

# Research on degradation of 2, 4-dichlorophenol and pentachlorophenol in water by electron beam irradiation

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**Abstract:** Electron beam was successfully used for the degradation of 2, 4-dichlorophenol (2, 4-DCP) and pentachlorophenol (PCP) in water. The effects of radiation doses on substrate degradation and dechlorination of solutions with concentrations of 50 mg/L for both chlorophenols were investigated. The effects of initial concentration, pH and absence of oxygen on the degradation were also investigated. The concentrations of 2, 4-DCP and PCP remaining in solution after irradiation were measured by high-performance liquid chromatograph (HPLC). The results show that an increased radiation dose leads to increased degradation of the chlorophenols and increased  $\text{Cl}^-$  yields. In all cases, the rate of degradation was found to be higher than the corresponding inorganic chloride yield from the parent compound. Deoxygenation was also found to increase the rate of degradation of the chlorophenols in water while degradation under alkaline condition was lower than at low to neutral pH.

**Key words:** electron beam; chlorophenols; degradation; dechlorination; deoxygenation

The effectiveness of the degradation of toxic organic pollutants in water by advanced oxidation processes (AOPs) especially the use of ionizing radiation in the form of  $\gamma$ -irradiation and electron beam irradiation has been demonstrated. The studies have also shown that electron beam irradiations are efficient in the destruction of several classes of hazardous organic compounds<sup>[1-8]</sup>.

Phenolic compounds and 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<sup>[9]</sup>. Both 2, 4-dichlorophenol (2, 4-DCP) and pentachlorophenol (PCP) are included in the United States Environmental Protection Agency (USEPA) list of priority pollutants and in the European Community (EC) directive concerning dangerous substances discharged into the aquatic environment<sup>[10]</sup>. The Integrated Wastewater Discharge Standard of China (GB 8978—1996) and Environmental Quality Standards for Surface Water (GB 3838—2002) also listed 2, 4-DCP and PCP among the priority organic pollutants whose maximum discharge concentration

should be regulated<sup>[11]</sup>.

Some papers have been published on the radiolytic degradation of monochlorophenols<sup>[6, 12]</sup>, 2, 4-DCP<sup>[9, 12]</sup> and PCP<sup>[13]</sup>. However all these irradiations were carried out using  $\gamma$ -irradiation sources. Up till now, there are very few research works done on the irradiation of aqueous solutions of chlorophenols using electron beam (EB) from high energy electron accelerators except for Ref. [14].

The goals of this study are to investigate the effect of electron beam irradiation doses on the destruction of 2, 4-DCP and PCP at different initial concentrations; the inorganic chloride produced; and the effect of initial pH and oxygen on the rate of **degradation and dechlorination**.

## 1 Experimental Materials and Methods

Chemically pure phenol, 2, 4-DCP and PCP were used without further purification. Solutions were made in deionized water. Eluents for high-performance liquid chromatography (HPLC) were water (twice distilled), methanol (HPLC-grade) and acetonitrile (HPLC-grade). 1.0 mol/L  $\text{H}_2\text{SO}_4$  and NaOH were used to adjust the initial pH of the solutions.  $\text{N}_2$  gas was used to remove oxygen in the deoxygenation solution experiments.

Electron beam irradiations using a 2 MeV electron beam accelerator were carried out at Applied Radiation Institute, Shanghai University, China. The electron beam scans an area of 120 cm in length and 7 cm in width. The solutions were placed in open containers

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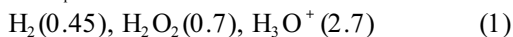
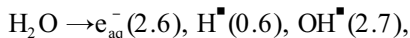
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exposed directly to the electron beam.

The determination of substrate degradation was performed by HPLC (Agilent 1100 series, Zorbax SB-C18 (5  $\mu$ m) column; flow rate: 1 mL/min; isocratic elution  $\varphi$  (water) :  $\varphi$  (methanol) :  $\varphi$  (acetonitrile) = 40 : 30 : 30 for 2, 4-DCP and 25 : 35 : 40 for PCP). 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  $\text{H}^\bullet$ , solvated electrons  $\text{e}_{\text{aq}}^-$ , hydroxyl radicals  $\text{OH}^\bullet$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  (Eq.(1))<sup>[2]</sup>.



While  $\text{OH}^\bullet$  is a powerful oxidizing agent,  $\text{e}_{\text{aq}}^-$  and  $\text{H}^\bullet$  are strong reducing agents. These three species are the most important in the destruction of toxic pollutants in water<sup>[15]</sup>. The values in parentheses represent  $G$  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. The unit is Gy.

In the presence of air,  $\text{H}^\bullet$  and  $\text{e}_{\text{aq}}^-$  are scavenged by oxygen, forming  $\text{HO}_2^\bullet$  and  $\text{O}_2^{\bullet-}$ .

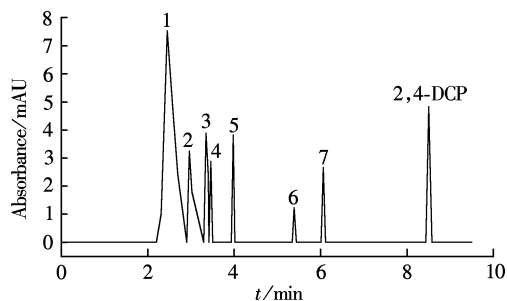


However, the superoxide radicals  $\text{HO}_2^\bullet$  and  $\text{O}_2^{\bullet-}$  have been shown to contribute insignificantly to the degradation of chlorophenols<sup>[12]</sup>. Thus in aerated solutions, the decomposition of chlorophenols is essentially due to  $\text{OH}^\bullet$  radical attacks.

### 2.1 Effect of radiation dose and initial concentration on degradation of chlorophenols

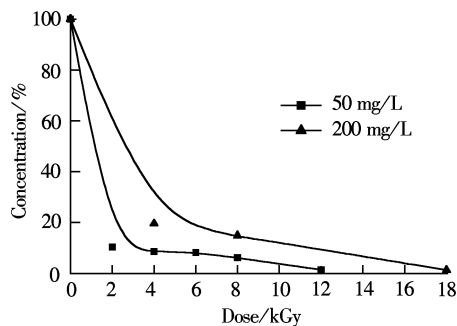
Radiation of the chlorophenols-containing water leads to the degradation of the original solute and formation of several intermediate products. Fig. 1 shows the HPLC chromatogram of 50 mg/L 2, 4-DCP after irradiation with a dose of 2 kGy at an absorbance wavelength of 280 nm. It can be seen from the graph

that several reaction intermediates have been formed along with the 2, 4-DCP (retention time  $t = 8.512$  min).



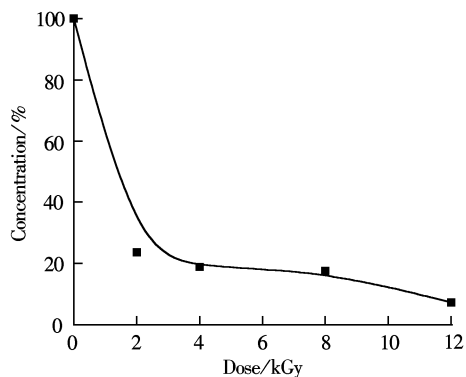
**Fig.1** HPLC chromatogram of 2, 4-DCP and reaction intermediates (1 to 7) after an irradiation dose of 2 kGy

Fig.2 shows the degradation of 50 mg/L and 200 mg/L 2, 4-DCP in aqueous solution at different irradiation doses. The result shows that the concentration of the original substrate decreases with increasing irradiation dose, which implies increasing degradation. Also, at any irradiation dose, the percentage of solute remaining in solution is lower for the 50 mg/L solutions than the 200 mg/L solutions, implying that the required irradiation dose to achieve certain percentage degradation increases with the increasing initial concentration of the solute.



**Fig.2** Degradation of 50 mg/L and 200 mg/L 2, 4-DCP in water by electron beam irradiation

Since PCP has a very low solubility at neutral to acidic pH, the experiments were conducted under alkaline conditions (pH = 11.6). From Fig. 3, the amount of PCP remaining in solution was also found



**Fig.3** Degradation of 50 mg/L PCP in water by electron beam irradiation

to decrease with increasing irradiation dose. The results cannot be compared with those obtained from the 2, 4-DCP solutions because the 2, 4-DCP experiments reported above were conducted without pH adjustment (neutral conditions).

2.2 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. In Fig. 4 and Fig.5, the yield of inorganic chloride (dechlorination), expressed as a percentage of total organic chlorine in the parent compound, were found to increase with increasing irradiation dose, but were much lower than that of decomposition of the original compound. This may be due to the formation of other organochlorides as intermediate products with increasing decomposition of the original compound.

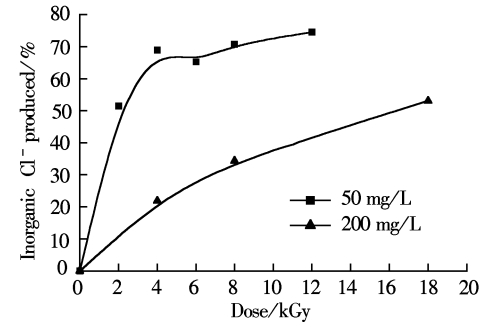


Fig.4 Inorganic Cl<sup>-</sup> produced during irradiation of 50 mg/L and 200 mg/L 2, 4-DCP

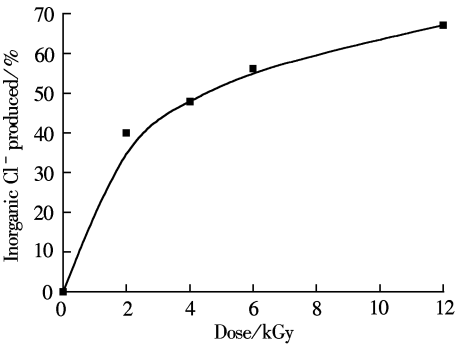


Fig.5 Inorganic Cl<sup>-</sup> produced during irradiation of 50 mg/L PCP in water

2.3 Effect of presence of oxygen on degradation and chloride formation

The results in Tab.1 and Tab.2 show that the rate of degradation is relatively higher in the deoxygenated solutions than the oxygen-containing solutions for 2,4-DCP; however the chloride yield in the deoxygenated solutions is found to be lower than that in the oxygen-containing solutions (DO = 9.0 to 9.5 mg/L) for both 2,

4-DCP and PCP. Thus, it can be concluded that for both 2, 4-DCP and PCP, deaeration leads to faster disappearance of the original substrate but not necessarily to mineralization as indicated by the chloride yield.

Tab.1 Deaeration and pH effect on 2, 4-DCP degradation and Cl<sup>-</sup> formation

Absorbed dose/kGy	Reaction	O <sub>2</sub> -containing solution	Deaerated solution	pH		
				3.1	7.2	11.3
2	Degradation	89.6	NA	86.8	89.6	41.3
	Chloride formation	51.5	49.2	38.9	51.5	38.9
4	Degradation	91.4	96.5	NA	NA	NA
	Chloride formation	68.9	46.6	44.0	68.9	NA
8	Degradation	93.8	97.0	NA	NA	NA
	Chloride formation	70.7	46.6	49.2	70.7	68.6

Note: NA indicates data not available.

Tab.2 Deaeration effect on PCP chloride formation

Absorbed dose/kGy	O <sub>2</sub> -containing solution / %	Deaerated solution / %
2	40.0	17.3
4	47.9	23.1
6	56.2	NA
8	NA	23.8

2.4 Effect of initial pH on degradation of chlorophenols

The result in Tab.1 shows that at pH values of 3.1 and 7.2, there was only little difference in the degradation of 2, 4-DCP at 2 kGy, but much lower degradation was observed for the alkaline (pH = 11.3) solution. In contrast however, the chloride yield at all the radiation doses was found to be higher under neutral conditions than either high or low pH, but lowest at low pH. This suggests that neutral pH conditions favor the mineralization of 2, 4-DCP. The lower degradation observed under alkaline conditions may be explained by the low yield of OH<sup>•</sup> radical under high pH conditions as shown in Fig.6.

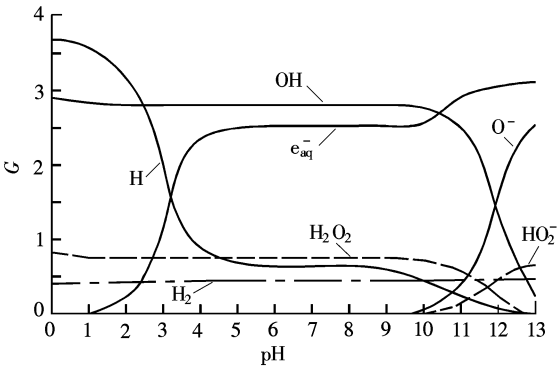


Fig.6 Effect of pH on the primary products of water irradiation (Source: Getoff, 1996)

3 Conclusion

Aqueous solutions of 2, 4-DCP and PCP have been successfully degraded by the use of high-energy electron beams. For 2, 4-DCP, the rate of degradation

and dechlorination were found to be dependent on the absorbed irradiation dose and initial concentration of the chlorophenols; increasing the radiation dose leads to increasing degradation of the original compound and increasing chloride formation.

The rates of degradation and dechlorination were also found to increase with increasing irradiation doses for the 50 mg/L, alkaline PCP solutions. In all the cases, the rate of dechlorination was lower than substrate degradation. Deoxygenation was also found to favor the decomposition of the two chlorophenols but led to less inorganic chloride formation. The rates of degradation of 2, 4-DCP under high pH conditions were also found to be less than half of those for neutral or low pH conditions.

## References

- [1] Cooper W J, Nickelsen M G, Meacham D E, et al. High energy electron beam irradiation: an innovative process for the treatment of aqueous based organic hazardous wastes [J]. *J Environ Sci Hlth*, **1992**, **A27**: 219–243.
- [2] Getoff N. Radiation-induced degradation of water pollutants-state of the art [J]. *Radiat Phys Chem*, **1996**, **47**(4): 581–593.
- [3] Gehringer P, Eshweiler H. Radiation-induced cleanup of water and wastewater [A]. In: Cooper W J, Curry R D, O'shea K E, eds. *Environmental Applications of Ionizing Radiation* [C]. John Wiley and Sons Inc, 1998. 325–340.
- [4] Nickelsen M G, Cooper W J, Kurutz C N, et al. Removal of benzene and selected alkyl-substituted benzenes from aqueous solution utilizing high energy electron irradiation [J]. *Environ Sci Technol*, **1992**, **26**: 144–152.
- [5] Sampa M H O, Duarte C L, Rela P R, et al. Remotion of organic compounds of actual industrial effluents by electron beam irradiation [J]. *Radiat Phys Chem*, **1998**, **52**, (1–6): 365–369.
- [6] Schmid S, Krajncik P, Quint R M, et al. Degradation of chlorophenols by  $\gamma$ -irradiation [J]. *Radiat Phys Chem*, **1997**, **50**(5): 493–502.
- [7] Song W, Zheng Z, Abual-Suud R, et al. Degradation and detoxification of aqueous nitrophenol solutions by electron beam irradiation [J]. *Radiat Phys Chem*, **2002**, **65**(4): 559–563.
- [8] Zele S R, Nickelsen M G, Cooper W J, et al. Modeling kinetics of benzene, phenol and toluene removal in aqueous solution using the high-energy electron-beam process [A]. In: Cooper W J, Curry R D, O'shea K E, eds. *Environmental Applications of Ionizing Radiation* [C]. John Wiley and Sons Inc, 1998. 305–416.
- [9] Trojanowicz M, Drzewicz P, Panta P, et al. Radiolytic degradation and toxicity changes in  $\gamma$ -irradiated solutions of 2, 4-dichlorophenol [J]. *Radiat Phys Chem*, **2002**, **65**(4): 357–366.
- [10] Jáuregui O, Galceran M T. Phenols [A]. In: Kleibohmer W, ed. *Environmental Analysis* [C]. Elsevier Science, 2001. 178–179.
- [11] China environmental protection standards: environmental quality and pollutants discharge [S]. Beijing: China Standards Press, 2003. 314–315. (in Chinese)
- [12] Zona R, Schmid S, Solar S. Detoxification of aqueous chlorophenol solutions by ionizing radiation [J]. *Wat Res*, **1999**, **33**(5): 1314–1319.
- [13] He Y, Liu J, Lu Y, et al. Gamma radiation treatment of pentachlorophenol, 2, 4-dichlorophenol and 2-chlorophenol in water [J]. *Radiat Phys Chem*, **2002**, **65**(4): 565–570.
- [14] Song W, Zheng Z, Hang D, et al. Radiolysis of chlorophenols by electron beam accelerator [J]. *J Nanjing University*, **2001**, **37**(6): 730–733. (in Chinese)
- [15] Lin K, Cooper W J, Nickelsen M G, et al. Decomposition of aqueous solution of phenol using high energy electron beam irradiation — a large scale study [J]. *Appl Rad Isot*, **1995**, **46**(12): 1307–1315.

# 水中 2, 4-二氯苯酚和五氯苯酚电子束辐射降解的研究

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**摘要:** 用电子束辐射降解水中的 2, 4-二氯苯酚(2, 4-DCP)和五氯苯酚(PCP), 研究辐照剂量对溶液初始质量浓度各为 50 mg/L 的 2 种氯代苯酚辐射降解和去除有机氯的影响. 同时研究了溶液不同的初始质量浓度、pH 值和去氧状态等条件对辐射降解的影响. HPLC 的测试结果表明: 随着辐照剂量的增加, 氯代苯酚的降解率增加, 溶液中的氯离子增加, 但辐照后溶液中仍有 2, 4-DCP 和 PCP 的残余物. 试验结果表明: 有机氯辐射降解的速度要比无机氯生成的速度快得多; 溶液的去氧也能加快氯代苯酚的降解; 在酸性到中性条件下比碱性条件下更利于有机氯裂解.

**关键词:** 电子束; 氯代苯酚; 降解; 除氯; 去氧

**中图分类号:** X703