

Degradation of chlorophenols in aqueous solution by electron beam irradiation

ADELEKE O. Francis¹ ZHOU Ruimin² ZU Jianhua² HE Linfeng¹

¹ (School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200072)

² (Shanghai Applied Radiation Institute, Shanghai University, Shanghai 201800)

ABSTRACT Electron beam was used for degradation of aqueous solutions of 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), and 2,4-dichlorophenol (2,4-DCP) in this research. The effect of absorbed dose on substrate degradation, dechlorination and pH of solutions with an initial concentration of 200mg/L each and another solution containing 50mg/L each of the three solutes mixed together were investigated. The results show that increased dose leads to increased degradation of the chlorophenols, increased Cl^- yield and decreasing pH value of the solutions. For the individual solutions containing 200mg/L of solutes, the rate of degradation and chloride ion yield was in the order of 2,4-DCP>4-CP>2-CP, while for the mixed 50mg/L solution, while 2,4-DCP still has the highest degradation rate, the degradation of 4-CP and 2-CP proceeded almost at the same rate. At a dose of 21kGy, the rate of degradation were 93.0% for 2-CP, 98.5% for 4-CP and 99.4% for 2,4-DCP (200mg/L individual solutions), and the chloride yield was 55.4%, 71.3% and 69.0% for 2-CP, 4-CP and 2,4-DCP respectively. The calculated dose required for 90% degradation of the original solute (D_{90}) are 18.0kGy (2-CP), 11.4kGy (4-CP) and 6.1kGy (2,4-DCP) for the 200mg/L solutions and 16.1kGy (2-CP), 15.6kGy (4-CP) and 12.8kGy (2,4-DCP) for the 50mg/L mixed solution.

KEYWORDS Electron beam, Chlorophenols, Degradation

CLC X703

1 Introduction

The effectiveness of degradation of toxic organic pollutants in water by use of ionizing radiations of γ -rays or electron beams 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^[1-8].

Phenolic compounds, especially chlorophenols, are one of the most common anthropogenic pollutants found in natural water and wastes, as they are used in productions of biocides, dyes and drugs, and they are formed during paper production and water disinfection by chlorine or chlorine dioxide^[9]. 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^[10]. The Integrated Water Dis-

charge Standard of China (GB 8978-1996) also listed 2,4-DCP, along with some other priority organic pollutants, as chemicals to which maximum discharge concentration should be regulated^[11].

Some papers have been published on the radiolytic degradation of monochlorophenols^[4,12] and 2,4-DCP^[9,12]. However these studies were carried out using γ -irradiation sources. There are almost no papers on irradiating aqueous solutions of chlorophenols using electron beam (EB) from high energy electron accelerators except for [13].

The goals of this study were to investigate the effect of absorbed dose on destruction of 2-CP, 4-CP and 2,4-DCP, the inorganic chloride produced and the pH change during the irradiation of aqueous solutions containing single substrate only and a mixed solution containing the three chlorophenols under investigation by electron beams.

上海市教委基金(03AQ96)资助

第一作者: Adeleke Olukunle Francis, 男, 1975年4月出生, 1998年毕业于尼日利亚联邦共和国 University of Ibadan, 在读硕士研究生

通讯联系人: 周瑞敏

收稿日期: 初稿 2004-04-19, 修回 2004-05-25

2 Materials and methods

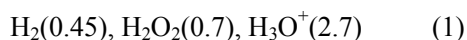
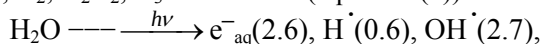
Chemically pure phenol, 2-chlorophenol (2-CP), 4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP) were used without further purification. Solutions were made in deionized water. Eluents for HPLC were water (twice distilled), methanol (HPLC-grade) and acetonitrile (HPLC-grade).

Electron beam irradiations using a 2MeV electron beam accelerator were carried out at Shanghai Applied Radiation Institute, Jiading Campus, Shanghai University. The electron beam scans an area of 120cm length and 7cm width. Polymer film dosimetry method was used for determination of the absorbed dose and the dose rate applied in this experiment was 1.75kGy/s.

The determination of substrate degradation was performed by HPLC (Agilent 1100 Series, Zorbax SB-C18 (5 μ m) column; flow rate: 1mL/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 225nm and 280nm for all compounds. Chloride ion measurement was done using Hach DR/2010 Spectrophotometer (Mercury (II) thiocyanate method), and pH meter was used to measure the pH values.

3 Results and discussion

The irradiation of water produces hydrogen atoms, $\text{H}^\cdot$; solvated electrons, e^-_{aq} ; hydroxyl radicals, $\text{OH}^\cdot$; H_2 ; H_2O_2 , H_3O^+ and OH^- (equation (1)).



The values in parentheses represent the G values. G is the number of reactive species formed or destroyed per 100eV of absorbed energy (1unit molecule/100eV = 0.10364×10^{-6} mol/J). In the presence of air, $\text{H}^\cdot$ and e^-_{aq} are scavenged by oxygen, forming $\text{HO}_2^\cdot$ and $\text{O}_2^{\cdot-}$ ^[3]. However, in aerated solutions, the decomposition of chlorophenols is due to $\text{OH}^\cdot$ radical attacks^[12]. A pulse radiolysis study^[14] of 2-CP in aqueous solutions suggests the formation of relatively stable OH adducts upon the addition of hydroxyl radical to the aryl ring of the substrate in neutral solutions. Therefore, it was expected that the degradation of the

studied chlorophenols would be mainly due to reactions with hydroxyl radicals.

3.1 Effect of irradiation on degradation and co-degradation

200mg/L solutions of 2-CP, 4-CP and 2,4-DCP, and a 50mg/L mixed solution were irradiated at doses of 8.8, 17.5, 21 and 26.3kGy. The amount of substrate remaining after irradiation was determined by HPLC. A chromatogram of the mixed solution both at 0kGy and 17.5kGy is given in Fig.1. The chromatogram shows that at a dose of 17.5kGy, the concentration of the substrate was much lower than for the non-irradiated solution (0kGy), and also reaction intermediates (not identified) have been formed.

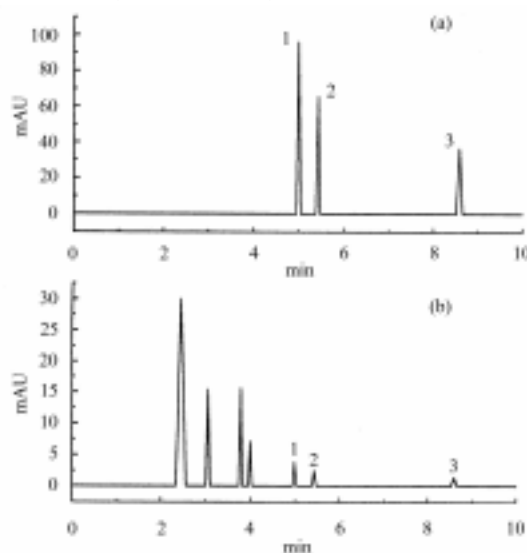


Fig. 1 HPLC chromatogram of 50mg/L mixed solution of 2-CP (1); 4-CP (2); and 2,4-DCP (3) and some reaction intermediates at absorbed doses of (a) 0kGy and (b) 17.5kGy

The degradation of all the chlorophenols was found to follow first order exponential decay with respect to the absorbed dose. The results of the degradation of both the 200mg/L solutions and 50mg/L mixed solution are given in Fig.2 and Fig.3 respectively.

In the case of the 200mg/L individual solutions, the efficiency of degradation was higher at initial doses and fell with increasing dose, probably due to competition with intermediates for $\text{OH}^\cdot$ radicals. In all cases, the rate of degradation was in the order of 2,4-DCP > 4-CP > 2-CP, which corroborate the results obtained in previous work^[13]. While in the 200mg/L solution, a dose of 8.8kGy led to a destruction of

96.4% of 2,4-DCP, this was reduced to 77.6% in the 50mg/L mixed solution containing the three chlorophenols. The same effect was observed for 4-CP whose degradation rate at 8.8kGy also fell from 82.8% (200mg/L solution) to 68.3% (mixed solution). However, for 2-CP, the presence of the other two chlorophenols did not seem to greatly affect its rate of degradation at 8.8kGy; being changed just from 70.3% (200mg/L solution) to 66.5% (50mg/L mixed solution).

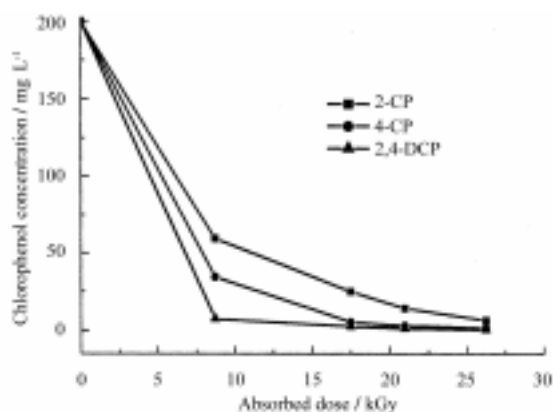


Fig.2 Effect of dose on the degradation of aqueous solutions of 200mg/L chlorophenols during irradiation by electron beam

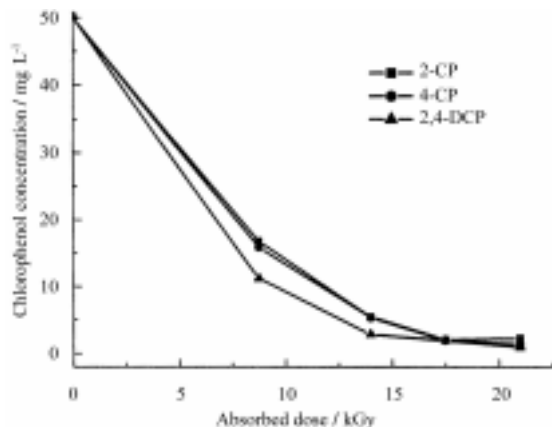


Fig.3 Effect of dose on the degradation of aqueous solutions of 50mg/L mixed chlorophenols during irradiation by electron beam

At a dose of 21kGy, the rates of destruction of the pollutants were 93.0% (2-CP), 98.5% (4-CP) and 99.4% (2,4-DCP) in the 200mg/L individual solutions, and 97.8%, 98.7% and 99.1% for 2-CP, 4-CP and 2,4-DCP respectively in the 50mg/L mixed solution. Fig.2 also shows that the degradation of both 2-CP and 4-CP almost proceeded at the same rate in the mixed solution.

3.2 Effect of irradiation on dechlorination

In addition to the degradation of the substrates during irradiation of chlorophenols, increasing amount of inorganic chloride ions were also found with increasing dose (Fig.4). The dechlorination rate was in the order of 2,4-DCP>4-CP>2-CP up to a dose of 17.5kGy and 4-CP>2,4-DCP>2-CP at 21 and 26.3 kGy. At 21kGy, the rate of dechlorination (as a percentage of chloride in the parent compound) was 55.4% (2-CP), 71.3% (4-CP) and 69.0% (2,4-DCP). For the 50mg/L mixed solution (Fig.5), the Cl^- yield at 21kGy was 66.1% of the total organic chloride.

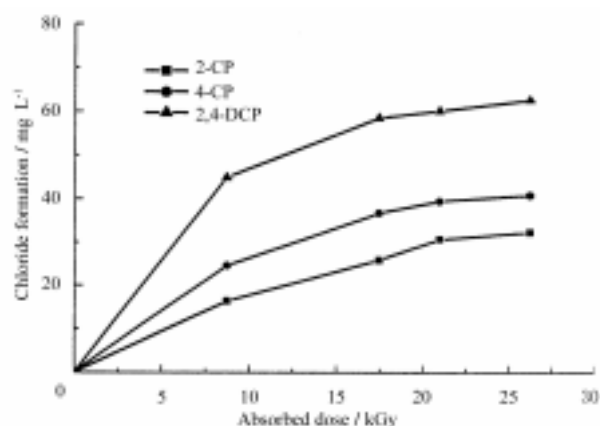


Fig.4 Effect of dose on chloride formation during degradation of 200mg/L chlorophenols solution by electron beam irradiation

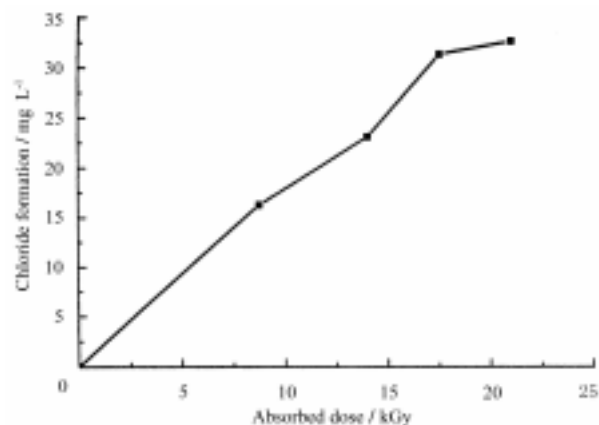


Fig.5 Effect of dose on chloride formation during degradation of 50mg/L mixed chlorophenols solution by electron beam irradiation

3.3 Determination of D_{90} and G for substrate degradation

First order exponential decay equations were fitted for the degradation of the solutes and the rate constant k was determined using ORIGIN. The dose re-

quired for 90% degradation, D_{90} ; and the destruction G values (G_D) of the solutes at D_{90} were also calculated. The results are given in Table 1.

Table 1 Electron beam–degradation of aqueous chlorophenols in deionized water solutions

Compound	Equation	R^2	D_{90}	G_D^a
200mg/L individual solutes				
2-CP	$y = y_0 e^{-0.13113x}$	0.99842	17.56	0.77
4-CP	$y = y_0 e^{-0.20180x}$	0.99990	11.41	1.18
2,4-DCP	$y = y_0 e^{-0.37543x}$	0.99981	6.13	1.74
50mg/L mixed solution				
2-CP	$y = y_0 e^{-0.14295x}$	0.99250	16.11	0.21
4-CP	$y = y_0 e^{-0.14810x}$	0.99400	15.55	0.22
2,4-DCP	$y = y_0 e^{-0.18063x}$	0.99867	12.75	0.21

^a $G_D \times 10^4$ (mol/J)

For the 200mg/L solutions, the rate constants k were 0.13113 (2-CP), 0.20180 (4-CP) and 0.37543 (2,4-DCP) and 0.14295 (2-CP), 0.14810 (4-CP) and 0.18063 (2,4-DCP) for the 50mg/L mixed solution. The calculated D_{90} are 18.0kGy (2-CP), 11.4kGy (4-CP) and 6.1kGy (2,4-DCP) for the 200mg/L solutions and 16.1kGy (2-CP), 15.6kGy (4-CP) and 12.8kGy (2,4-DCP) for the 50mg/L mixed solution.

The destruction G values (G_D) were calculated from (Nickelsen and Cooper, 1992):

$$G_D = \frac{(\Delta R_D)(N_A)}{(D)(6.24 \times 10^{15})} \quad \text{mol/J} \quad (2)$$

Where ΔR_D is the change in organic solute conc. (mol/L); D is the dose (kGy); N_A is Avogadro's number; 6.24×10^{15} is the constant to convert kGy to 100eV/L.

The G values, which are also indications of efficiency of the radiation degradation, were found to be much lower for the mixed solution than for the individual solutes. This indicates that degradation of the studied chlorophenols were more efficient with individual substrate than in the presence of other chlorophenols in solution.

3.4 Effect of irradiation on pH of solutions

The pH changes observed during the irradiation of the solutions are summarized in Table 2. The radiolytic degradation of monochlorophenols initially leads to the formation of various hydroxybenzenes (phenol, catechol, resorcinol, hydroquinone, hydroxyquinone) and that leads to the formation of simple carboxylic acids (formic, oxalic, maleic, muconic) [9]. Formate

and acetate ions were detected using ion chromatograph in irradiated 50mg/L solutions of 2,4-DCP at doses ≥ 10 kGy [9]. Thus, the pH change observed with increasing dose might be due to the formation of reaction intermediates.

Table 2 Change of pH during electron beam–irradiation of chlorophenols at different doses

Dose /kGy	pH			
	Individual solutes (200mg/L)			Mixed solution. (50mg/L each)
	2-CP	4-CP	2,4-DCP	
0	7.25	7.76	7.12	7.42
8.75	3.71	3.67	3.13	3.59
14	3.65	3.48	3.06	3.38
17.5	3.44	3.26	3.04	3.24
21	3.36	3.22	2.97	3.23
26.25	3.30	3.20	2.96	—

4 Conclusions

Aqueous solutions of 2-CP, 4-CP and 2,4-DCP have been successfully degraded by the use of high-energy electron beams. The relative rate of degradation and dechlorination was 2,4-DCP>4-CP>2-CP. In a mixed solution containing the three chlorophenols, the rate of degradation and dechlorination and the radiation chemical yield, G , decreased significantly while the D_{90} increased. The pH of the solutions also decreased with increasing irradiation dose.

At a dose of 21kGy, the amount of original solute degraded were 93.0% (2-CP), 98.5% (4-CP) and 99.4% (2,4-DCP) in the 200mg/L individual solutions, and 97.8%, 98.7% and 99.1% for 2-CP, 4-CP and 2,4-DCP respectively in the 50mg/L mixed solution.

Acknowledgements

Adeleke O. Francis would like to express his gratitude to the governments of the People's Republic of China and Federal Republic of Nigeria for providing the opportunity to study in China. The authors also thank Dr. Li Hong for her assistance with the HPLC.

References

- Cooper W J, Nickelsen M G, Meacham D E, *et al.* J Environ Sci Hlth, 1992, **A27**(2): 219-243
- Nickelsen M G, Cooper W J, Kurutz C N, *et al.* Environ Sci Technol, 1992, **26**(1): 144-152
- Getoff N. Radiat Phys Chem, 1996, **47**(4): 581-593
- Schmid S, Krajnik P, Quint R M, *et al.* Radiat Phys Chem, 1997, **50**(5): 493-502

- 5 Sampa M H O, Duarte C L, Rela P R, *et al.* Radiat Phys Chem, 1998, **52**(1-6): 365-369
- 6 Gehringer P, Eshweiler H. In Environmental Applications of Ionizing radiation. (Ed. Cooper, W. J *et al.*) John Wiley and Sons Inc., 1998. 325-340
- 7 Zele S R, Nickelsen M G, Cooper W J *et al.* In Environmental Applications of Ionizing radiation. (Ed. Cooper W J *et al.*) John Wiley and Sons Inc., 1998. 395-416
- 8 Song W, Zheng Z, Abual-Suud R, *et al.* Radiat Phys Chem, 2002, **65**(6): 559-563
- 9 Trojanowicz M, Drzewicz P, Panta P, *et al.* Radiat Phys Chem, 2002, **65**(3): 357-366
- 10 Jáuregui O, Galceran M T. In Environmental Analysis. (Ed. W. Kleibohmer), Elsevier Science. 2001. 178-179
- 11 张自杰. 排水工程(下册), 第四版, 北京: 中国建筑工业出版社, 1999. 624-625
- 12 ZHANG Zijie. Water Supply Engineering (Vol 2), 4th ed, Beijing: China Construction Industry Press, 1999. 624-625
- 13 宋卫华, 郑正, 杭德生, 等. 南京大学学报(自然科学), 2001, **37**(6): 730-733
- 14 刘士姮, 汪世龙, 孙晓宇, 等. 辐射研究与辐射工艺学报, 2004, **22**(1): 13-18
- SONG Weihua, ZHENG Zheng, HANG Desheng, *et al.* J Nanj Univ (Nat Sc), 2001, **37**(6): 730-733
- LIU Shihuan, WANG Shilong, SUN Xiaoyu, *et al.* J Radiat Res Radiat Process, 2004, **22** (1): 13-18

水溶液中氯代苯酚的电子束辐射降解研究

奥陆克¹ 周瑞敏² 俎建华² 何林锋¹

¹ (上海大学环境化学学院 上海 200072)

² (上海大学辐射应用研究所 上海 201800)

摘要 利用电子束辐射降解水中的 2-氯苯酚 (2-CP), 4-氯苯酚 (4-CP) 和 2,4-二氯苯酚 (2,4-DCP), 研究了辐照剂量对初始浓度各为 200mg/L 的三种氯代苯酚以及浓度各为 50mg/L 的三种混合物辐射降解、去除有机氯及溶液 pH 值的影响。用 HPLC 测定了辐照溶液中 2-CP、4-CP 和 2,4-DCP 的含量, 测试结果表明, 随着辐照剂量的增加氯代苯酚的降解增加, 溶液中的氯离子增加, pH 值减小。浓度为 200mg/L 的三种溶液, 在同样的辐射剂量率下, 其辐射降解速度和氯离子产率的顺序为 2,4-DCP>4-CP>2-CP; 对浓度各为 50mg/L 氯代苯酚的混合物溶液, 2,4-DCP 的辐射降解速度最大, 4-CP 和 2-CP 的降解速度几乎相同。在辐照剂量为 21kGy 时, 对浓度为 200mg/L 的三种溶液, 其辐射降解率分别为 93.0% (2-CP)、98.5% (4-CP) 和 99.4% (2,4-DCP), 氯离子产率为 55.4%、71.3%和 69.0%, 降解率为 90%所需剂量 (D_{90}) 分别为 18.0kGy (2-CP)、11.4kGy (4-CP) 和 6.1kGy (2,4-DCP)。浓度各为 50mg/L 混合体系中的 D_{90} 值分别为 16.1kGy (2-CP)、15.6kGy (4-CP) 和 12.8kGy (2,4-DCP)。

关键词 电子束辐射, 氯代苯酚, 降解

中图分类号 X703