Gamma Radiolytic Degradation of Heptachlor in Methanol and Monitoring of Degradation by HPLC

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Summary: Removal of known insecticide Heptachlor (HPTC) in methanol solution by γ-rays under varied experimental conditions has been optimized. Air saturated solution of HPTC was irradiated at γ-rays dose from 1 to 10 kGys. The extent of radiolytic degradation was monitored by reversed phase high performance liquid chromatography (HPLC) coupled with UV detector. At dose of 10 kGys ≥ 98 % of HPTC was degraded. The degradation of HPTC occurs by $CH_3O^{\bullet}$ and $^{\bullet}CH_2OH$ radicals generated by methanol radiolysis. It is concluded that γ-rays can remove Persistent Organic Pollutants (POPs) form environmental matrices. It can decrease the harmful properties of these POPs by their transformation into less resistant fragments to biological / natural elimination in the aquatic atmosphere.

Keywords: Heptachlor, Gamma radiations, POPs, Removal and HPLC.

Introduction

Chlorinated cyclodiene insecticides' including HPTC has been incorporated along with 12 Persistent Organic Pollutants (POPs) in the United Nation Environment Programme (UNEP) of Stockholm Convention signed in 2001. These cyclodiene pesticides contaminate environment in several countries thus needs for remediation measures [1]. HPTC is used to eradicate termites, ants and soil insects [2]. HPTC is incorporated in human body using contaminated food and during respiration where applications were done improperly [2]. Its effects appear in hyper-excitation of nervous system, liver harm, digestive system problems, pain and unconsciousness [3, 4]. Both HPTC and its epoxide are extremely poisonous to marine life [5]. Its water solubility is 0.056 mg L^{-1} [6]. The acceptable daily intake (ADI) is 0.0001 mg/kg/day [7] and maximum containment level (MCL) is 0.0004 mg L^{-1} [8]. HPTC and its epoxide are quite stable and resistant to environmental degradation with half-life of 250 days [9]. In water, it readily undergoes hydrolysis in anaerobic atmosphere by microorganism into epoxide and in vegetation the major breakdown product is its epoxide [3, 10].

HPTC was photo-degraded in ethanol [1], degraded by anaerobic process [11], activated carbon and Pseudomonas fluorescence free cell culture was used for its eradication [12], removal by biomimetric absorbent [13] and advanced oxidation processes (AOPs) such as per-oxidation by chlorine/ozone are used for its removal with subsequently chemical precipitation with aluminum sulfate and activated carbon adsorption [14]. In Pakistan, residue of HPTC has been found in various food items. Thus, removal of Heptachlor is essential [15]. The γ-rays based radiation techniques are important in removal of chlorinated pesticides due to the penetrating power of γ-rays in samples dissolved in water and organic solvents [16]. Currently γ-rays based removal of PAHs [17, 18], pesticides and organic contaminants are reported [19-25].The aim of this research was to study the radiolytic degradation of HPTC in methanol, its reaction with radiolytic species which may be generated by methanol radiolysis. Degradation of HPTC by γ-rays was followed by HPLC which, revealed formation of several radiolytic products at initial γ-rays doses and at 10 kGys all the HPTC along with the degradation products (DPs) were degraded. Thus, γ-rays have good potential for removal of POPs in contaminated water.

Results and Discussion

The HPTC has a molecular formula ($C_{10}H_5Cl_7$), IUPAC name is 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetra-hydro-4,7-methano-1H-indene and molecular weight (MW), 373.32 and its structure is depicted in Fig. 1. In a variety of radicals generated processes the role of γ-rays is important. Usually, pesticides degradation is done in water where different types of radicals are generated. This reported study of HPTC γ-rays degradation is undertaken in methanol due its poor solubility in water [6]. The low solubility of most of the POPs in neutral aqueous media may prevent their γ-rays irradiation in water. For this reason we choose

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methanol as solvent. The role of solvent is important in radiolytic degradation of organic molecules. The radiolysis of methanol is outlined as under.
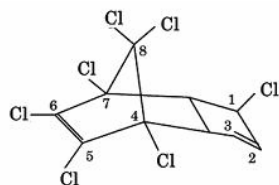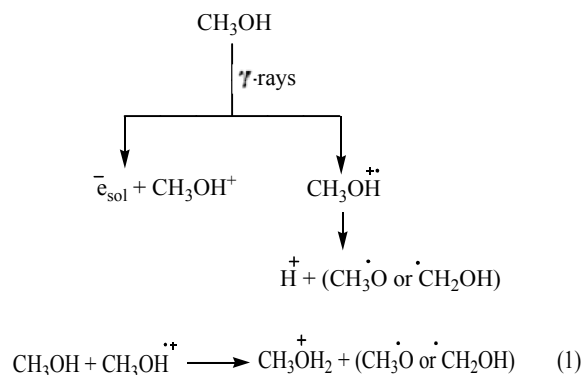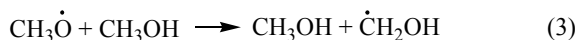

Fig. 1:   Structural formula of heptachlor.

Gamma Radiolysis of Methanol

The radicals generated by γ-rays interaction with methanol are $CH_3\dot{O}$, $\dot{C}H_2OH$, H and e^-_{sol}. [26]. The possible radical generateion mechanism is as follow.

$$CH_3OH$$

$$\downarrow \gamma\text{-rays}$$

$$\bar{e}_{sol} + CH_3OH^+ \qquad CH_3\overset{+\cdot\cdot}{O}H$$

$$\downarrow$$

$$\overset{+}{H} + (CH_3\dot{O} \text{ or } \dot{C}H_2OH)$$

$$CH_3OH + CH_3\overset{\cdot\cdot+}{O}H \longrightarrow CH_3\overset{+}{O}H_2 + (CH_3\dot{O} \text{ or } \dot{C}H_2OH) \qquad (1)$$

Additionally, the interaction of transient with methanol is also favored [27].

$$CH_3OH + \dot{H} \longrightarrow H_2 + CH_3\dot{O} \text{ or } \dot{C}H_2OH \qquad (2)$$

$$CH_3\dot{O} + CH_3OH \longrightarrow CH_3OH + \dot{C}H_2OH \qquad (3)$$

The radicals $CH_3\dot{O}$ (G = 2.5) and $\dot{C}H_2OH$ (G = 1) are generated by methanol interaction with γ-rays and these radicals participate in redox degradation of HPTC [28, 29].

Reversed Phase HPLC Separation Parameters for HPTC Degradation Products

Reversed Phase liquid chromatography is a good separation technique used for identification and estimation of organic compounds. HPTC and its epoxide analysis are reported on stereo selective

HPLC column to monitor its endocrine disruptor activity [30]. In the current study RP-HPLC mode along with UV detection was adopted to assess the amount of degradation together with number of products formed in methanol. The standard HPTC at 50 mgL^{-1} was analyzed on RP column without exposure to gamma dose. Linear response of HPTC concentration and its UV response were observed on RP column as depicted in Fig. 2.
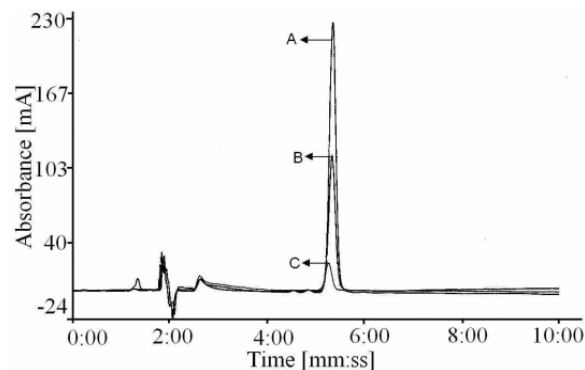

Fig. 2:   Linear response of HPTC concentration and its UV response on Hyperclone BDS-C$_{18}$ column (150 mm ×4.6 mm), HPLC Eluent 80 % Methanol in water, flow rate 0.8 mL min^{-1}, UV detection 240 nm, HPTC standard A 50, B 25, C 5 mg L^{-1} respectively

Monitoring of HPTC Degradation

The extent of degradation of HPTC at varied γ-rays dose can be estimated using spectrophotometry. But, for a real HPTC degradation, liquid chromatography is valuable and useful in estimating the actual amount after γ-rays degradation together with DPs formed. The amount of HPTC degradation versus γ-rays dose from 1 to 10 kGys is depicted in Fig. 3. The peak height of HPTC decreases with increase of γ-rays dose and it reduces to base-line at 10 kGys. At this γ-rays dose it was totally eliminated. Fig. 4 A depicts the HPTC standard overlays at 50 mgL^{-1} concentration without γ-rays dose and Fig. 4 B at 10 kGys HPTC degradation.

Various authors have reported HPTC and related chlorinated pesticides degradation by dehydrohalogenation and dehalogenation mechanism [23, 31].
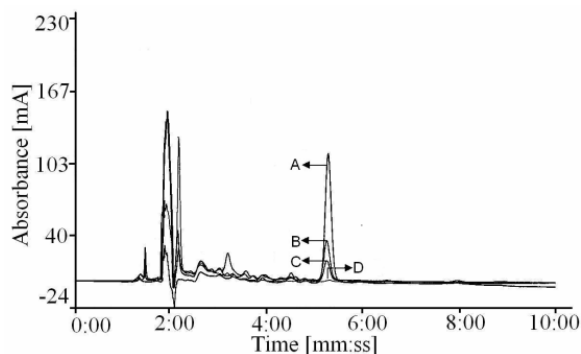
Fig.3:   Extent of γ-rays degradation of 50 mg L^{-1} HPTC at varied dose of 1 to 10 kGys in methanol, LC conditions as in Fig. 2, A 1, B 5, C 7, D 10 kGys, respectively
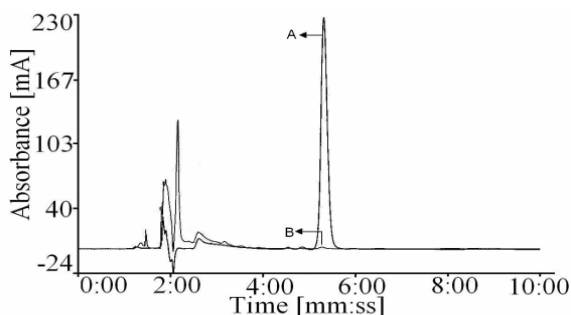

Fig. 4:   Overlays of 50 mg L^{-1} HPTC standard and its 10 kGys degraded sample. A without γ-rays exposure, B 10 kGys γ-rays dose

Fig. 5:   Trend of G-value variation of HPTC at varied γ-rays dose.
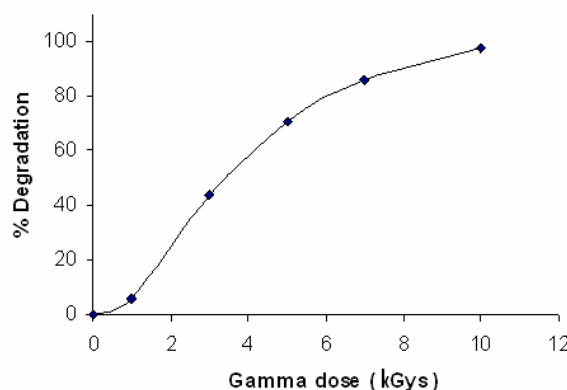
Fig. 6:   Degradation trend of 50 mg L^{-1} HPTC at varied γ-rays dose

The chemical radiation yield is given in G-value which is the number of molecules degraded or created per 100 eV of absorbed γ-rays dose and is calculated by using following formula [32].

$$G = \frac{[\Delta R] \times N_A}{D \times 6.24 \times 10^{17}}$$

The [ΔR] is the amount of HPTC in mole L^{-1} after gamma irradiation, N_A is Avogadro's number, D is the γ-rays dose in kGys and 6.24×10^{17} is conversion factor to 100 eV L^{-1}. The G-values at varied γ-rays dose was estimated using RP-HPLC method and is depicted in Fig. 5 and amount of HPTC elimination at 50 mgL^{-1} versus varied γ-rays dose is depicted in Fig. 6.

Although on industrial scale, methanol is not used as solvent for POPs degradation. However, it can be used as model organic solvent for studying the radiolysis of POPs in laboratory environment due to their enhanced solubility for studying reaction pathways [32, 33].
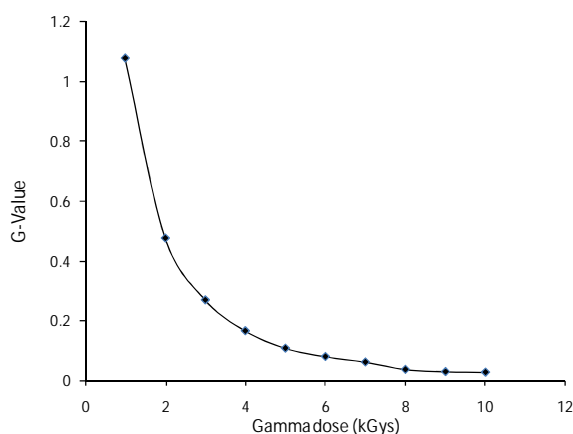
The radicals generated in methanol are different from those produced during irradiation of water. However, our radiolytic study will contribute to the general understanding of radical reactions occurring in an irradiated system. The degradation trend of HPTC was increased when water was introduced into the methanol medium, such water /methanol system may represent radiolysis process that occurs in water. This enhanced increased in degradation upon addition of water was due to the generation of hydroxyl radical as shown by the following reaction in radiolysis of water by γ-rays.

$$H_2O \xrightarrow{\quad} (2.7)\,\dot{O}H + (0.6)\,\dot{H} + (2.6)\,e^- + (0.45)\,H_2 + (0.7)\,H_2O_2 + (2.6)\,H^+$$
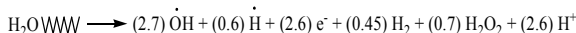
The integer in digression is the G-value and is the number of radicals generated per 100 eV of γ-rays dose. The hydroxyl radical produced in the above equation is a power oxidant having an

oxidation potential of 2.8 volts and this was the main cause of improved degradation of HPTC in water/methanol media as compared to methanol alone.

Experimental

Chemicals and Reagents

Lichroslov grade methanol was obtained from Fluka, Switzerland. HPTC was from Dr. Ehrenstorfer GmbH, Germany; its 1000 mg L^{-1} solution was prepared in methanol. This solution was refrigerated for preparation of working standards.

Instrumentation

The quaternary gradient pump CE-4102, UV-Visible detector CE-4300 and data station V 4.1 were from Cecil Instruments, U.K. The Rheodyne injector (7725i) with 20 µL loop and RP column Hyperclone BDS C$_{18}$ (150 mm x 4.6 mm) were from Phenomenex, USA.

Irradiation of HPTC Samples

^{60}Co commercial radiation source at PARAS Lahore at γ-rays dose rate of 372 Gyh^{-1} was used for HPTC irradiation. 50 mg L^{-1} of HPTC standard in methanol was irradiated for γ-rays dose of 1 to 10 kGys

Conclusions

Gamma irradiation offers numerous striking benefits such as capability to confirm that the toxic compound and its amount has been reduced to minimal level. It provides opportunity of in-situ elimination of toxic substance due to piercing nature of γ-rays. It can also eliminate water borne pathogens that are of immense community health alarm. The conventional chlorination practice of water is unsuccessful to eliminate pathogen like Cryptosporidium parvum and Mycobacterium avium. These are easily eliminated using γ-rays which is chemical less management of water supplies. At present water treatment processes with minimal or no chemical utilization are more environmental friendly [34].

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