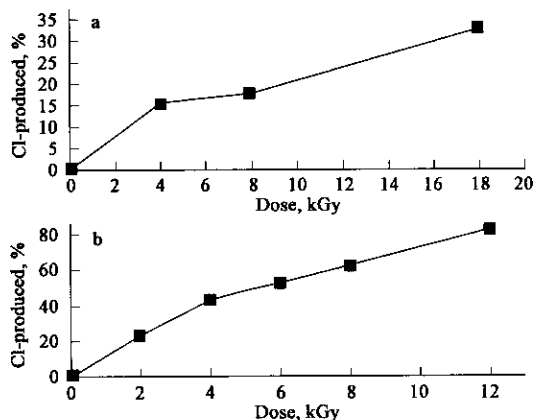

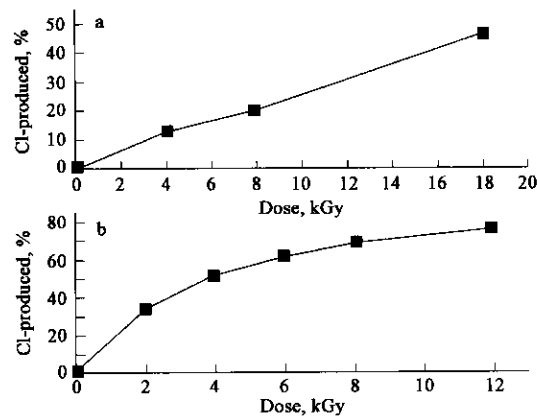Fig. 4　Inorganic Cl⁻ produced during irradiation of (a) 150 mg/L and (b) 50 mg/L 2-CP in water

Fig. 5　Inorganic Cl- produced during irradiation of (a) 200 mg/L and (b) 50 mg/L 4-CP in water

2.4　Effect of presence of oxygen on degradation and chloride formation

To study the effect of presence of oxygen on the degradation of chlorophenols, oxygen-containing solutions and deaerated solutions of 2-CP and 4-CP were irradiated. The DO of the oxygen containing solutions was between 9.0 mg/L and 9.5 mg/L while deaeration was achieved by passing N_2 gas into the solution to displace the oxygen. Results (Table 1) showed that both the rate of degradation and chloride formation at all doses were considerably higher in the deaerated solutions than the oxygen-containing solutions. 99.2% degradation was observed for the deaerated 2-CP compared to 81.2% in the oxygen-containing solution at a dose of 8 kGy. For 4-CP, 98.9% (deaerated) and 91.9%

(oxygen-containing) degradation was observed at a dose of 8 kGy.

In the presence of oxygen, $H^{\bullet}$ and e_{aq}^{-} are scavenged to form $HO_2^{\bullet}$ and $O_2^{\bullet -}$ (Equations (2) and (3)) and it is believed that these superoxides, except for $OH^{\bullet}$, are responsible for the oxidation and subsequent degradation of chlorophenols. However, the mechanism and the reason for the observed higher degradation rate in deaerated solutions is not known, as most previous works performed with aerated solutions (Getoff, 1988; Schmid, 1997; Zona, 1999; He, 2002; Trojanowicz, 2002). In a previous study on the degradation of trichloroethylene (Getoff, 1996), higher chloride yield was also observed in the airfree solutions and it was suggested that it might be due to specific e_{aq}^{-} attack on the Cl^{-} atom of the compound, in combination with $OH^{\bullet}$ reaction forming OH-adduct which undergo spontaneous decomposition.

Table 1   Degradation (%) and chloride formation (%) of 50 mg/L monochlorophenols in water after irradiation in the presence and absence of oxygen

Absorbed dose, kGy	2-CP				4-CP					
	4		8		2		4		8	
	Degr.	Cl^-	Degr.	Cl^-	Degr.	Cl^-	Degr.	Cl^-	Degr.	Cl^-
O_2-containing soln.	75.4	43.4	81.2	62.3	65.3	34.7	85.4	52.1	91.9	68.8
Deaerated soln.	85.5	72.1	99.2	82.4	86.3	71.0	98.8	81.2	98.9	97.4

2.5   Effect of initial pH on degradation of chlorophenols

Table 2 gives the result of the degradation of the two monochlorophenols under acidic, neutral and alkaline conditions at a dose of 4 kGy. 1.0 mol/L H_2SO_4 and 1.0 mol/L NaOH solutions were used to adjust the pH of the chlorophenols solutions. The result showed that at pH values of 3.1 and 7.2, there was no significant difference in the degradation of both 2-CP and 4-CP, but lower degradation was observed for the alkaline(pH 11.3) solution. This may be explained by the low yield of OH radical under high pH conditions as shown in Fig. 6.

Table 2   Degradation(%) of 50 mg/L monochlorophenols in water after irradiation(absorbed dose = 4 kGy) as a function of initial pH of solution

Initial pH	2-CP	4-CP
pH 3.1	75.5	84.7
pH 7.2	75.4	85.4
pH 11.3	45.8	63.8

3   Conclusions

Aqueous solutions of 2-CP and 4-CP have been successfully degraded by the use of high-energy electron beams. The relative rate of degradation and dechlorination was 4-CP > 2-CP. The rate of degradation was found to be dependent on the absorbed dose and initial concentration of the chlorophenols. The rate of dechlorination was also found to be dependent on the absorbed irradiation dose. For the 50
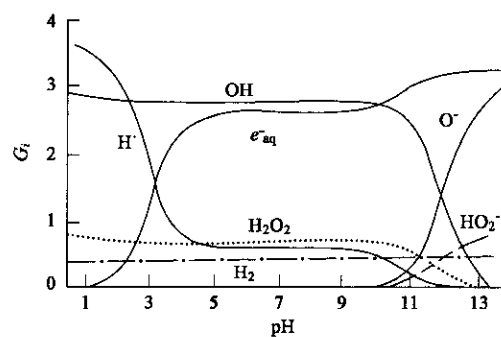

Fig. 6   Effect of pH on the primary products of water irradiation G_i values indicated the initial yield

(number of the species per 100 eV absorbed energy) (Source: Getoff, 1996)

mg/L solutions, 81.2% (2-CP) and 91.9% (4-CP) degradation was achieved at a radiation dose of 8 kGy. The rate of dechlorination was lower than substrate degradation and was 62.3% and 68.8% for 2-CP and 4-CP respectively at a dose of 8 kGy. Deaeration and low to neutral pH conditions were also found to favor the rate of degradation of the studied chlorophenols.

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