Photolytical Degradation Products of Pentachlorophenol in Aqueous Solution and Organic Solvents

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The photolytical degradation of pentachlorophenol in water, ethyl alcohol, and ethyl acetate was investigated to provide an understanding of its persistence and the nature of its degradation products. The photodegradation of pentachlorophenol in water was found to be most efficient resulting in complete dechlorination and production of acetic acid, oxalic acid, and chloride ion as final products. The chlorinated degradation products of pentachlorophenol in water (2,3,4,6-tetrachlorophenol; 2,3,5,6-tetrachlorophenol; 2,4,5-trichlorophenol; 2,3,6-trichlorophenol; 2,6-dichlorophenol; dichlorobenzenediol), ethyl alcohol (2,4,6-trichlorophenol; 2,3,6-trichlorophenol; 2,5-dichlorophenol; 2,3-dichlorophenol), and ethyl acetate (2,3,6-trichlorophenol; 2,4-dichlorophenol) were identified. A theoretical determination of the degradation products using density functional theory computations of atomic charge distribution that correlated with the experimental findings of this study is proposed.

Key Words: UV radiation, chlorophenols, DFT calculation

INTRODUCTION

The use of ultraviolet (UV) radiation alone or in combination with oxidizing agents and catalysts to degrade chlorophenols has been reported in literature. In general, the addition of catalysts or oxidants enhances the photodegradation process. The efficacy of sulphonated phthalocyanine complexes as catalysts and sensitizers to photodegrade chlorophenols was established by Ozoemena et al. (2001). Pandiyan et al. (2002), Rao et al. (2003), and Kim et al. (2007) used titanium dioxide as catalyst in the photooxidation of chlorophenols. Pandiyan et al. (2002) found that in the presence of titanium dioxide, polychlorinated phenols are more difficult to dechlorinate than monochlorinated phenols. Antonaraki et al. (2002) studied the photolysis of chlorophenols using UV and visible light in combination with hydrogen peroxide or a polyoxometallate catalyst, and related the decomposition rate with the position and number of chlorine atoms in the phenolic ring. They found that a chlorine atom in the *meta* position accelarates the photodecomposition process. The

photochemical decomposition of chlorophenols using UV light and various oxidants such as hydrogen peroxide, ozone or Fenton's reagent involves free radical formation (Benitez et al. 2000; Ghaly et al. 2001).

Although a complete mechanistic model for the photodegradation of chlorinated organic compounds including polychlorophenols is not yet available, a number of reaction pathways and degradation products have been proposed (Hirvonen et al. 2000; Hong et al. 2000; Burrows et al. 2002; Hong & Zeng 2002; Suegara et al. 2005; Czaplicka 2006). Low molecular weight chlorophenols and organic acids, for example, are commonly reported as photodegradation products of pentachlorophenol. The degradation products vary with factors like radiation source and the use of oxidants or catalysts.

Pentachlorophenol is an industrial and agricultural chemical with many uses, e.g., as general disinfectant, insecticide, and fungicide or anti-fouling agent. Pentachlorophenol is a common environmental pollutant and its use has been banned or restricted in many countries in Southeast Asia including the Philippines (UNEP 2002).

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It is listed as one of the compounds of concern in a global report on persistent toxic substances (UNEP 2003). It is found not only in water, soil, and sediments but also in fish and in human milk and tissues (Mussalo-Rauhamaa et al. 1998; Hong et al. 2005; Ge et al. 2007; Kiguchi et al. 2007). The World Health Organization (WHO) classifies pentachlorophenol as a highly hazardous compound (WHO 1996). It exhibits toxicity in organisms and in experimental animal models (Freire et al. 2005; Yang et al. 2005; Villela et al. 2006; Yin et al. 2006).

The degradation of environmental pollutants by UV irradiation provides a potential route in developing acceptable treatment methods. Studies aimed at remediating surface water or wastewater polluted with pentachlororophenol are understandably carried out in aqueous solutions (Hirvonen et al. 2000; Hong et al. 2000; Benitez et al. 2003; Gunlazuardi & Lindu 2005). In the present investigation, the use of UV radiation (without catalysts, oxidants or sensitizers) to treat pentachlorophenol in aqueous and organic solvents was studied. The photolytical degradation products of pentachlorophenol in water, ethyl alcohol, and ethyl acetate were identified and compared with literature data. In addition, density functional theory calculations of atomic charge distribution were used to explain the formation of chlorinated products identified in this study.

MATERIALS AND METHODS

All chemicals were analytical grade quality (acetone, 99.8%; ethyl alcohol, 99.5%; ethyl acetate, 99.5%; methyl alcohol, 99.8%; acetonitrile, 99.8%; diethyl ether, 99.5%; acetic acid, 99.0%, formic acid, 98.0%; oxalic acid, 99.5%; sulfuric acid, 97.0%) and purchased from Wako Pure Chemical Industries, Ltd. (Japan) and Cica-Reagent Chemical Co., Inc. (Japan). The water was prepared and purified by passing through an Organo PF Filter Model III apparatus and a Millipore Simpli Lab UV Ultrapure System in series.

Pentachlorophenol and the chlorinated phenolic degradation products were identified using analytical standards: pentachlorophenol, 99.8% (Wako Pure Chemical Industries, Japan); 2,4-dichlorophenol, 99.9% (Kanto Chemical Co., Inc., Japan); 2,5-dichlorophenol, >98%, 2,6-dichlorophenol, >99%, 2,3,6-trichlorophenol, >98% and 2,4,5-trichlorophenol, >99% (Tokyo Kasei, Japan); 2,4,6-trichlorophenol, 99.5% and 2,3,4,6-tetrachlorophenol, 98% (Dr. Ehrenstorfer GmbH, Germany); 2,3,5,6-tetrachlorophenol, 99% (Cambridge Isotope Laboratories, Inc.).

The UV irradiation set-up, described in detail elsewhere (Suegara et al. 2005; Espino et al. 2006), is composed of a 1.7 W low pressure mercury (Hg) lamp with 254 nm main wavelength of radiation (Germipak UV cell GCL212) and 4 mL UV-Vis quartz cells (GL Sciences Inc., Japan). The radiation intensity of the lamp measured using a UVX radiometer (UVP, Inc., U.S.A.) was 6.72 mW cm^{-2}.

The decrease in pentachlorophenol concentration and the appearance of the chlorinated products were monitored using a high pressure liquid chromatograph combined with electrochemical detector (HPLC-ECD) (HP1100 LC and HP1049A ECD, Hewlett Packard) and on a TSK gel ODS 80T column with dimensions of 2.4 mm i.d. x 25.0 cm L (TOSOH Corporation, Japan). The chromatographic conditions were as follows: 45:55 v/v water:acetonitrile isocratic elution; 0.9 ml/min flow rate; 1.2 V potential; 40° C operating temperature; 100 µl injection volume. Pentacholorophenol was quantified using standard calibration solutions (r^2=0.9998 in water, r^2=0.9994 in ethyl alcohol, r^2=0.9995 in ethyl acetate).

For the analysis of the degradation products using liquid chromatography-electrospray ionization-mass spectrometry (LC-ESI-MS), an irradiated aqueous solution of pentachlorophenol was acidified with concentrated formic acid to pH 2.4 and extracted using an Oasis HLB+ sorbent (Waters, Milford, MA). Conditioning of the solid-phase was done using 3 mL 1:9 v/v methyl alcohol:diethyl ether, 2 mL methyl alcohol and 2 mL 1 % formic acid solution. Sample loading was at 4 mL/min. A 1 mL of 1 % formic acid solution was used to wash the solid-phase before air drying it for 5 min. Elution was carried out with 1 mL methyl alcohol followed by 3 mL 1:9 v/v methyl alcohol:diethyl ether. The solid-phase extraction set-up was operated with a microtube pump (EYELA Rikakikai Tokyo). The extract was concentrated to a final volume of 1 mL using a gentle stream of N_2 gas. The concentrated extract was then analyzed on a Shim-pak FC ODS column (2.0 mm i.d. x 150 mm L) using an LCMS-2010A system (Shimadzu, Japan). The LC-ESI-MS conditions were: 50:50 v/v 0.1 % formic acid:acetonitrile isocratic elution; 0.2 mL/min flow rate; 2.0 µL injection volume; +4.5 kV and –3.5 kV ESI voltage for positive and negative modes, respectively; 1.5 L/min gas spray flow; 0.2 kP gas pressure; 250° C ionization temperature; 100-600 m/z scan range at 1.0 sec/scan.

The chloride ion concentrations in the irradiated aqueous and ethanolic solutions were measured using an IC7000 Series II ion chromatographic analyzer (Yokogawa Analytical Systems, Japan) and on an Excelpak ICS-A23 column with the following conditions: 5 x 10^{-3} M sodium carbonate and 15 x 10^{-3} M sulfuric acid eluent solutions;

1.0 mL/min flow rate; 40° C operating temperature. Acetate and oxalate ion measurements were carried out using a Dionex ICS-90 ion chromatography system (Dionex Corporation, CA, USA) with IonPac AG12A 4 x 50 mm guard and IonPac AS12A 4 x 200 mm analytical columns. The chromatographic and operating conditions were: 2.7×10^{-3} M sodium carbonate / 0.3×10^{-3} M sodium bicarbonate eluent at 1 mL/min flow rate; 25 μL injection volume; 25 min run time; 1600 psi average system backpressure; 14 μS average background conductance; suppressed conductivity detection with AS12S-ULTRA (4 mm) auto-suppression recycle mode.

The total organic carbon (TOC) measurements were performed using a TOC-5000A analyzer (Shimadzu, Japan) and following the combustion-infrared technique and EPA Methods 415.1 and 415.2 (1999).

Atomic charge distribution in the pentachlorophenol molecule was determined by density functional theory (DFT) calculations on a Gaussian 98 W program (Frisch et al. 1998) and B3LYP method with 6-311G basis set for molecular geometry optimization.

RESULTS

Degradation of pentachlorophenol in water and organic solvents
The decrease in pentachlorophenol concentration (Figure 1) confirmed the degradation of pentachlorophenol when exposed to UV light in the different solvents. After 8 min of UV irradiation, pentachlorophenol degraded completely in water while in ethyl alcohol or ethyl acetate it required over 60 min of irradiation before it was no longer detectable. Its degradation in water and organic solvents fitted the first-order reaction equations :

$$\ln [PCP]_t / [PCP]_o = -kt \qquad (1)$$

and

$$t_{1/2} = \ln 2 / k \qquad (2)$$

where $[PCP]_t$ and $[PCP]_o$ are concentrations of pentachlorophenol at time t and time 0, respectively, k is the rate constant, and $t_{1/2}$ is the half-life. The slopes of the linear plots (r^2=0.978 to 0.992) of $\ln [PCP]_t / [PCP]_o$ against time determined the rate constants. The rate constants and half-lives, calculated on data points from the start of irradiation to complete or greater than 70 % decomposition are presented in Table 1.
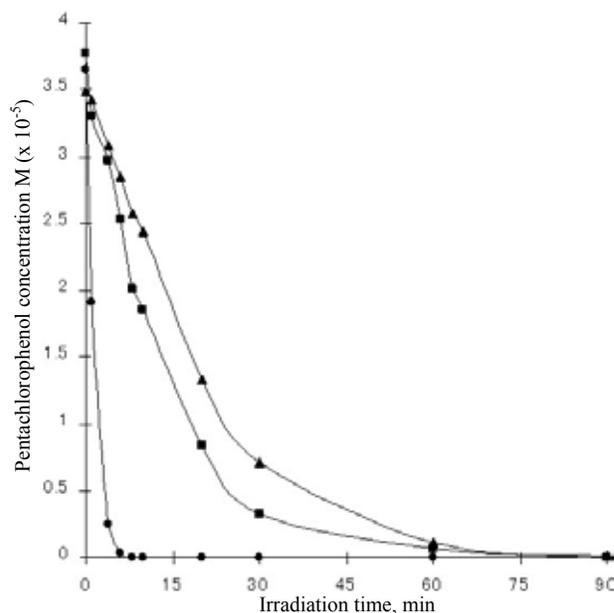

Figure 1. Decrease in concentration of pentachorophenol in water (●), ethyl acetate (■) and ethyl alcohol (▲) exposed to UV light using a low pressure Hg lamp (254 nm). [3.76×10^{-5} M initial concentration]

Table 1. First-order rate constants and half-lives of the degradation of pentachlorophenol (7.51×10^{-5} M initial concentration) in different solvents

Solvent	Rate constant (min^{-1})	Half-life (min)
Water	0.600	1.2
Ethyl acetate	0.068	10
Ethyl Alcohol	0.039	18

Final photodegradation products
Figure 2A shows the appearance of chloride ion, acetic acid, and oxalic acid as pentachlorophenol in water photodegraded. Both organic acids persisted in solution after over 60 min of UV light exposure, although oxalic acid was found in lower concentrations than acetic acid. In the irradiated solution of pentachlorophenol in ethyl alcohol (Figure 2B), only chloride ion and acetic acid were detected. Acetic acid also remained in the solution after more than 60 min of irradiation.

Total organic carbon was measured in the irradiated aqueous solutions to monitor the extent of photodecomposition. A decrease in TOC and total carbon concentrations with a corresponding increase in inorganic carbon concentration was observed (Figure 3), suggesting that pentachlorophenol and its degradation products mineralized into oxides of carbon during an extended
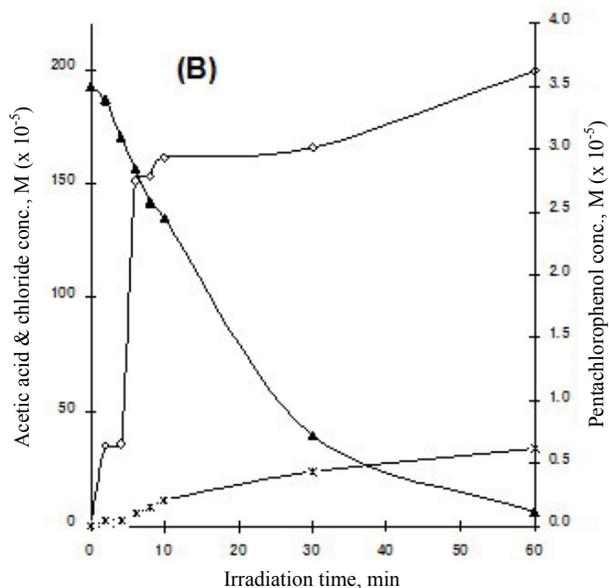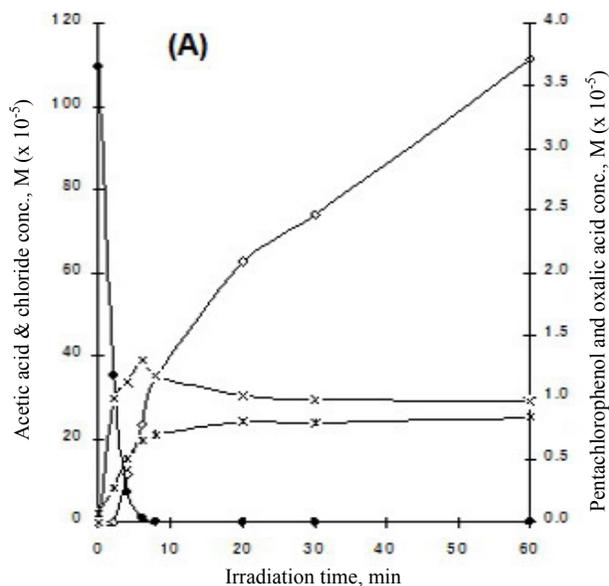
Figure 2. Final products formation [acetic acid (◇); oxalic acid (x); chloride (∗)] in the photodegradation of pentachlorophenol in (A) water (●) and (B) ethyl alcohol (▲)

Figure 3. Total carbon (□), organic carbon (Δ) and inorganic carbon (○) concentrations in irradiated solutions of pentachlorophenol in water

2,3,6-trichlorophenol and 2,6-dichlorophenol were produced when pentachlorophenol photodegraded in water. Similar to pentachlorophenol, these products degraded completely after 8 min of UV irradiation. Among the degradation products of pentachlorophenol in water, 2,6-dichlorophenol and 2,4,5-trichlorophenol figured prominently. In the irradiated solutions of pentachlorophenol dissolved in ethyl alcohol or in ethyl acetate, fewer degradation products were formed. In the ethyl alcohol solutions, 2,4,6-trichlorophenol, 2,3,6-trichlorophenol, 2,5- dichlorophenol and 2,3-dichlorophenol were detected. These products persisted in solution long after pentachlorophenol has completely decomposed. The degradation product 2,3-dichlorophenol was found to be stable under UV light exposure of over 5 h while the other products required at least 4 h of irradiation before they were no longer detectable in solution. In ethyl acetate, only 2,3,6-trichlorophenol and 2,4-dichlorophenol were detected. These products degraded in less than 20 min of UV irradiation.

Monochlorophenols were not detected in any of the irradiated pentachlorophenol solutions. An extract of the aqueous solution of pentachlorophenol that was irradiated for 3 min was found to contain a dichlorobenzenediol.

Atomic charge distribution computations
The calculated atomic charge distributions on the C atoms are shown in Figure 5, whereas the atomic charge distributions for O, H, and Cl atoms are available upon

period of UV light exposure, over 13 h in this study. The formation of acetic and oxalic acids, in part, accounts for the measured TOC.

Chlorinated photodegradation products
Figure 4 shows the appearance of chlorinated degradation products in the irradiated solutions of pentachlorophenol in the different solvents. 2,3,5,6-Tetrachlorophenol, 2,3,4,6-tetrachlorophenol, 2,4,5-trichlorophenol,
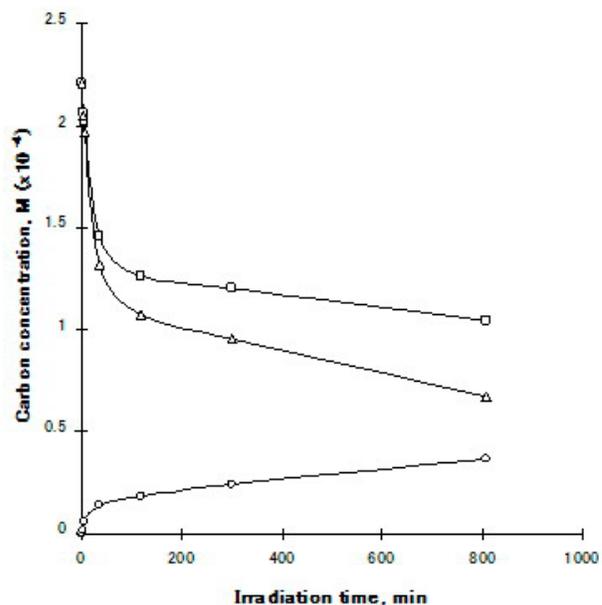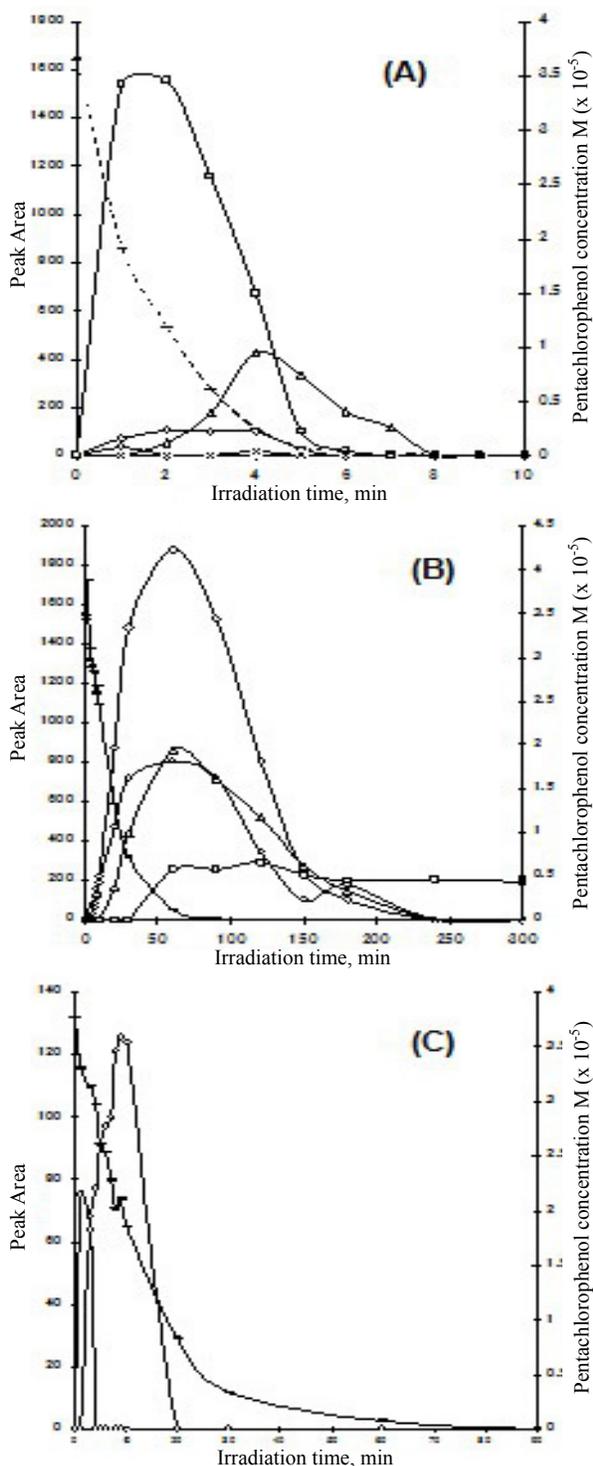
Figure 4. Formation of chlorinated degradation products in irradiated solutions of pentachlorophenol (—) in (A) water [2,3,5,6-tetrachlorophenol (◇); 2,3,4,6-tetrachlorophenol (○); 2,4,5-trichlorophenol (Δ); 2,3,6-trichlorophenol (X); 2,6-dichlorophenol (□)], (B) ethyl alcohol [2,4,6-trichlorophenol (◇); 2,3,6-trichlorophenol (○); 2,5-dichlorophenol (Δ); 2,3-dichlorophenol (□)], and (C) ethyl acetate [2,3,6-trichlorophenol (◇); 2,4-dichlorophenol (○)]

request. The atomic charge distributions on C atoms at the *ortho* positions were all positive (1.606 to 1.751) compared with the negative charge distributions (–0.116 to –1.132) on C atoms at the *meta* and *para* positions. Dechlorination will likely occur in C atoms with negative atomic charge distribution because the relative localization of electrons on these atoms will result to a weak C-Cl bond. The Cl atoms in the *meta* or *para* position to the hydroxyl group are thus expected to be readily removed during photodegradation through reductive dechlorination.

DISCUSSION

Pentachlorophenol dissolved in the very polar water solvent photodegraded faster than when it was dissolved in ethyl alcohol or ethyl acetate. This is consistent with other studies that showed fast photodegradation rates for organic compounds in aqueous solution. Kim & O'Keefe (2000), for example, found that polychlorinated dibenzodioxins and furans are more photoreactive in pure water than in 60 % v/v acetonitrile-water. Another example is the photodegradation of the pesticide ethiofencarb wherein the degradation kinetics is affected by solvent polarity : $t_{1/2}$ in water > $t_{1/2}$ in methanol > $t_{1/2}$ in hexane (Sanz et al. 1999). In terms of environmental fate, pentachlorophenol exposed to UV radiation will decompose fast in water but will persist in matrices such as soil suspensions, sediments or lipophilic tissues. The reported half-lives of pentachlorophenol are between 23 and 178 d in soils and from 10 to 24 h in fish tissues (UNEP 2002).

Ideally, UV radiation treatment of organic pollutants should result in complete decomposition and produce innocuous or mineralized by-products. In this study, pentachorophenol formed low molecular weight chlorophenols, organic acids, and chloride ions as degradation products. Although the degradation rate was faster in water than in ethyl alcohol or ethyl acetate, more degradation products were detected in water. When an aqueous solution of pentachlorophenol was exposed to UV light, tetra-, tri- and dichlorinated phenolic compounds appeared within 2 min of irradiation. After 2 min, over 30 % of the Cl in pentachlorophenol was already in solution (Figure 6). Between 6 and 8 min, complete dechlorination (i.e., 100 % Cl in solution) of pentachlorophenol and its degradation products occurred. This explains why chloride ion concentration is higher in the aqueous solution than in ethyl alcohol solution after 60 min of irradiation (Figure 2). At this time, pentachlorophenol and its chlorinated products were still detected in the ethyl alcohol solution (shown in Fig. 4B) making the chloride ion concentration less than in aqueous solution.
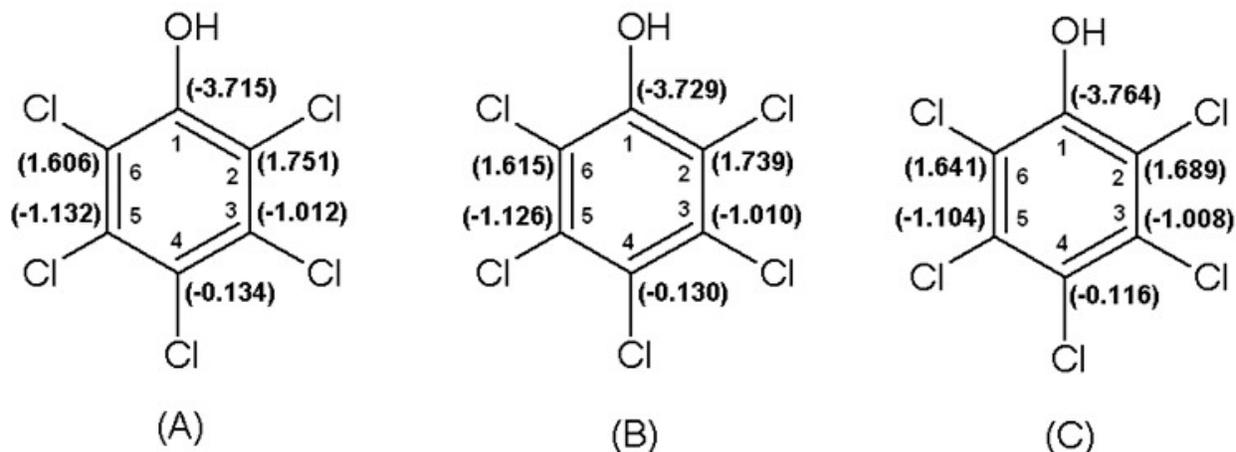
Figure 5. Atomic charge distribution on C atoms of pentachlorophenol solvated in (A) water, (B) ethyl alcohol and (C) ethyl acetate computed using Gaussian DFT B3LYP/6-311G. [*ortho* C-2 & C-6, *meta* C-3 & C-5, *para* C-4]
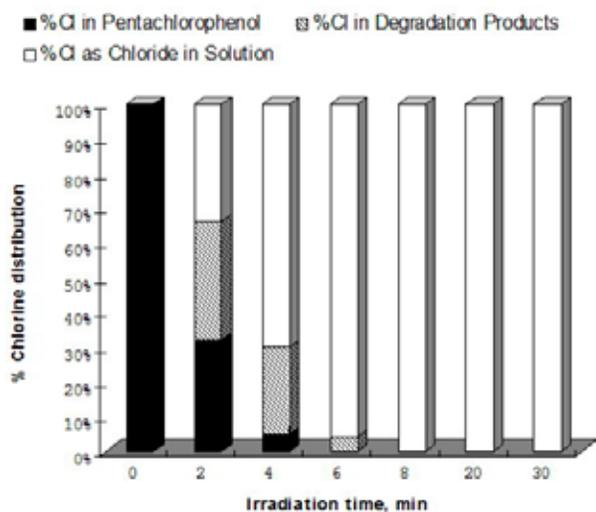

Figure 6. % Chlorine in the photodegradation of pentachlorophenol in water

Based on the decrease in TOC and the increase in inorganic carbon and chloride ion concentrations (Figs. 2A & 3), mineralization of pentachlorophenol occurred in the aqueous solutions. When pentachlorophenol degraded, however, oxalic acid and acetic acid were formed indicating incomplete mineralization. These organic acids were still detected after over 60 min of UV light exposure (Fig. 2A) suggesting that higher energy or longer exposure to UV light is needed for complete mineralization. After 13 h of irradiation, organic carbon was still detected indicating the persistence of the organic acids. Although oxalic acid and acetic acid persisted in the irradiated aqueous solution, total dechlorination of pentachlorophenol was achieved. The UV radiation treatment of pentachlorophenol in water, therefore, is environmentally sound because the final waste stream contains dechlorinated and low molecular weight organic compounds that are far less harmful than the parent compound.

Hong et al. (2000) demonstrated that irradiating pentachlorophenol in aqueous solutions using a high pressure Hg lamp produces not only simple chlorinated phenolic compounds, but also dimeric products including heptachlorodibenzo-p-dioxin and octachlorodibenzo-p-dioxin that are more toxic than pentachlorophenol. In the present study, these harmful compounds were not detected when extracts of the irradiated aqueous solutions were silylated with N,O-bis(trimethylsilyl)-trifluoroacetamide and analyzed by GC-MS. It was noted, however, that the aqueous solutions became reddish in color between 2 and 4 min of irradiation. This color faded after 6 min. Concentrating an aqueous solution of pentachlorophenol that was irradiated for 3 min gave an intense purple to red color. Figure 7 shows HPLC-ECD chromatograms of the concentrated and non-concentrated irradiated solutions showing more products detected in the concentrated solution. An LC-ESI-MS analysis of the concentrated extract identified 4 compounds including pentachlorophenol and the 2 tetrachlorophenols. Based on mass spectral analysis and molar mass estimations, the fourth compound was identified as a dichlorobenzenediol. The isomeric form of this compound, however, remains to be elucidated. Considering the chlorine balance measurements, this degradation compound that required preconcentration for detection also decomposes when exposed to UV radiation.

Table 2 presents the photolytical degradation products of pentachlorophenol in the different solvents as well as other products reported in similar studies.
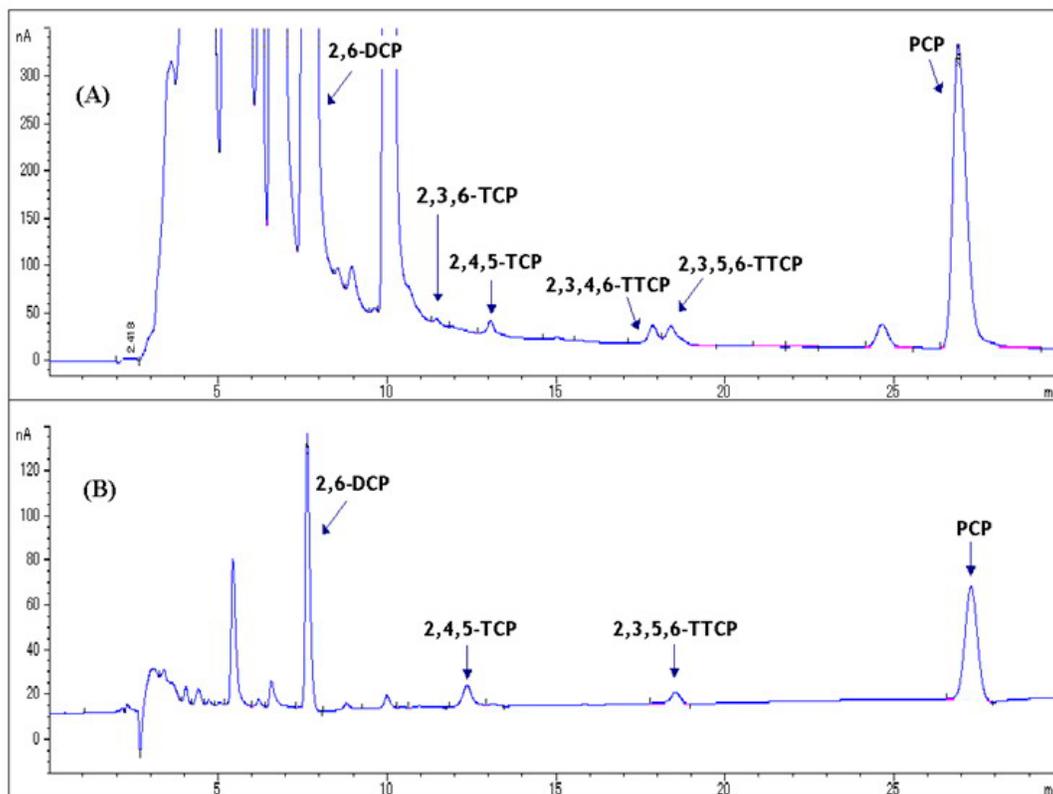
Figure 7. HPLC-ECD chromatograms of pentachlorophenol in water irradiated for 3 min: (A) concentrated by solid-phase extraction and (B) without sample preconcentration

Table 2. Identified photolytical degradation products of pentachlorophenol in different solvents

Solvent	This study. UV light source: Low pressure Hg lamp Analytical Methods: HPLC-ECD, LC-MS and Ion Chrom.[a]	Suegara et al. 2005 UV light source: Low pressure Hg lamp Analytical Methods: HPLC-UV, GC-MS and Ion Chrom.[b]	Hong et al. 2000 UV light source: High pressure Hg lamp Analytical Method: GC-MS with MSTFA[d] derivatization
Water	2,3,4,6-Tetrachlorophenol 2,3,5,6-Tetrachlorophenol 2,4,5-Trichlorophenol 2,3,6-Trichlorophenol 2,6-Dichlorophenol Dichlorobenzenediol Acetic acid Oxalic acid Chloride	2,3,4,6-Tetrachlorophenol 2,3,5, 6-Tetrachlorophenol 2,5-Dichlorophenol Chloride	3,5-Dichlorophenol 2,3,5-Trichlorophenol Tetrachlorophenol Pentachlorophenol Chlorohydroquinone Dichlorohydroquinone Trichlorohydroquinone Tetrachlorohydroquinone 1,2,4-Trihydroxytrichloroquinone Tetrachlorocatechol Pentachlorobenzene Hexachlorobenzene Other dimeric products
Ethyl alcohol	2,4,6-Trichlorophenol 2,3,6-Trichlorophenol 2,5-Dichlorophenol 2,3-Dichlorophenol Acetic acid Chloride	n.s.[c]	n.s.
Ethyl acetate	2,3,6-Trichlorophenol 2,4-Dichlorophenol	n.s.	n.s.

[a] analyzed for formate, acetate, oxalate and chloride ions
[b] analyzed for chloride ions only
[c] n.s. : not studied
[d] MSTFA : N-methyl-N-trimethylsilyltrifloroacetamide

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Different photolytical conditions result in different photolytical products. Several polychlorinated, polyhydroxylated, and dimerized intermediates are formed when pentachlorophenol in water degrades using a high pressure Hg lamp. In contrast, fewer degradation products are detected when a low pressure Hg lamp is used. In the present study, 2,3,6-trichlorophenol was commonly detected as degradation product in the three solvents. Interestingly, all of the chlorinated products have Cl atoms in the C-2 position of the molecule and some have Cl atoms in the C-6 position. This can be explained by the relative stability of the *ortho* C-Cl bonds of chlorophenols. It is known that chlorophenols with a substituent in the *ortho* position exhibit intramolecular H-bonding between the hydroxyl group and the Cl atom (Crespin et al. 1999; Silvi et al. 2002). In 2-chlorophenol, for example, its *syn* conformer is more stable than its *anti* conformer as a result of intramolecular H-bonding (Akai et al. 2001). Intramolecular H-bond is not formed in the *anti* conformer unless the chlorinated phenol is substituted at both *ortho* positions. This was demonstrated in an IR spectral analysis of pure pentachlorophenol (Czaplicka & Kaczmarczyk 2006) where free hydroxyl groups were not observed suggesting the presence of intramolecular H-bonds. These H-bonds seem to limit the reactivity of Cl atoms in C-2 and C-6 of pentachlorophenol during photolysis.

Additionally, theoretical measurements of charge distribution on C atoms of pentachlorophenol can explain the relative stability of the *ortho* C-Cl bond. Atomic charge distribution can provide a qualitative impression of the electron-attracting or repulsion capacity of an atom as it holds on to a bond. In the pentachlorophenol molecule, a localization of electrons on the C atom promotes a weak C-Cl bond, i.e., the sites of weak C-Cl bonds are on C atoms with negative atomic charge distribution. Based on the calculated charge distributions, Cl atoms bonded to *ortho* C atoms will not easily dissociate. This is consistent with the experimental results where the degradation products of pentachlorophenol in the different solvents have Cl atoms still attached to C-2; most have Cl atoms bonded to C-2 and C-6. In the degradation of pentachlorophenol in water, 2,6-dichlorophenol was observed in relatively higher amounts (higher peak areas) compared to the other products (Fig. 4A). The atomic charge distribution on C-2 of pentachlorophenol in water is more positive than the charge distribution on C-2 of pentachlorophenol solvated in ethyl alcohol or ethyl acetate making its *ortho* C-Cl bond stronger. This explains the formation of 2,6-dichlorophenol that was detected only in the irradiated aqueous solutions.

In bond dissociation energy measurements of polychlorinated phenols (Suegara et al. 2005), C-Cl bonds in C-2 and C-6 have the highest bond dissociation energies confirming that Cl atoms in the *ortho* positions are more difficult to dissociate. DFT calculations of bond dissociation energy and atomic charge distribution can, therefore, be used together to confirm the degradation products of pentachlorophenol. If these calculations are used to propose a probable isomeric form of the dichlorobenzenediol detected in the irradiated aqueous solutions, then this degradation product would be a 2,6-dichloro-1,4-benzenediol.

Several reaction mechanisms and pathways for the degradation of pentachlorophenol are reported in literature. The identified photolytical degradation products in this study provide additional data to support these pathways.

CONCLUSIONS

The extent of photodegradation of pentachlorophenol depends on solvent polarity. In aqueous solution, pentachlorophenol undergoes fast degradation where it is dechlorinated to form low molecular weight chlorophenols and organic acids and mineralized to produce chloride ions and carbon dioxide. Its degradation in organic solvents requires longer UV irradiation and produces less degradation products. The DFT atomic charge distribution measurements suggest that the C-Cl bond in the *ortho* position of the pentachlorophenol molecule is most stable. This agrees with the experimental results where the chlorinated products retain their Cl atoms in C-2 and C-6 of the molecule.

ACKNOWLEDGMENTS

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