



GAMMA RADIATION TREATMENT OF PENTACHLOROPHENOL, 2,4-DICHLOROPHENOL AND 2-CHLOROPHENOL IN WATER

Yongke He, Jun Liu, Jilan Wu
Department of Technical Physics,
Beijing University,
Beijing, China

Abstract. The aim of this work was to investigate γ radiation treatment of pentachlorophenol (PCP), 2,4-dichlorophenol (DCP) and o-chlorophenol (o-CP) in water. The dechlorination of PCP, DCP and o-CP has been studied using γ radiation as well as ozonization. $G(\text{Cl}^-)$ is always much higher than the corresponding $G(-\text{PCP})$, this means that some primary radiolytic products are unstable during post irradiation. PCP is much easier to be decomposed under irradiation than that of simple chlorophenol. Some stable radiolytic intermediates were detected. Primary analysis reveals some quinones among the final products with toxicity that remains unclear. In the pulse radiolytic experiment, it was determined that about 53% of radicals undergo electrotransfer and others undergo addition when OH radicals react with PCP. The values of COD(Mn) after irradiating PCP in dosage were determined. It is recommended to bubble ozone simultaneously when radiation (or electron beam) treat CPs contaminating water.

1. INTRODUCTION

Chlorination is widely used in drinking water treatment for disinfection and often seriously increase the level of toxic chlorinated organic by-products, and it is not surprising to find chlorophenols (CPs) among them [1]. Therefore research is needed in the applicability of radiation in water treatment.

Pentachlorophenol(PCP) and its salts, primarily the sodium salt have gained wide applications both in industry and agriculture and they are among the common environmental pollutants. In the seventies PCP was used in China in the fight against snail fever and as a herbicide. Its biodegradation is slow, and hence it is not surprising that it is still observed in many drinking water resources. CPs are toxic at concentrations of few $\mu\text{g}/\text{L}$ and are also persistent, thus are listed in the US-EPA list of priority pollutants and in the European Community Directive 76/464/EEC as dangerous substances discharged into the aquatic environment [2, 3]. Since 1996, an IAEA project on the treatment of PCP in drinking water has been implemented.

OH radical is a very strong oxidant and react with most organic compounds at a diffusion control rate with little selection, and as a result, the concerned hazardous compound remains undestroyed at rather high absorbed dose applied. Model systems should be studied to obtain necessary data required for figuring out the radiolytic processes and making a practical estimation upon pertinent G values and rate constants. Pulse radiolysis is of quite help for kinetic studies. OH-radical-induced dechlorination of PCP, DCP and o-CP has been studied. To reduce the absorbed dose required, other methods like ozonation might be used in combination. Our works focus on the remediation of drinking water polluted with PCP and other CPs by the methods of γ radiation as well as ozonization. From the time of drinking water treatment prior to ensuring promising methods, one must confirm its reasonableness carefully. In this case, accompanying the degradation of PCP DCP and o-CP under irradiation, some stable intermediates have been detected, with potential toxicity considered. In the present paper, we report some latest results concerning to the radiation treatment of PCP, DCP and o-CP.

2. EXPERIMENTAL

Chemicals of the highest purity were commercially available and used without further purification. Prior to irradiation the solutions were saturated with air or N₂O. The pH of solutions were adjusted by 0.1M NaOH. Irradiation was carried out in ⁶⁰Co facilities in Beijing University and dose rates were determined with a Fricke dosimeter.

The decomposition of CPs were measured by HPLC on C₁₈ columns. The mixture of methanol and water was used as fluent, where proportions and flow rates changed with different objects. PCP was detected at 320 nm and o-CP and DCP were detected at 280 nm. MS was performed with APCI (atmosphere pressure chemical ionization) source, negative mode, referring to Puig [4] with modification.

The yield of chloride ion was measured by ion selective electrode (Orion 9417B type), spectrophotometry (according to Florence) [5] and HPLC (Dionex 2010i), respectively.

Chemical Oxygen Demand (COD) was determined as described by Yu [6].

3. RESULTS AND DISCUSSION

3.1. Gamma radiolysis of PCP

Table I compiles G values of PCP consumption and Cl⁻ formation in different atmospheres.

TABLE I. COMPILATION OF G VALUES OF PCP CONSUMPTION AND CHLORIDE IONS FORMATION UNDER TIRRADIATION

	Air		N ₂ O ^a		N ₂ O+NaN ₃ ^b		N ₂
[PCP] ₀ (mol l ⁻¹)	1.3×10 ⁻⁴	1.5×10 ⁻⁵	1×10 ⁻⁴	1×10 ⁻⁴	1×10 ⁻⁴	1×10 ⁻⁴	1.6×10 ⁻⁵
pH	9.7	5	5	9	10	9	9
G(-PCP) (10 ⁻⁷ mol J ⁻¹)	0.90	0.55	2.9	2.9	2.9	1.9	1.2
G(Cl ⁻) (10 ⁻⁷ mol J ⁻¹)	6.0	ND	4.4(7.9) ^c	6.0(9.9) ^c	8.2(9.9) ^c	6.5(7.5) ^c	4.8
Dose range (Gy)	0~140	0~32	0~150	0~150	0~150	0~150	0~500

^a: N₂O saturated solution; ^b: N₂O saturated solution with [NaN₃] = 210⁻³ M; ^c post-irradiation storage.

From the above, G(-PCP) is always much lower than G(OH), indicating that the phenoxy radicals formed may regenerate some PCP during their decay. G(Cl⁻) is always much higher than the corresponding G(-PCP). We confirmed this by different ways including ion selective electrode, spectrophotometry and sometimes HPLC. This means that some primary irradiation products are unstable during post-irradiation storage, which release Cl⁻ continuously and meanwhile consume no further PCP.

From Fig. 1, both the G(-PCP) and G(Cl⁻) were strongly dependent on doses. It reveals that when higher doses were applied, the intermediates would compete with PCP in capturing OH or e⁻_{aq}.

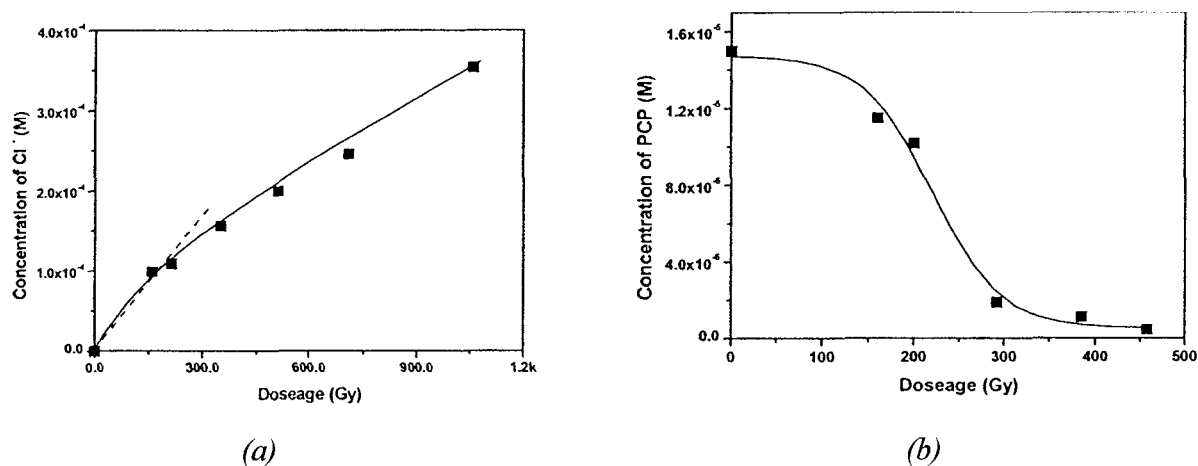
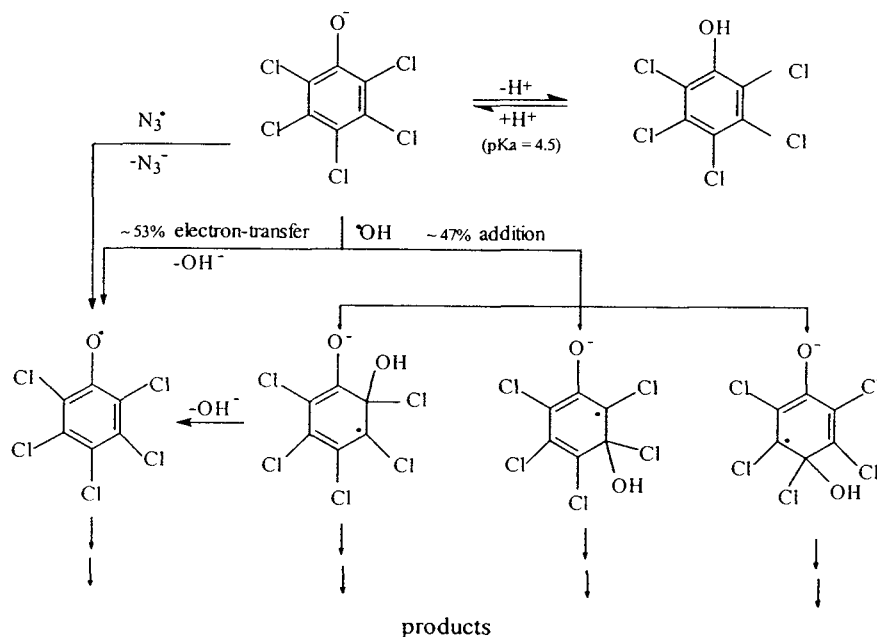


FIG. 1. (a) Dependence of $G(\text{Cl}^-)$ on dose, $1.6 \times 10^{-4} \text{ M}$ PCP, pH 9.6, air saturated solution; (b) Dependence of $G(-\text{PCP})$ on dose, $1.5 \times 10^{-5} \text{ M}$ PCP, pH 5, air saturated solution.

3.2. Pulse radiolysis and mechanism of PCP degradation

When radiolytically generated OH radical reacts with PCP at the beginning stage two pathways compete with each other: electron transfer and radical addition [7].



In a pulse radiolysis experiment, using optical and conductivity detection alternatively, Fang determined [8] that about 53% OH radicals undergo electron transfer and the others undergo addition when OH radicals react with PCP. Though further detailed mechanism relating to the release of Cl⁻ from pentachlorophenoxy radical and deprotonated hydroxytetrachlorophenoxy radical still leaves to be found. Based on Table I, we can properly draw out that in both ways only a part of PCP is eventually consumed and more than one Cl⁻ is released from a destroyed PCP molecule.

Comparing rate constants of OH and e⁻_{aq} reacting on chlorophenols, quinones and chloranils with that on pentachlorophenol ($k(\text{Cl}_5\text{C}_6\text{O}^- + \cdot\text{OH}) = 8.610^9 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) [7], it is easy to understand that both the $G(-\text{PCP})$ and $G(\text{Cl}^-)$ are strongly dependant on the dose. The consumption of PCP and the release of Cl⁻ are reduced evidently as dose increases. Thus, some unexpected situations might take place. For example, if dose applied is insufficient, the water still retains undesirable chloranils.

3.3. γ Radiolysis of o-CP and DCP

Table II shows the compilation of G values of 2,4-dichlorophenol and 2-chlorophenol.

TABLE II. G VALUES OF O-CP AND DCP; PH5, AIR SATURATED SOLUTION

[CP] ₀ M	o-CP			DCP	
	110^{-3}	410^{-4}	110^{-5}	4.410^{-4}	110^{-5}
G(-CP) $10^{-7}\text{mol}\cdot\text{J}^{-1}$	4.2	1.8	1.2	2.0	0.3
G(Cl ⁻) $10^{-7}\text{mol}\cdot\text{J}^{-1}$	0.3	0.2	ND	1.2	ND
Dose range (Gy)	0~432	0~420	0~32	0~420	0~300

With increasing concentration, the G value of decomposition is increased. It reveals that there existed competition reaction of OH radicals with radiolytic products. From Table II, it can be seen that the elimination of Cl from PCP is much easier than that from o-CP and DCP. The reason is very clear that as the chlorine atom attracts electron, the benzene ring in PCP is in a more stress.

Approaching to more practical case, the experiments of degradation of DCP and o-CP on dose were done. The results are shown in Figs 2 and 3.

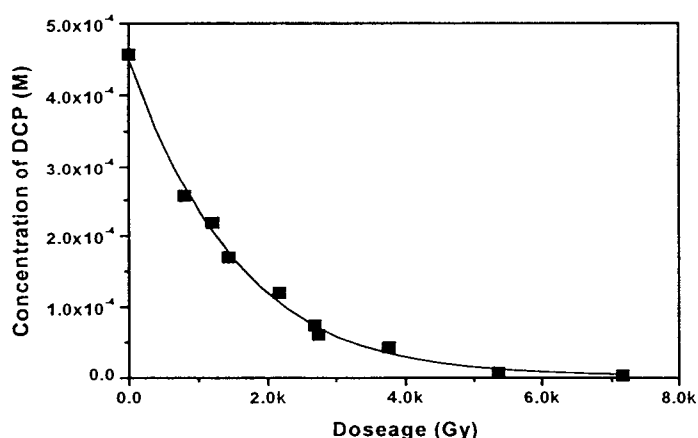


FIG. 2. The dependence of degradation of DCP on dose; pH5, air saturated 4.4×10^{-4} M DCP solution.

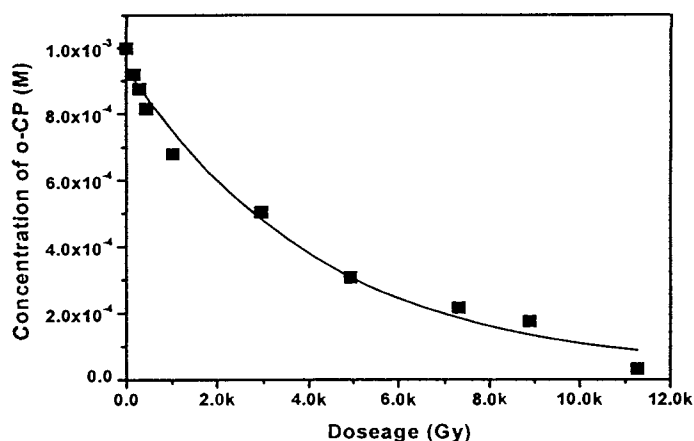


FIG. 3. The dependence of degradation of o-CP on dose; pH5, air saturated 1×10^{-3} M o-CP solution.

The dose used to decompose the parent compound is higher than that calculated from corresponding G values. It displays once again that the intermediates compete to scavenge OH radical against parent compound.

3.4. Intermediate radiolytic products

From the view of drinking water treatment, prior to ensuring a promising methods, one must confirm its reasonableness carefully. In this case, accompanying the degradation of PCP under irradiation, we detected some stable intermediates:

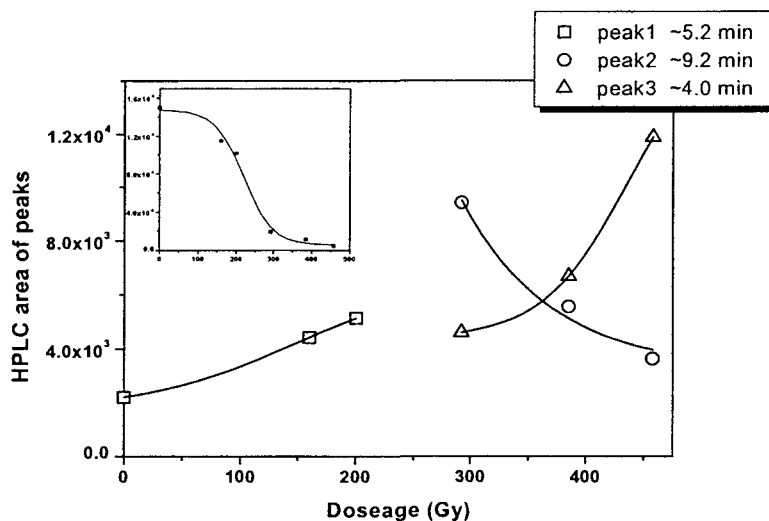


FIG. 4. Growth and decay of intermediate radiolytic products of PCP ($1.5 \times 10^{-5} M$, pH5, air saturated solution). Peak 1 disappeared when absorbed dose is higher than 300 Gy; There is no signal of peak 2 and peak 3 when dose is lower than 200 Gy. Insert is corresponding degradation of PCP, c.f. Fig. 1(b).

It can be seen that, even in the case of γ radiolysis of $1.5 \times 10^{-5} M$ PCP, when dose applied was about 500 Gy, the accumulation of a second radiolytic product was still going on. Measuring chemical oxygen demand (COD_{Mn}) after irradiating PCP in different dosages supports the result above.

TABLE III. DEPENDENCE OF COD ON DOSE FOR pH5, AIR SATURATED $6.3 \times 10^{-5} M$ PCP SOLUTION

Dose (Gy)	0	530	1600	2800
COD_{Mn} (mg/L)	10.5	10.5	9.4	3.4

At absorbed dose of 530 Gy about half of PCP is consumed, yet the COD value doesn't change. The COD value decreased markedly only when the dose was high enough to consume almost all PCP. We suggest 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 phenoxy radicals towards O_2 .

Therefore, it is necessary to separate these compounds, determine their structure and evaluate their toxicity. The unknown compound may be 2-chloro-p-benzoquinone; its UV spectrum is shown in Fig. 5.

In model systems where water was contaminated by o-CP and DCP, more intermediates were produced which underwent more complex change than those contaminated by PCP during irradiation. This may be due to the difference of primary degradation mechanism between PCP and o-CP and DCP.

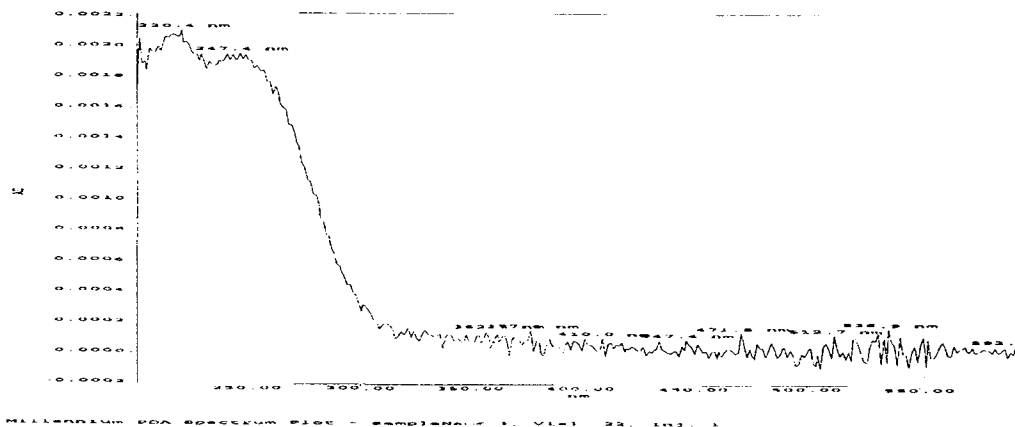


FIG. 5. UV Spectrum of unknown compound taken from the HPLC-DAD of γ irradiated pH5, air saturated $1.5 \times 10^{-5} M$ PCP solution.

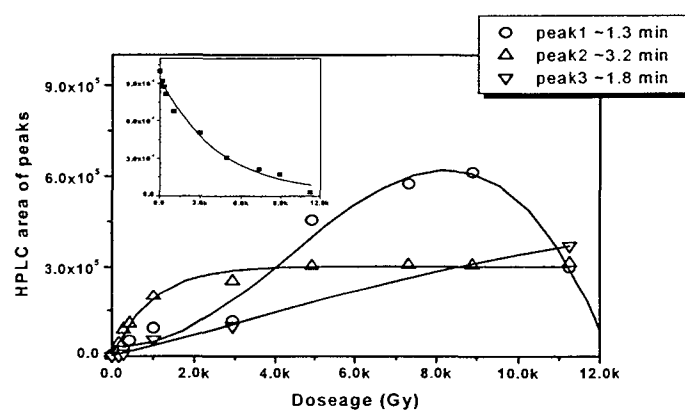


FIG. 6. Growth and decay of intermediate radiolytic products of *o*-CP ($1.010^{-3} M$, pH5, air saturated solution); insert is the corresponding degradation of *o*-CP, c.f. Fig. 3.

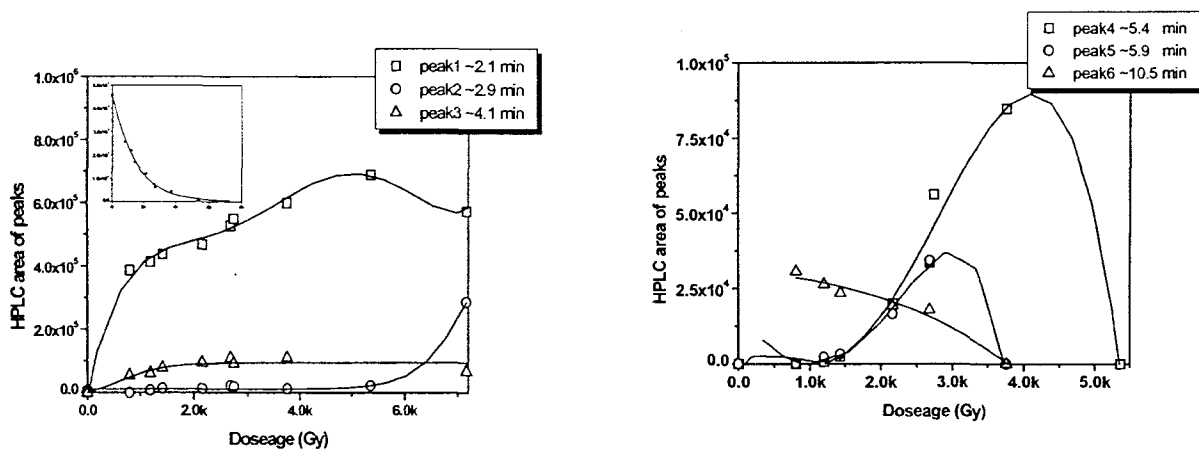


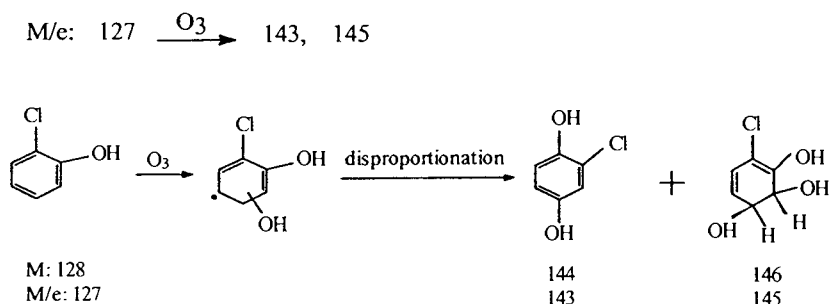
FIG. 7. (a) and (b) Growth and decay of intermediate radiolytic products of DCP ($4.42 \times 10^{-4} M$, pH5, air saturated solution); insert is the corresponding degradation of DCP, c.f. Fig. 2.

3.4. Combination of ozonization and γ irradiation

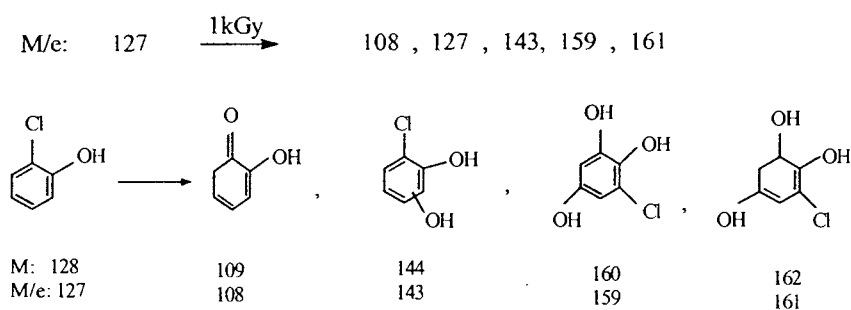
It is believed that O_3 can breakdown unsaturated carbon-carbon bonds and therefore destroy the benzene ring of aromatic compounds, whereas radiation treatment alone usually requires relatively high dose to achieve the same effects, even in the presence of O_2 .

We tried ozonization and obtained MS spectra of ozonization products as well as that of irradiation products. The two series of MS spectra are so similar in the case of o-CP and DCP. Combined with information obtained from HPLC analysis, we propose that during ozonization CPs were degraded in similar way as irradiation, i.e. OH radical attacks rather than through predicted C=C cleavage.

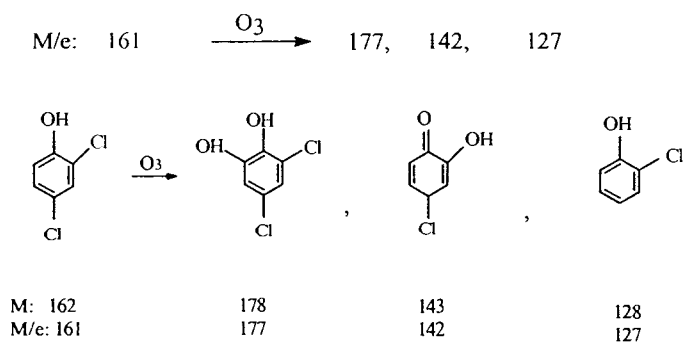
Ozone treatment of o-CP:



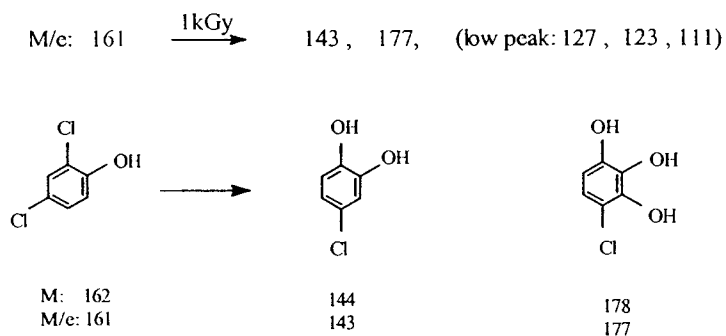
γ radiolysis of o-CP:



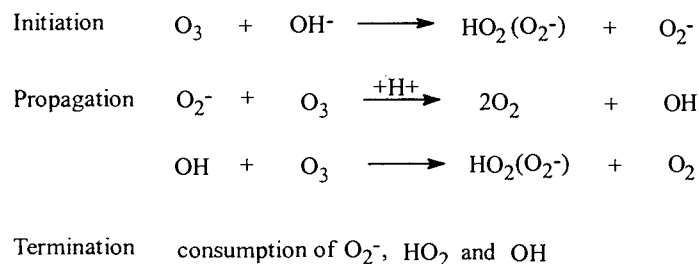
Ozone treatment of DCP:



γ radiolysis of DCP:

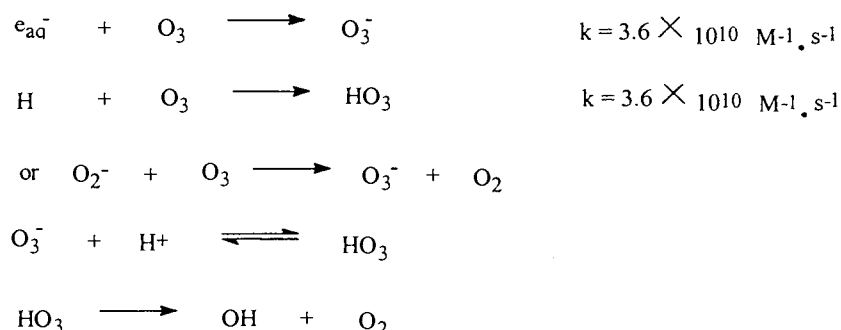


This agrees with Weiss's chain decomposition mechanism of ozone in water [9, 10]:



The peroxy radicals (HO₂· or ·O₂⁻) may perform similar manner on CPs like OH radicals [11].

However, O₃ can convert radiolytically generated reducing species (hydrated electron and H atom in the absence of O₂, or ·O₂⁻ under aeration) to oxidizing OH radicals and thus can improve the efficiency of radiation-induced oxidation. Therefore, ozone may be considered a good partner of ionizing radiation in some water treatment [10].



Moreover, PCP exhibited its specialty among CPs towards ozonization. PCP degraded quickly during ozonization and left far less by-products.

4. CONCLUSION

If γ irradiation method is used to treat city water (drinking water), potential toxicity of radiolytic intermediates must be considered. Though the chronic toxicity equivalency factors (TEFS) of pentachlorophenol is greater than that of monochlorophenol (1:0.04) [12], the content of chlorophenol is 35 times greater than that of PCP in some city drinking waters. In addition, PCP is much easier to be decomposed under γ irradiation than that of simple chlorophenol; however, we should pay more attention to the radiolytic intermediates of simple chlorophenols. Future work should be done such as separation and identification of intermediates, its formation and decay kinetics, evaluation of the toxicity of intermediates and so on.

Evaluation of treatment efficiency by final product analysis is necessary. COD and TOC are common indices of the qualities of water and wastewater, as for the evolution of their qualities after radiation treatment. The fact is that some simple organic compounds such as formic acid and acetic acid are non-toxic, yet they are included in COD and TOC values. While formic acid can easily be oxidized to CO₂ by OH radical in the presence of O₂, it requires very high doses to further oxidize acetic acid to CO₂. Therefore, basic research to

obtain detailed mechanistic information, especially detailed product spectra, is needed for both designing and optimizing the treatment process.

It is recommended to bubble ozone simultaneously when γ radiation (or EB) treats CPs contaminating water. Ozone itself, in water can, react on CPs through OH and HO₂ radicals, and it can also convert radiolytically generated reducing species into oxidizing OH radicals and therefore enhance the efficiency of radiation-induced decomposition.

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