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Gamma Radiolytic Degradation of 4-Chlorophenol Determination of Degraded Products with HPLC and GC-MS

S. Bilal Butt[1*], M. Nasir Masood[1], Nasir Hayat Hengra[2] and M. Mansha Ch[2]

[*1]*Central Analytical Facility Division, PINSTECH*

[2]*Pakistan Institute of Engineering and Applied Sciences, P.O. Nilore, Islamabad, Pakistan*

Abstract

Contamination by chlorophenols of surface water and groundwater is an emerging issue in environmental science and engineering. After their usage as pesticide, herbicide and disinfectant, these organic compounds subsequently enter the aquatic environment through a number of routes. Some of the chlorophenols are slightly biodegradable, while others are more persistent and mobile in the aquatic environment especially chlorophenols. Gamma radiolytic degradation is one of advance oxidation process that has been thought to be one of the promising treatments to deal with this problem. This radiolytic study was carried out in methanolic 4-CP (4-chlorophenol) samples. Among several factors effecting radiolytic degradation of 4-CP, dose and concentration are important that were evaluated under atmospheric conditions. A degradation yield (G –value) for 4-CP of 0.38 and 1.35 was achieved in 20 and 100mg/dm^3 solution. It was observed that degradation yield decreases with increasing 4-CP concentration. Gamma radiolysis produce free radicals in solvent which further react with 4-CP molecules to generate different products. The identification of degradation products was proposed using HPLC and GC-MS.

Keywords: *Gamma radiolysis, degradation, 4-CP, Degradation efficiency, Dose, Mechanism*

Introduction

There are many available techniques to eliminate the chlorophenols from environment which may be divided into two broad categories, conventional and advance oxidation processes (AOPs). The conventional methods employed are thermal, physiochemical and biological. Gas Phase Chemical Reduction (GPCR), Base Catalysed Decomposition, Sodium Reduction, Paralysis /gasifiers and Supercritical water oxidation are well established and commercially available techniques under this category [1].

The thermal incineration is a method recommended for many chlorophenols. The horse radish peroxide enzyme has been reported a successful enzymatic detoxification for biological treatment of chlorophenols in drinking water and waste water. The conventional physiochemical treatment system which consists of the series of steps like flocculation, sedimentation and adsorption on activated carbon is commercially applied in many pesticide industries [2]. Secondly advanced catalytic oxidation processes (AOP) have gained attention as emerging clean and efficient technology for air and water treatment. Ultrasonic Irradiation, Photocatalytic degradation using TiO2, Electron Beam Injection and gamma radiolytic degradation are promising AOP which are currently under study [1]. For purification of polluted natural waters, numerous advanced oxidation technologies are in process of investigation or in use. These technologies are based on the generation of OH radicals, which break down organic pollutants (Figure 1) [3].

The gamma radiolysis degradation is also an important AOP process which has recently gain attention as a potential remediation technology.

*Corresponding Author E-mail: bilalbutt86@yahoo.com

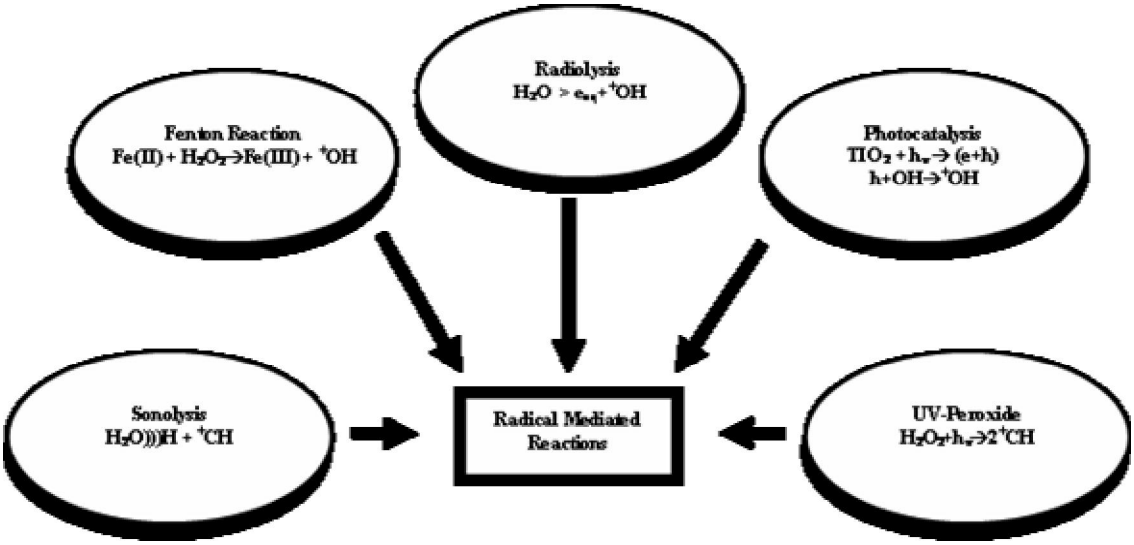

Figure 1. **Some important AOPs employed for water treatment**

This method proved successful for the destruction of various classes of organic pollutants such as halogenated alkyl hydrocarbons, aromatic hydrocarbons and chlorobenzene [4].

The purpose of present study is to monitor degradation of 4-CP in methanolic solutions.

The use of radiation for the degradation of water pollutants has one step ahead to solve environmental problems. The primary mechanisms of chlorophenols degradation in air are hydroxyl radical and photolysis [5]. Many degraded products and degradation mechanism have been reported [6-8]. Radiation induced degradation was carried out keeping in mind that decomposition of requires species occur as well as the total toxicity of resultant solution should also decrease [6]. The efficiency of the radiation induced degradation depends upon many factors like kind and energy of radiation, absorbed dose, dose rate, pollutant concentration as well as synergistic effects of radiation and ozone or/and catalysts and molecular structure of the pollutant [9, 6].

The degraded products and the efficiency of radiolysis process have been evaluated mainly with reverse phase HPLC-UV. But the most reliable and sensitive tool is gas chromatography coupled with mass spectrometer (GC-MS) [10]. The aim of this study is to identify the products of radiolytic degradation of 4-CP and determine the effect of the various experimental factors on removal efficiency and effectiveness of radiolytic degradation.

Methods and Materials

Chemicals

All reagents used were of analytical grade. The Methanol was purchsed from Merck, Germany. Doubly distilled / deionized water was used for preparation of mobile phase for HPLC and other solutions. The stock solution of 4-CP was 1.26 kg/L with purity 98%. Its 1000 mg/dm^3 stock solution was used to make required concentration solution and was kept under darkness. Distilled/deionized water was prepared from Syborn deionizer, USA. The irradiated samples were filtered through 0.45 mm PTFE syringe filter, Sartorious, Germany.

To monitor the dose effect on gamma radiolysis process, nine solutions of p-chlorophenol 1 to 100 mg/L were prepared. In order to facilitate the direct analysis on GC-MS, the standards were prepared in methanol. Five standard solutions of each have 100 mg/L concentration of 4-CP ware prepared to monitor dose effect. The doses given were 1, 4, 8, 12 and 20 KGy.

Gamma irradiation

Post operational fuel elements of Pakistan Atomic Research Reactor (PARR-1) were used as a

source of Gamma-irradiation. Calibration of dose intensity was carried out in a Gamma-Cell and Reactor Core using Teletector probe, FAG, FR Germany and it was 24.3 and 243 Gy/h respectively. The 10–20 ml solutions in glass vials containing 1–100 mg/L 4-CP were irradiated for the required radiation dose.

Analytical procedures

The HPLC solvent delivery system consisted of quaternary gradient pump K-1001 and solvent organizer K-1500 were from Knauer, Germany. For sample injection a loop of 20 µL was used in combination with Rheodyne injector 7725i. A UV-VIS HPLC detector.

Hitachi L-7420 spectrophotometer was used for monitoring of 4-chlorophenols. The absorption was measured at 254 nm. The reverse phase column was Discovery C 18 from Supelco, USA. For data handling a Varian-4270 printer/plotter and software Eurochrom 2000, basic edition V2.05 were used. The wave length was set at 254 nm. The mobile phases were 66% methanol and potassium hydrogen phosphate (KHP) buffer. The latter mobile phase prepared by mixing buffer solution, methanol and tetrahydrofuran in volume ratio 50:45:5 respectively. The buffer was prepared by adding 0.02 moles (0.137g in 50ml) in doubled distilled water. The detection limit for the substrates was ~2 µmol dm^{-3}. Concentrations below this value are indicated as "total decomposition".

Operational conditions for GC-MS

The degradation process was monitored with GC-MS, Varian, USA gas chromatograph model 3800 coupled to mass spectrometer Saturn-2000 equipped with a capillary column CP Sil 5.25 mmX15 m. Carrier gas: Helium with constant pressure 10 psi, Split ratio 5, injection volume 5ul, Hamilton glassy syringe 7101 N. For UV absorption analysis a phoenix double beam UV-VIS spectrophotometer was employed with scanning range from 190 to 800 nm.

Results and Discussion

The studies were carried out to evaluate the effect of 4-CP concentration and dose on degradation efficiency.

Effect of concentration variation

Radiolytic degradation monitoring was carried out at varied concentration of (4-CP) while keeping dose constant. It was observed that increases in 4-CP concentration decrease the radiolytic yield. It was observe that more than 90 % efficiency could be achieved for samples having concentration of 4-CP less then 5mg/dm^3. Radiolysis efficiency reaches 100 % for samples containing 1 mg/L or less sample concentration as shown in Figure 2. Low degradation efficiency may be due to dimmer formation that shifts equilibrium back word at high concentrations. This equilibrium also depends upon the pH, which lowered with reaction hence causes to shift reaction back word.

The degradation efficiency of 13.67 % was achieved for 100 mg/dm^3 with formation of four degraded products. Radiolytic degradation observed for 90 mg/dm^3 was 33 %, which is greater as compared to 100 mg/dm^3 at same dose.

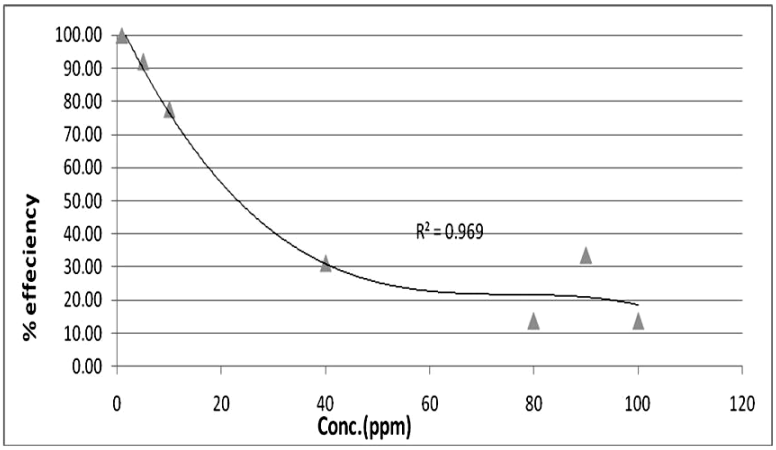

Figure 2. **Trend of degradation efficiency verses concentration of 4-CP.**

Dose Variation at constant concentration

The gamma dose effect was monitored by giving different doses from 1 to 20 kGy to samples having same concentration. Two studies each at 20 and 100 mg/dm3 4-CP concentrations were carried out respectively. Firstly results of 100 mg/dm^3 are discussed. The HPLC chromatographs given in Figure 3 show the effectiveness of radiolysis measured generally by the G value. According to Literature, when the G value of radiolytic degradation is equal to 1, it means that 1.04mmol of a substance is formed or degraded by 1Mrad (10KGy). Therefore, the formation of a determined amount of the degraded organic pollutants by a radiation dose (kGy) can be expressed as that by varying dose, the amount of degraded products formed increases.

$$Y = 0.104.\ D.G \qquad (1)$$

Where Y is concentration of degraded pollutant (4-CP in this case), D is dose applied and G is radiolytic yield [11]. A good efficiency means that more molecules degraded per unit dose (high G value).

The radiolysis trend for 100mg/dm^3 at varied dose is shown in Figure 4. It shows that degradation increases linearly in specified dose range. Radiolytic yield of 4-CP degradation in methanol by Gamma-irradiation (G-4-CP), i.e., the number of molecules degraded by 100 eV was calculated by the slop of curve shown in Figure 4.

Identification of degraded Products with varied dose

Identification of degraded products formed in the solutions which were irradiated with 1, 4, 8, 12 and 20 KGy dose was carried out. The GC-MS chromatograph for parachlorophenol and the mass spectra along with it best possible match in NIST (National Institute of Science & technology, USA) library are shown in Figure 5 and Figure 6.

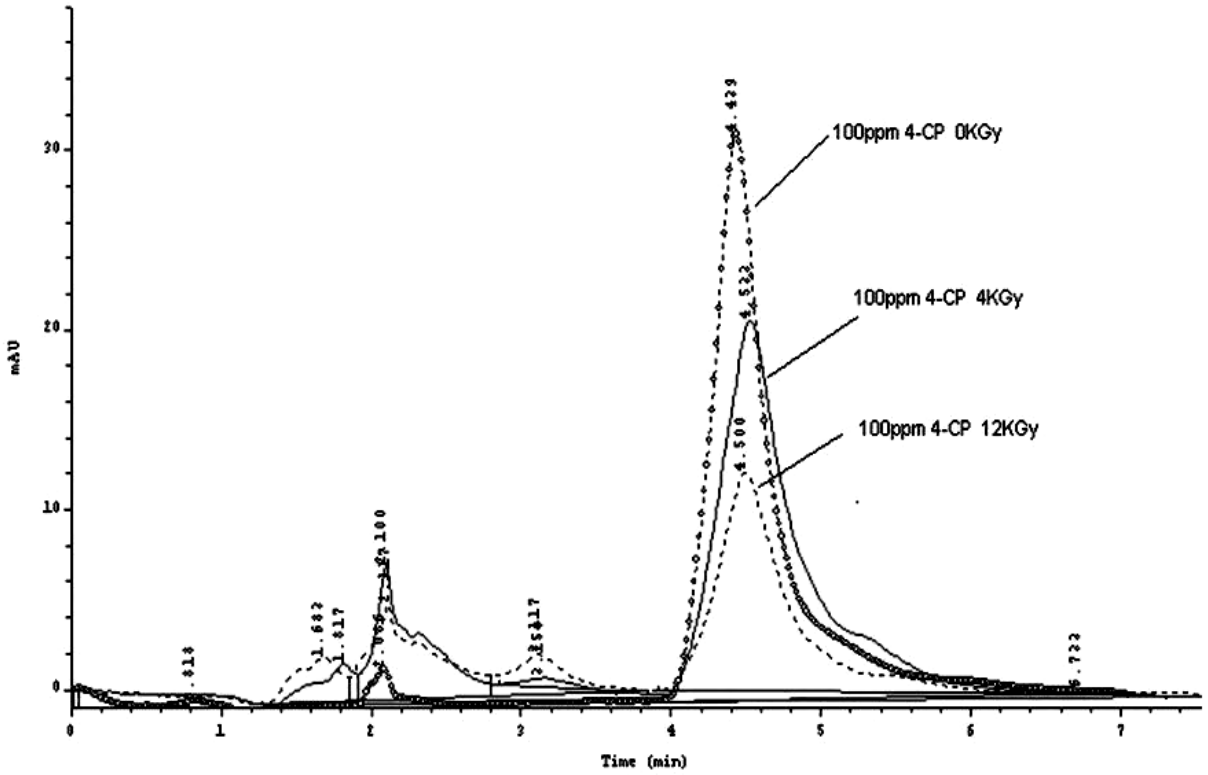

Figure 3. **HPLC analysis of 100 mg/L 4-CP with 0, 4 and 12KGy gamma irradiated solutions. Mobile phase 66% methanol, flow rate 0.7ml/min; wave length=254nm.**

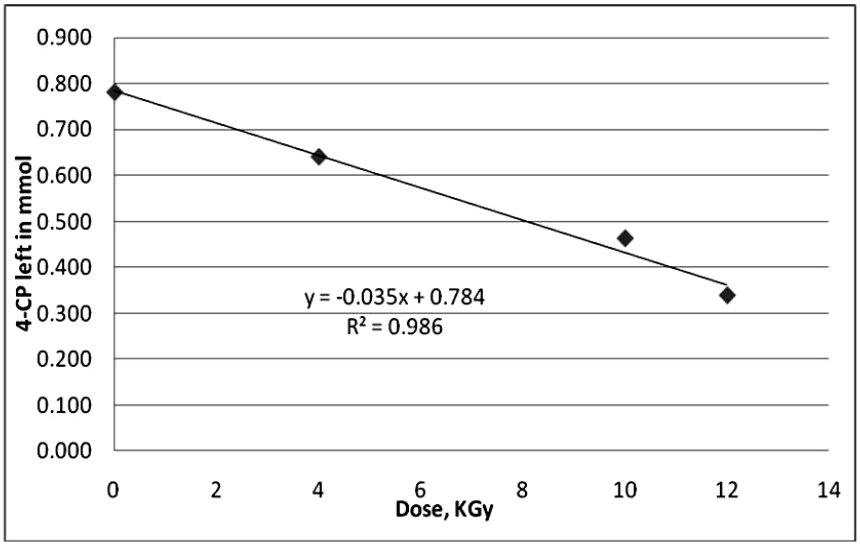

Figure 4. **Degradation Efficiency at varied dose for 100 mg/L 4-CP.**

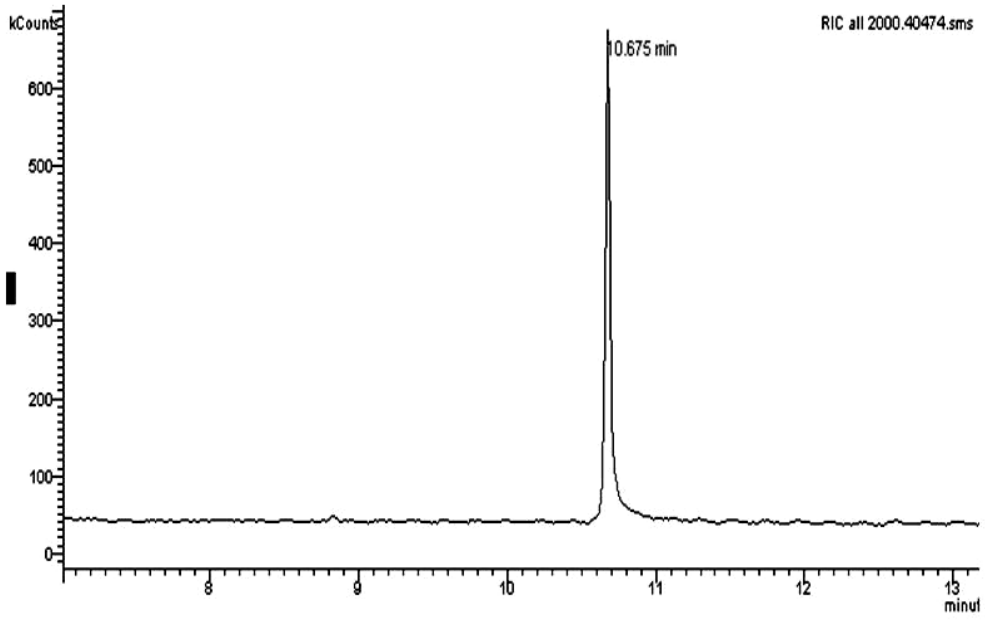

Figure 5. **The GC-MS Chromatograph for 40 mg/L. Volume injected 0.5 µL. with split 1:5.**

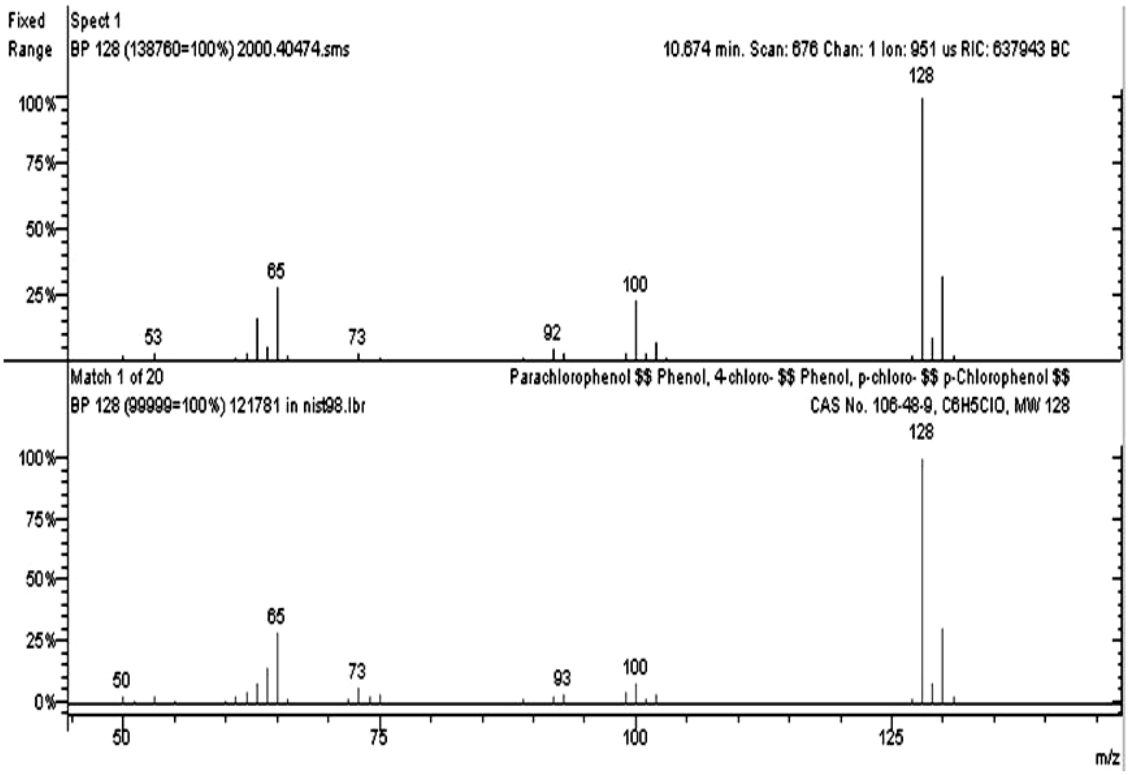

Figure 6. **Mass spectra of 4-CP along search spectra has best similarity with sample spectra. 4-CP peak appears at GC-MS total ion chromatograph shown in Figure 5 at retention time 10.67min.**

Molecular Mechanism of Radiolytic degradation

The compounds with electron donor groups like OH group have antioxidant properties, therefore these are considered difficult to decompose. The most reactive oxidizing species are the OH radicals. They can split off an H-atom or electron of an organic molecule. However, their preferred reaction sites are the double bonds. In the case of aromatic compounds the OH· species react on various ring positions, where the ortho- and para-sites are the preferred ones. These transients further abstract oxygen to be converted into peroxyl radicals [12].

Methanol yields ·CH3-OH, ·CH2-OH, CH3O·, e- and H· radicals when it interacts with gamma radiations. These free radicals are very reactive and attach on 4-CP molecules present in solution. Degradation of 4-CP in methanol proceeded through these radicals to generate different products.

Conclusion

It was found that with increasing 4-CP concentration degradation efficiency decreases exponentially. But in case of dose variation at constant concentration, a linear increase in efficiency was noted. The gamma radiolytic technique is effective for pollutants degradation in water and waste water. 4-CP at low concentration can be removed efficiently. The degraded products identified help in establishing degradation mechanism. In future this data can be used to establish water purification systems.

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S. Bilal Butt is working as deputy chief scientist in Central Analytical Facility Division, PINSTECH. His area of interest is monitoring of tracer level of environmental organic pollutants using chromato-graphic techniques and their removal by ionization radiation.