



## Radiolysis of pentachlorophenol (PCP) in aqueous solution by gamma radiation

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### Abstract

Steady-state radiolysis experiments were performed to investigate the  $\gamma$ -irradiation treatment of pentachlorophenol (PCP) in aqueous solution. The effect of initial concentration on the PCP degradation was also investigated. The experimental results showed that  $\gamma$ -irradiation was able to degrade PCP in aqueous solution successfully, and the radiolytic degradation process of PCP could be described by the first-order kinetic model. When the initial concentration of PCP was 25 and 50 mg/L and the radiation dose was 4 and 6 kGy, respectively, the degradation efficiency was 100%. A luminescence bacterial test was used for evaluating the toxicity of the radiolytic intermediate products. Total detoxification of a 75 mg/L PCP solution could be achieved by carrying out the irradiation procedure at the dose of 15 kGy.

**Key words:** ionizing irradiation; pentachlorophenol (PCP); kinetics; dechlorination; toxicity

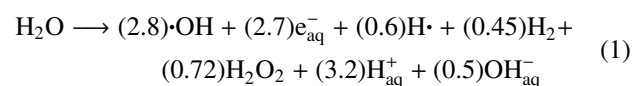
### Introduction

Pentachlorophenol (PCP) is a widespread soil and water contaminant due to its past extensive use mainly for wood preservation and other pesticide applications all over the world. Because of its toxicity, recalcitrance, and potential adverse health effects, PCP has been regulated as one of the priority pollutants by the US and China Environmental Protection Agency. In China, PCP was once used heavily as a herbicide, and its sodium salt was used widely in the fight against schistosomiasis in the past century. Even today, the annual production in China is about  $1 \times 10^7$  kg, one-fifth of the world production of PCP (Hu and Wang, 2007).

Pentachlorophenol is a persistent organic pollutant (POPs) with high biological toxicity due to its stable aromatic ring system and chlorine substituents. Conventional physicochemical and biological processes are not efficient for its degradation (Piringer and Bhattacharya, 1999; Wang *et al.*, 2000; Pera-Titus *et al.*, 2004). Therefore, intense efforts have been made to find efficient and cost-effective treatment methods to degrade this type of refractory organic pollutants. In recent years, one promising group of destructive technologies have emerged for water and wastewater treatment, commonly referred to as advanced oxidation processes (AOPs). AOPs are based on the generation of highly oxidative hydroxyl radicals for the breakdown of organic contaminants, such as photocatalysis, ozone-based oxidation, Fenton's reaction, sonolysis,

supercritical oxidation, ionizing radiation, and various combinations of them. Among these methods, ionizing radiation appears to be one promising alternative for hazardous organic wastewater treatment. The usefulness of ionizing radiation for efficient degradation of a large variety of biorefractory pollutants has been successfully demonstrated (Kurucz *et al.*, 1995; Getoff, 1996; Duarte *et al.*, 2002; Mezyk *et al.*, 2004; Popov and Getoff, 2005; Hu *et al.*, 2006).

In pH range of 6–8.5, radiolysis of air-free water leads to the formation of a suite of radical species (Eq.(1)) (Getoff, 1998; Wasiewicz *et al.*, 2006).



The numbers in brackets (G values) indicate the relative number of each species formed per 100 eV absorbed energy and can be converted into the SI units of  $\mu\text{mol/J}$  by multiplying with a factor of 0.1036. These reactive radicals react with each other and with other ions and solutes present in the solution. The chemical reactions initiated by the three highly reactive species ( $\cdot\text{OH}$ ,  $\text{e}_{\text{aq}}^-$ ,  $\text{H}$ ) are principal important with respect to ionizing radiation process in aqueous solutions. The highly reactive hydroxyl radical ( $\cdot\text{OH}$ ) is traditionally believed to be the active species which is responsible for the destruction of pollutants. Because of its high standard reduction potential of 2.8 V in acidic media (Pera-Titus *et al.*, 2004), these radicals would be able to oxidize almost all organic compounds to carbon dioxide and water. The hydrated electron ( $\text{e}_{\text{aq}}^-$ )

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is the strongest known reducing agent (reduction potential  $-2.9$  V) and reacts very rapidly with halogenated organic compounds through dissociative electron capture (Alfassi *et al.*, 1994; Al-Sheikhly *et al.*, 1997):



The purpose of this study was to investigate the effect of  $\gamma$ -irradiation dose on the destruction of PCP at different initial concentrations. The change of absorption spectra, the concentrations of PCP and  $\text{Cl}^-$  ions produced, and pH value of the solutions, as well as the acute toxicity removal during the radiolysis of PCP were analyzed.

## 1 Materials and method

### 1.1 Materials and sample preparation

All the chemicals were used without further purification. PCP has two forms: pentachlorophenol and the sodium salt of pentachlorophenol. Because the sodium salt dissolves easily in water but pentachlorophenol does not, chemically pure PCP-Na was used. Eluents for HPLC were water (twice distilled) and methanol (HPLC-grade). NaOH was used to adjust the pH of the irradiated solutions for toxicity test.

Throughout the experiments, all solutions (200 ml) were made in deionized water and were contained in 250 ml gastight Pyrex glass vials. The solutions were also irradiated in these vials. The initial pH of all solutions was in the range of 6.5–7.0 without any adjustment.

### 1.2 Radiation experiments

The gamma radiolytic experiments were carried out using a  $^{60}\text{Co}$  irradiation facility with a dose rate of 284 Gy/min. Dosimetry was performed using the standard Fricke dosimeter. Solutions were irradiated with different doses and all experiments were performed at ambient temperatures.

### 1.3 Analytical methods

The remaining concentration of PCP was determined by HPLC (Agilent 1100LC, Pump L-6200, UV-Vis detector L-4000, using an inverse-phase C18 column, USA). The elution was performed using  $\text{H}_2\text{O}$ /methanol (65/35, V/V). The samples were measured at 320 nm at a column temperature of  $40^\circ\text{C}$  with a flow rate of 0.8 ml/min. The injection volume was 20  $\mu\text{l}$ . The evolution of UV-Vis absorption spectra of PCP in aqueous solution prior to and after different dose irradiation was recorded by Lambda 800 UV-Vis Spectrometer (PerkinElmer Instruments, USA). The concentration of  $\text{Cl}^-$  ions released upon radiolysis was determined by ion selective electrode (Orion 86804, Thermo Orion Inc., USA).

## 1.4 Toxicity measurement

The normalized method (GB/T 15441-1995) is based on the measure of bioluminescence from the marine bacteria *Photobacterium phosphoreum* T3. The main property of these bacteria is their capacity to emit light. The luminous intensity, decided by the quantity and activity of living bacteria, is negatively proportional to the acute toxicity of solutions, and it was measured at  $20\text{--}25^\circ\text{C}$  using a luminometer (DXY-2, the Institute of Soil Science, Chinese Academy of Sciences). The salt content (NaCl) of the samples must be 3%. After 20 min of incubation, the bacterial light intensity is determined photometrically using 3% NaCl solution as reference. From the change in the luminescence intensity, the percentage inhibition after incubation and the toxicologic parameter EC50 (effective concentration required to decrease bacterial luminescence by 50%) can be calculated.

*Photobacterium phosphoreum* T3 is sensitive to medium acidity (Shi *et al.*, 2004), and toxicity of pentachlorophenol increases as pH of water decreases, but the  $\gamma$ -irradiation of an aqueous solution resulted in a pH decrease owing to the formation of protons (Eq.(1)) and the oxidation of dissolved organic compounds into carboxylic acids. Hence, sample acidity was neutralized by adding sodium hydroxide according to the norm.

## 2 Results and discussion

### 2.1 $\gamma$ -Radiolysis of PCP

Preliminary laboratory-scale experiments in open air were run with the initial PCP-Na concentration of 50 mg/L. The initial pH is 6.8. Table 1 shows the pH values of the PCP solutions at different irradiation doses, which decreased with the increasing radiation doses. This is mainly because that the  $\text{H}_{\text{aq}}^+$  left while the  $e_{\text{aq}}^-$  was consumed, and the accumulation of soluble carboxylic acids produced

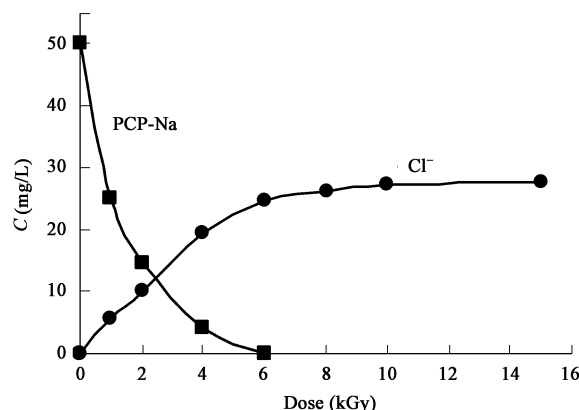


Fig. 1 Evolution of the PCP and  $\text{Cl}^-$  concentrations ( $C_0 = 50$  mg/L).

Table 1 pH values of pentachlorophenol solutions at different irradiation doses

Dose (kGy)	0	1	2	4	6	10	15
pH	6.8	4.0	3.6	3.3	3.2	3.2	3.1

$C_0 = 50$  mg/L.

during the radiation also had a contribution (Song *et al.*, 2002; Popov and Getoff, 2005).

Figure 1 shows the evolution of the PCP-Na and  $\text{Cl}^-$  concentrations. The decomposition of PCP-Na and release of  $\text{Cl}^-$  increased with the increasing radiation dose. At the dose of 6 kGy, PCP is degraded completely and the dechlorination efficiency is about 80%, which indicate that some kinds of intermediate products still contain  $\text{Cl}^-$ , such as tetrachlorophenol and trichlorophenol (He *et al.*, 1994).

The absorption spectra of 50 mg/L PCP-Na solutions at different absorbed doses are shown in Fig.2. Pentachlorophenol has a strong absorption band in ultraviolet area with the wavelength of 248 and 320 nm. The characteristic peak value of PCP decreased markedly with increasing absorbed doses. This agreed with the degradation of PCP-Na (Fig.1). The new absorption around 295 nm emerged because of the hypsochromic shift caused by the pH decrease.

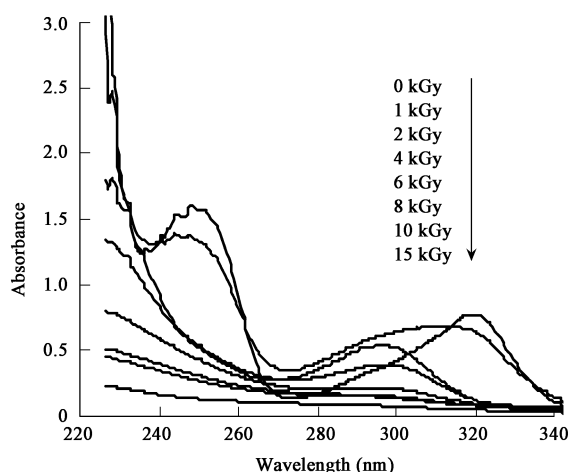
## 2.2 Products analysis

The destruction of PCP and the formation of the degradation products as a function of absorbed dose were measured by HPLC. The chromatogram of 50 mg/L PCP-Na solution irradiated with an absorbed dose of 1 kGy

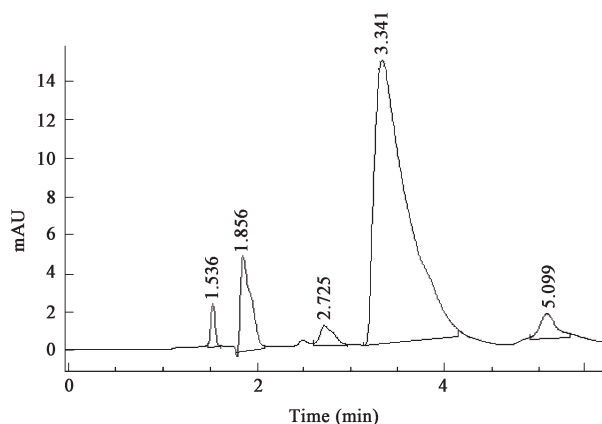
is shown in Fig.3. Besides the highest peak of PCP with the retention time of 3.34 min, several other peaks were found in the HPLC chromatogram with a UV detector at  $\lambda_{320\text{ nm}}$ . Fig.4 shows the changes of these peak areas, which indicate the production and degradation of intermediates during the radiation treatment. It is important to note that the  $\gamma$ -radiation treatment turned the initial colorless solutions to light pink at the radiation doses of 1 and 2 kGy, but it turned colorless again at the dose of 4 kGy. This is in great agreement with the production and degradation of the intermediate with the retention time of 5.10 min in Fig.4, which indicates that this intermediate is the reason of color change. In addition, we also found that the release of  $\text{Cl}^-$  increased during postirradiation storage (24 h, there was no further consumption of PCP) (Fig.5), suggesting some unstable products formed may further release  $\text{Cl}^-$ .

## 2.3 Kinetics of PCP $\gamma$ -irradiation degradation

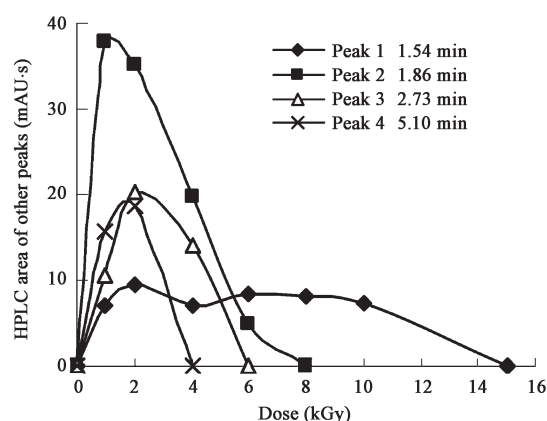
Aqueous solutions, 25, 50, 75, 100 mg/L PCP-Na, were irradiated at 1–15 kGy, and the results are shown in Fig.6. PCP-Na in water can be efficiently decomposed by  $\gamma$ -radiation. The required irradiation dose to remove 100% of the PCP-Na was 4 and 6 kGy at the initial concentration of 25 and 50 mg/L, respectively. Even at the



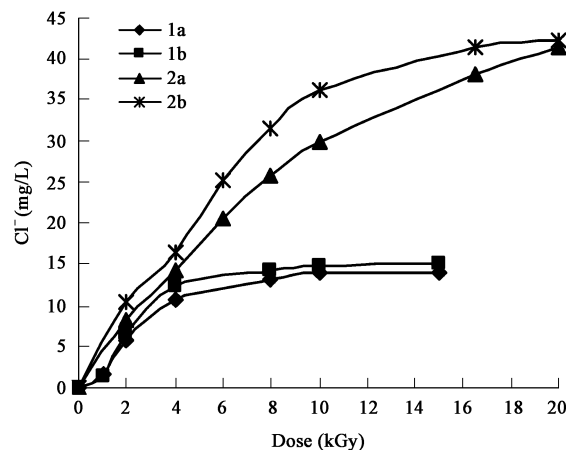
**Fig. 2** UV-Vis spectra of 50 mg/L PCP aqueous solutions irradiated at different irradiation doses.



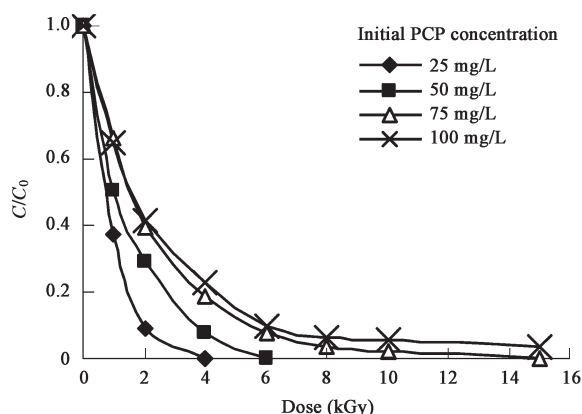
**Fig. 3** HPLC chromatogram of PCP after an irradiation dose of 1 kGy ( $C_0 = 50$  mg/L).



**Fig. 4** Change in concentration of intermediates by radiolysis of PCP ( $C_0 = 50$  mg/L).



**Fig. 5** Increasing release of chloride ions during 24 h postirradiation storage. 1:  $C_0 = 25$  mg/L; 2:  $C_0 = 75$  mg/L. a: determined at once after irradiation; b: determined after 24 h postirradiation storage.



**Fig. 6** Removal of PCP at different initial concentrations with increasing irradiation dose.  $C$  and  $C_0$  are actual and initial concentration of PCP-Na.

high concentrations of 75 and 100 mg/L, the concentration of PCP-Na decreased by more than 90% when 6 kGy were applied. The initial degradation rate is higher than that of the later stage. This is because the intermediates competed with PCP-Na for the reactive radicals, and with the decrease of PCP concentration, the probability reactive radicals attacking PCP became less and more reactive radicals recombined. It is obvious that at higher PCP-Na concentration, the course of degradation process is somewhat slower, but the absolute sum of PCP-Na degraded is higher. Also, with the decrease of the PCP-Na concentration, the dose needed for complete degradation is strongly reduced.

Usually, the concentration of a solute in water decreases exponentially with the irradiation dose, which can be expressed as:

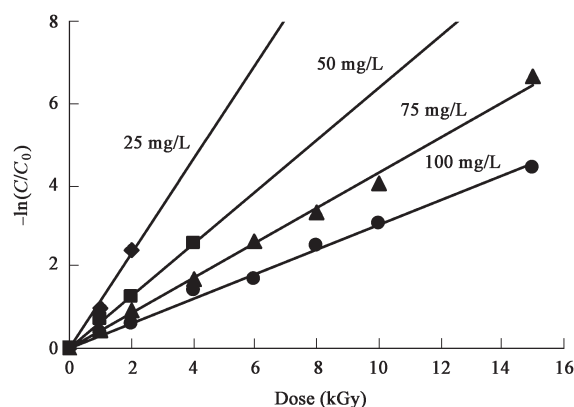
$$C = C_0 e^{-dD} \quad (3)$$

where,  $D$  is the irradiation dose necessary to achieve the corresponding concentration  $C$ , and  $d$  ( $\text{kGy}^{-1}$ ) is the dose constant in units of a reciprocal dose, which is analogous to a pseudo-first order, time-dependent rate constant (Mincher *et al.*, 2002; Kurucz *et al.*, 2005). The dose constant  $d$  is affected by various factors, including pollutant concentration, pH, the molecular structure of the pollutant, kind of radiation, dose rate, and so on (Getoff, 2002). It is useful to compare the decomposition rates at different conditions of the pollutant decomposition. The modification of Eq.(3) is shown as the following:

$$-\ln(C/C_0) = dD \quad (4)$$

Figure 7 and Table 2 show the rates of decomposition of PCP at different initial concentrations and are in an excellent agreement with the modified pseudo-first order reaction mechanism (Eqs.(3) and (4)). The dose constant  $d$  was the largest at the lowest initial concentration of PCP, and it was smaller at a higher initial concentration. According to the data in Table 2, the relationship between  $d$  and the initial concentrations could be worked out and expressed as a power function in Eq.(5):

$$d = 25.4496 C_0^{-0.9539}, \quad R^2 = 0.9943 \quad (5)$$



**Fig. 7** Initial concentration dependency of the radiolytic decomposition rate constant (dose constant) by  $\gamma$ -irradiation.

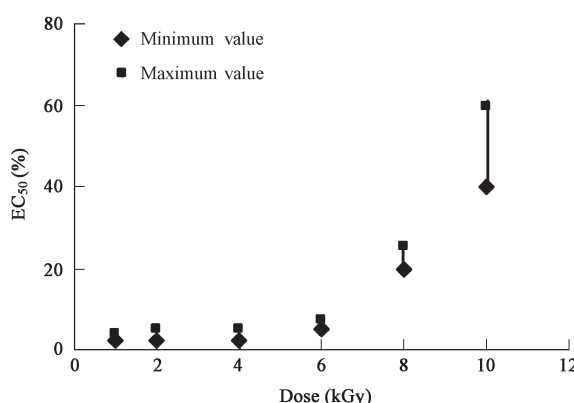
**Table 2** Change in dose constant ( $d$ ) with different initial PCP concentration

$C_0$ (mg/L)	$d$ ( $\text{kGy}^{-1}$ )	$R^2$
25	1.15	0.9882
50	0.63	0.9989
75	0.43	0.9967
100	0.30	0.9943

Therefore, the radiation dose needed under the same experimental conditions can be calculated easily if the initial concentration and removal efficiency are assumed.

## 2.4 Evolution of toxicity

Usually, the degradation products formed in the ionizing radiation processes are mainly low molecular-weight compounds, which are assumed to be less toxic and more biodegradable than the original compounds. Based on this fact, much research work has been conducted on combining ionizing irradiation or other advanced oxidation processes with biological treatments. But it has been reported that there would be some more toxic products formed during the oxidative treatment prior to the complete mineralization of the pollutants (Borrely *et al.*, 2000; Drzewicz *et al.*, 2005). On the other hand, we need to know the approximate irradiation dose when the toxicity of the wastewater is degraded acceptable to the environment



**Fig. 8** Radiation effects on acute toxicity of 75 mg/L PCP solution evaluated by bioluminescent bacteria tests.

or subsequent biological treatment processes. Consequently, the evolution of acute toxicity for 75 mg/L PCP-Na solution during the irradiation was evaluated, using the luminescent bacteria test according to a normalized method (GB/T 15441-1995). The results are shown in Fig.8. It is important to note that the lower the  $EC_{50}$  value, the higher the toxicity. It is obvious that the acute toxicity of the PCP-Na solution degraded with the increasing irradiation dose, and the degradation of the acute toxicity was complete at the 15 kGy dose. It basically agreed with that the dechlorination is of detoxification process. In the future research work, it must be taken into account that for toxicity evaluation, more than one biological species should be used to confirm the treatment efficiency.

### 3 Conclusions

On the basis of the experiments on the  $\gamma$ -irradiation of PCP in aqueous solutions, the following conclusions can be drawn. (1) The  $\gamma$ -irradiation treatment is an efficient and promising technology for the degradation of PCP in aqueous solutions. At rather low dose of 6 kGy, the  $\gamma$ -irradiation was able to remove all PCP-Na at the initial concentration of 50 mg/L and more than 90% of PCP-Na at the initial concentrations of 75–100 mg/L; (2) the decomposition rate of PCP by  $\gamma$ -irradiation was pseudo-first order kinetic over the applied initial concentrations, and the dose constant was strongly dependent on the initial concentration; (3)  $\gamma$ -irradiation decreased the toxicity of the PCP-Na solution immensely. It indicates that it is practical to apply biological treatment after suitable  $\gamma$ -irradiation at certain dose, which may reduce the required absorbed dose significantly.

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