RADIATION INDUCED DECOMPOSITION OF PENTACHLOROPHENOL (PCP) IN WATER

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Abstract

The decomposition of PCP in water induced by γ - irradiation has been studied at low PCP concentration under varions conditions. PCP is consumed linearly with increasing absorbed doses. PCP could be decomposed almost completely by γ - irradiation at relatively high doses. Chloride ions are increased simultaneously with the consumption of PCP. The amount of chloride increases also linearly with the increasing absorbed dose. At relatively high absorbed dose, almost all chloride atoms in PCP are eliminated. Chemical oxygen demand (COD) has been measured after irradiation. Ozone is a powerful oxidazing agent for PCP. After saturation of 1.09×10^{-4} mol. dm^{-3} PCP aqueous solution with ozone, PCP concentration drops to 1.6×10^{-5} mol.dm^{-3}. The combination of ozonation-ionizing radiation treatment is very effective, which greatly decreased the dose needed. pH and chemical oxygen demand also have been measured after ozonation and irradiation.

INTRODUCTION

In China a certain chemical plant is well known not only for its huge throughput of chlorinated organic compounds, but also for the fact that it is the unique assigned plant in China to manufacture hexachlorocyclohexane (HCCH) in case of the plague of locusts. Moreover, it used to synthesize a large amount of pentachlorophenol (PCP) to kill oncomelania, which is the intermediate host of blood fluke in some provinces of China and still manufactures PCP as main composition of some herbicide. Drinking water in some district has possibly been polluted by HCCH and PCP and their precursor hexachlorobenzene (HCB). Besides, according to a report [1] by Shanghai Running Water Company, 22 chlorinated organic compounds are formed after the daily treatment of the running drinking water with chlorine, 6 of which are among the EPA list of chlorinate organic compounds to be prior controlled. The level of chlorinated phenols is not significantly altered. HCB and other chlorinated benzene increase considerably after the treatment. Therefore, our envisaged efforts would focus on the remediation of drinking water polluted with PCP, HCB and other halogenated organic compound by the mehods of advanced oxidation processes (AOP) such as the combination of ionizing radiation and ozonation.

EXPERIMENTAL

The radiation chemical yield of PCP consumption has been determined spectrophotometrically (λ_{max} = 320 nm, ε = 6900 dm^3 mol^{-1} cm^{-1}) and checked by high-performance-liquid-chromatography (HPLC) on a 12.5 cm C_{18} column employing ethanol-water (v:v = 88:12) containing 0.1% acetic acid as the eluent. The yield of chloride ion has

been measured by the mercury(II) thiocyanate method according to ref. [2] with minor modification. In brief, a certain amount of irradiated sample is extracted by diethyl ether to minimize the possible effects of phenolic compounds. Chloride ions in water phase react with $Hg(SCN)_2$ quantitatively, and the liberated SCN^- is subsequently converted into $[Fe(SCN)_6]^{3-}$ which can be easily measured spectrophotometrically (λ_{max} = 460 nm, ε = 2600 $dm^3 mol^{-1} cm^{-1}$). Chemical oxygen demand has been titrated as described in ref. [3]. The ozone concentration in the solution by measuring optical density at 260 nm was determined, taking ε = 2900 $dm^3 mol^{-1} cm^{-1}$ [4]. The dose was deter009minded with Fricke dosimeter.

RESULT AND DISCUSSION

Decomposition of Pentachlorophenol with γ-Radiation

The decomposition of PCP in water induced by γ-irradiation has been studied at low PCP concentration under various conditions (different atmosphere or different pH). Figure 1 shows the UV spectra of PCP aqueous solutions after γ-irradiation at different doses. PCP exhibits a characteristic absorption at 320 nm (ε = 6900 $dm^3 mol^{-1} cm^{-1}$) while most of substituted or non-substituted phenols (except pyrograllol, and p-hydroxyphenol) have negligible absorption there. Therefore the decrease of absorbance at 320 nm should quantitatively response for the consumption of PCP.

As shown in Figure 2, PCP is consumed linearly with increasing dose. At the later stage where most PCP are consumed and the remaining couldn't compete for OH radicals with products efficiently, thus the consumption rate (G value) decreases. Yet PCP could be consumed almost completely by γ-irradiation at relative high doses ($cf.$ Fig. 1). The G values of PCP consumption are calculated from the slope of such plots as shown in Fig. 2 and complied in Table 1.

Table 1 The compilation of G values for PCP consumption and release of chloride

pH	air		N_2		N_2O	
	G(-PCP)	G(Cl⁻)	G(-PCP)	G(Cl⁻)	G(-PCP)	G(Cl⁻)
5	-0.22	1.1	N.D.	2.4	N.D.	2.7
9	-0.37	1.7	-1.2	4.8	-1.5	7.1

Note: G values in the units of 10^{-7} mol J^{-1}; N. D. not determined.

Chloride ions released simultaneously with the consumption of PCP. The amount of chloride eliminated increases also linearly with the increasing absorbed dose (Fig. 2). From the slope of such plots of concentration of chloride $vs.$ absorbed dose the G values of chloride elimination are calculated and complied in Table 1. At relative high absorbed dose, almost all chloride atoms ($i.e.$ five times of initial amount of PCP) are eliminated.

As shown in Table 1, the radiation chemical yields are very low. The pulse radiolytic study of PCP [5] suggested that OH radicals react with PCP by attacking the benzene ring to generate dihydroxypentachlorocyclohexadienyl, pentachlorophenoxyl, and semiquinone radicals [3]. At pH 8 the phenoxyl radicals prevail (77%) [4]. Phenoxyl radicals often react very slowly with O_2 but usually react with O_2^- very fast [6,7]. O_2^- can add to phenoxyl
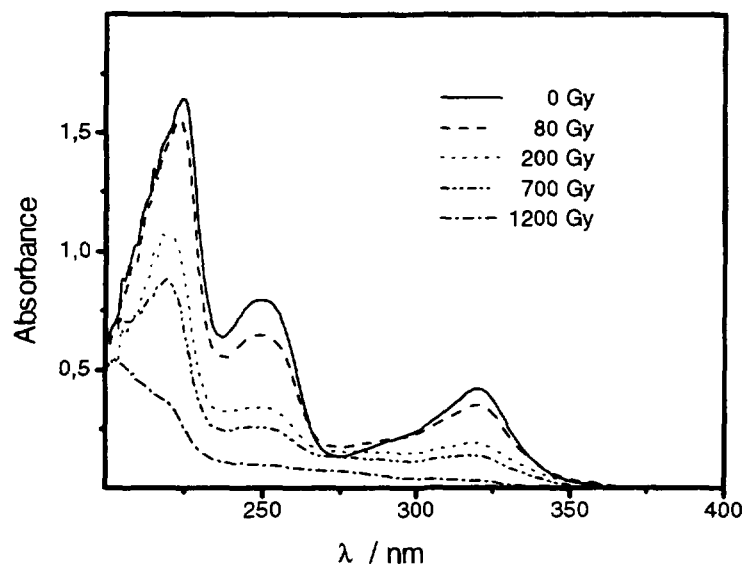
Fig. 1 UV spectra of PCP solution prior to and post γ-irradiation at different doses.
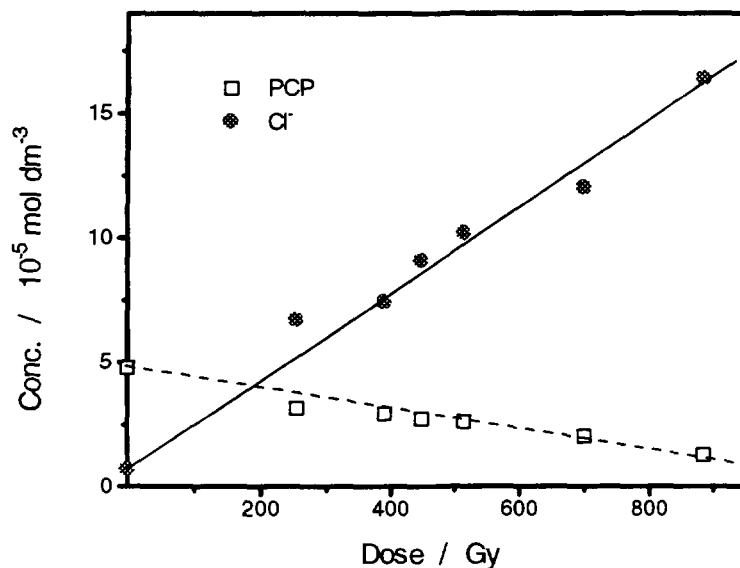Air saturated, pH 11, $[PCP]_0$ 6.3 x 10^{-5} mol dm^{-3}, Dose rate: 0.3_1.6 Gy s^{-1}

Fig.2 Dose dependent consumption of pentachlorophenol and release of chloride.
Air saturated, $[PCP]_0$ 4.8 x 10^{-5} mol dm^{-3}, Dose rate 0.3_1.6 Gy s^{-1}.

radicals and subsequently regenerate phenols by O_2 elimination or result stable adducts. The very low yield of PCP decomposition in air saturated solution (where hydrated electrons are converted into O_2^-) indicates that O_2^- react with PCP derived phenoxyl radical mainly to regenerate PCP. Table 1 also shows that the G value of PCP consumption increases with increasing   pH.   One   possible   reason   is   that   at   high   pH   the dihyroxypentachlorocyclohexadienyl radicals formed by the addition of OH radical to PCP tend to generate semiquinone radicals by Cl^- elimination rather than to generate pentachlorophenoxyl radicals by OH^- elimination, since at high pH both OH groups in the dihyroxypentachlorocyclohexadienyl radicals are deprotonated. The chemical yields of Cl^- elimination are about five times as large as that of PCP consumption at relative low absorbed

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dose ($\leq$500 Gy, *i.e.* the consumption of PCP is not more than a half) under all conditions investigated. This means that the γ-irradiation induced PCP dechlorination is somehow cooperatively, *i.e.* the products formed by the dechlorination of PCP induced by OH radical attack tend to dechlorination thoroughly. The products are polyphenols and thus are better reductants than PCP, therefore they can reduce phenoxyl radicals to PCP while they themselves are degraded. This might contribute to the much higher chloride yield, yet the detailed mechanism remains unknown.

Chemical oxygen demand (COD_{Mn}) has also been measured after irradiation. The results are shown in Table 2. At absorbed dose of 530 Gy about half of PCP is consumed (*cf.* Fig. 2), yet the COD value doesn't not change. The COD value decrease markedly only when the dose is high enough to consume almost all PCP. This suggests that at the early stage the benzene ring open is negligible in the consumption of PCP induced by OH radicals though O_2 is present, which agrees to the low reactivity of phenoxyl radical towards O_2.

Table 2 COD_{Mn} values of irradiated PCP. $[PCP]_0 = 6.3 \times 10^{-5}$ mol dm^{-3}, pH 5.3, air-saturated, dose rate 0.3~1.2 Gy s^{-1}

Dose / *Gy*	0	530	1600	2500
COD_{Mn} / *mg dm*$^{-3}$	10.5	10.5	9.4	3.4

The Combination of Ozonation-Ionizing Radiation Treatments

As the commercially available ozone generator is quite expensive, we requested and cooperated with the Environmental Research Center of Tsinghua University to develop a simplified device for the present project. The newly built ozone generator is under examination. Ozone is a powerful oxidazing agent but the reaction is almost selective to the unsaturated parts of the molecule to be oxidized. PCP is a special compound, in which benzene ring have six substituted groups. Ozone itself can decompose PCP. As shown in Figure 3, PCP is consumed considerably with increasing ozone inital concentration. PCP concentration drops from 1.09×10^{-4} mol dm^{-3} to 1.60×10^{-5} mol dm^{-3}, when ozone concentration is to 1.80×10^{-4} mol dm^{-3}.
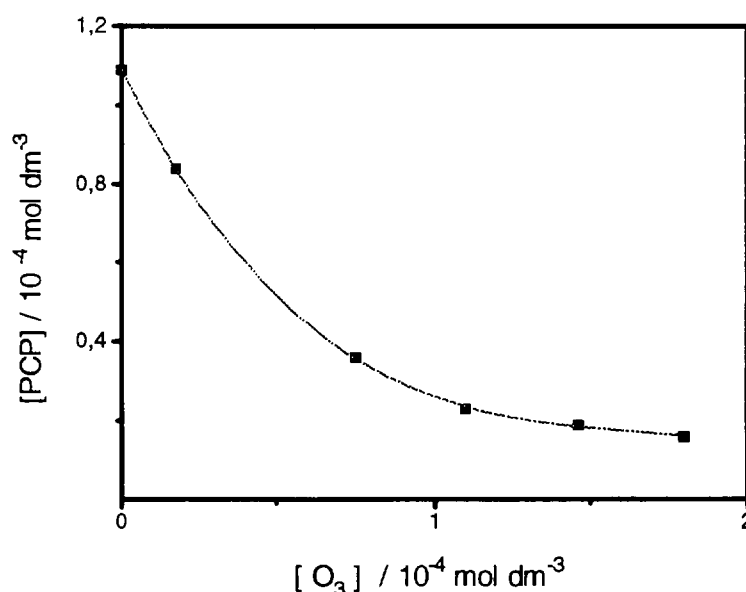

Fig.3 The effect of the concentration of ozone on the consumption of pentachlorphenol

The combination of ozonation with γ-irradiation treatment greatly decreased dose applied. Comparing with to γ-irradiation treatment, only 1/3 dose is needed by combination method. Chloride ions realeased with the decomposition of PCP. The change of chloride ion concentration by ozonation and γ-irradiation is summarized in Table 3. The pH value of the irradiated solution is distinctly reduced. By comparing UV absorption spectra of decomposition products with carboxylic acid , one can suggest that the decomposition product may be carboxylic acids, but further identification is needed. The variation of pH values and chemical oxygen demand (COD) have been measured. The results are complied in Table 3.

Table 3   Effects of absorbed dose on chloride ion, COD_{Mn} and pH value of ozonized PCP aqueous solution

Dose / Gy	0	183	367	565	734
$[Cl^-] / 10^{-4}$ moldm^{-3}	3.20	3.50	4.90	4.70	5.1
COD_{Mn} / mg dm^{-3}	13.5	9.37	8.92	8.92	7.57
pH	3.74	3.64	3.95	3.53	3.49

Note: $[PCP]_0$ 1.09 × 10^{-4} mol dm^{-3}, pH 9.44, COD_{Mn} 18.23 mg dm^{-3}, Dose rate 0.8~ 3.2 Gy s^{-1}

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