CHAPTER 5

ADSORPTION STUDIES OF PESTICIDES WITH PALM SHELL CARBON

5.1 Introduction

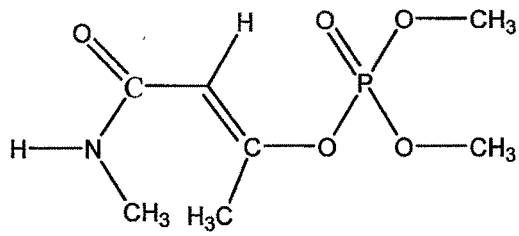
Large amounts of pesticides are currently used throughout the world for agricultural and public health purposes. Numerous studies have reported that a great part of ground and surface water contamination is caused by direct losses (e.g. spills during filling operations, leakages of spray equipment, spray leftovers, spills of rinsing water of treatment equipment, etc.)[5.1,5.2]. The potential environmental damage caused by pesticides provokes interest for its remediation and/or prevention.

The Organophosphorus and Organochlorine pesticides are bioaccumulative and relatively stable, as well as toxic and carcinogenic. They are used frequently for agricultural, forestry and domestic activities [5.3]. They are leached to ground water and runoff to surface water. Monocrotophos and Chloropyrifos are two of the widely used pesticides and often found in surface and ground water in residual form [5.4]. Choropyrifos, o,o- Diethyl-o-(3,5,6-trichloro-2-pyridyl)-phosphorothioate, has significant importance because of its wide distribution, extensive use and persistence[5.42]. Monocrotophos (1,3-hydroxyl-N-methyl-cis-crotonamide, dimethyl phosphate) possesses systemic and residual activity in addition to its high contact toxicity [5.34].

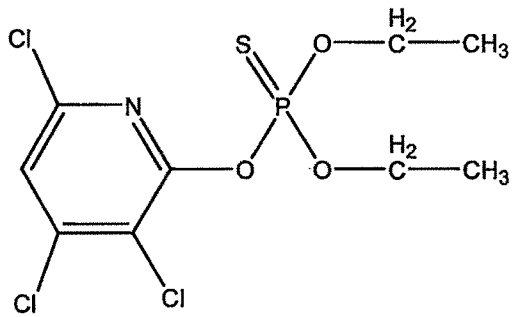
Therefore, the adsorption potential of acid treated palm shell powder (APSP) for monocrotophos an organophosphorous pesticide and chloropyrifos an organochlorine pesticide was evaluated. It was decided to monitor the adsorption characteristics of APSP for the pesticides both by monitoring the concentration of pesticides and also by measuring the COD contributed due to the pesticides.

The details of the efforts directed that led to the development of a method for the removal of pesticides are presented in the following pages

Structures



Monocrotophos



Chlorpyrifos

5.2 Material and method:

5.2.1 Materials:

The adsorbates used in this study were pesticides Monocrotophos and Chloropyrifos obtained from Baroda Agrochemicals Limited, BASKA. Their chemical structure and main physical properties are shown in Table1.Stock solution of chloropyrifos was prepared in acetonitrile since it provides complete solubilization. Working chloropyrifos pesticide solutions were prepared by diluting the stock solution with double distilled water. Stock solutions of monocrotophos were prepared by dissolving accurately weighed amount of monocrotophos in double distilled water and subsequently diluting to the required concentration.

The methods used for the preparation and characterisation of the adsorbent APSP used for this study is mentioned in chapter 3.

5.3 Batch Adsorption Experiments:

The batch experiments were carried at ambient temperature (~ 30°C) in a thermostated shaker at an agitation speed of ~150 rpm. A known mass of APSP was added to stoppered conical flasks filled with 25 mL of pesticide solution and was shaken for a fixed time interval. A blank, without APSP, was maintained to observe any adsorption of pesticides on the glass surface or degradation during the equilibration. The experiments were conducted at real pH values of pesticide solutions. In the studied concentration ranges pH values of Monocrotophos and Chloropyrifos were 2.74–3.00 and 5.30–5.58, respectively. The initial and equilibrium pesticide concentrations were determined. After filtering the supernatants through Whatman filter paper no: 41, COD and absorbance of the filtrate were measured.

For Spectroscopic measurements a calibration graph was prepared by taking known pesticide concentrations in 25 mL of aqueous solution and extracting them by shaking the samples (25 mL) with toluene (10 mL) for 1 min. After shaking, the samples were allowed to stand for 1 min and 1 g of anhydrous sodium sulfate was added to each tube to remove any trace of moisture from the toluene. Pesticide concentrations in the toluene layer were analysed spectrophotometrically after determining the wavelength that provided maximum absorbance. The wavelengths of maximum absorption for Monocrotophos and Chloropyrifos were 328.5nm and 291.5nm respectively. Calibration graph [Figure 5.1] for each pesticide was prepared and the concentration of each pesticide

residue after adsorption on APSP in further experiments was determined by referring to the calibration graph of the respective pesticide.

The percentage removal of the pesticide and the amount adsorbed (mg/g) were calculated by the following relationship:

$q_e = (C_i - C_e)/m;$

Where, C_i-initial concentration of pesticide in mg/L; C_e – Equilibrium concentration of pesticide in mg/L; m – Mass of adsorbent g/L; q_e – Amount of pesticide adsorbed per gram of adsorbent.

COD measurements were done by closed reflux and titration according to the procedure outlined in standard methods [5.10]. The COD of the samples were estimated before and after adsorption by APSP.

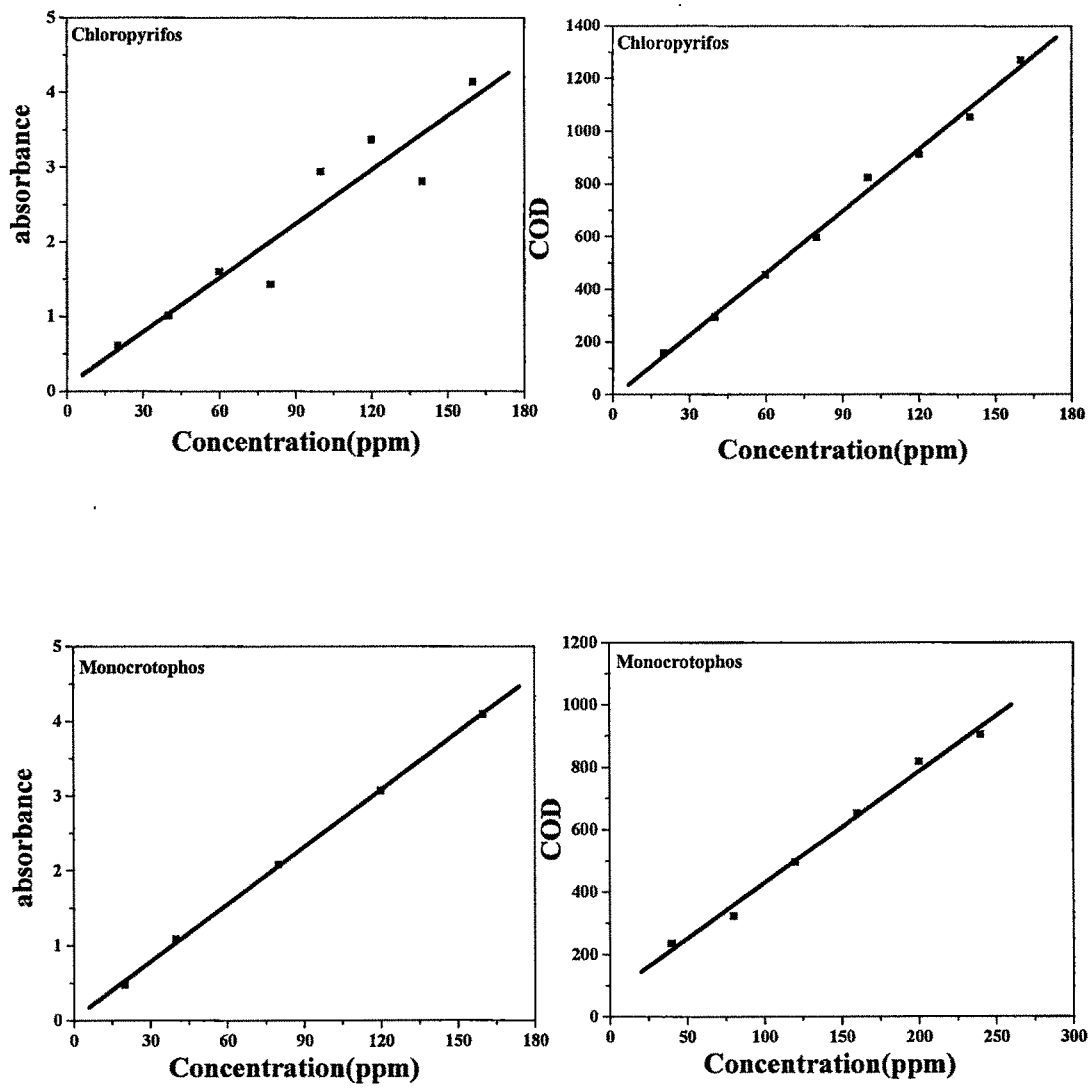


Figure 5.1: Calibration graphs of Pesticides

5.4 Optimization Parameters:

5.4.1 Effect of time on uptake of pesticide:

Table 5.1 and Figure 5.2 shows the effect of contact time in the range of 30–200 min on the percent adsorption of monocrotophos and chloropyrifos onto APSP using both spectrophotometric and COD measurements. Percent adsorption increases with increasing agitation time and is seen as a two stage process in the case of chloropyrifos acquiring equilibrium at 180 min. In the case of monocrotophos also equilibrium was achieved within 180 min. It was decided to equilibrate for 180 min in all further investigations for both chloropyrifos and monocrotophos. Chloropyrifos was transported into the macro pores within 120 min of contact time with APSP in the first phase. During the second phase (after ~ 120 min), a slight decrease in the adsorption rate was noted, most likely because of slow diffusion of the pesticides into the smaller pores and irregularities on the adsorbent surface [5.11]. A number of adsorption studies have been published which show considerable variation in the time needed to establish equilibrium [5.9]. When equilibrium conditions are reached, the adsorbate molecules in the solution are in a state of dynamic equilibrium with the molecules adsorbed by the adsorbent. Overall, the pseudo adsorption equilibrium was reached within 3 h for the pesticides under study. After pseudo equilibrium, less than a ~2% variation of pesticide concentration in the solution was observed even after keeping overnight. The results are consistent with those reported by El Bakouri et al. [5.12-5.14] for drin pesticides adsorption on modified organic waste residues and acid treated agricultural stones for endosulfan, and also in accordance with results reported by Kyriakopoulos et al. [5.5] and Kumar and Phillip [5.15] for alachlor, amitrole, trifluralin and prometryn adsorption

on porous polymeric adsorbents and endosulfan adsorption on clay and composted Indian soils, respectively, where equilibrium was established in a period of around 4h. Experimental data obtained from spectrophotometric and COD measurements for monocrotophos and chloropyrifos in the studied concentration range correlated well with each other.

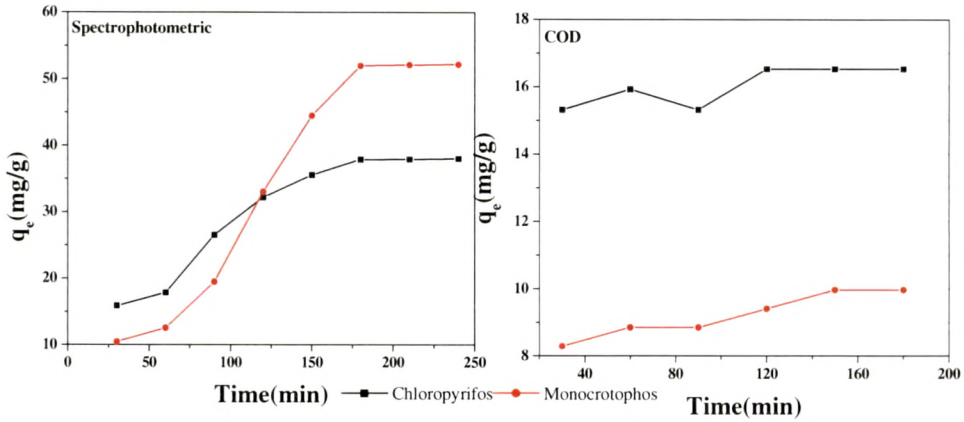


Figure 5.2: Effect of time on amount of pesticide adsorbed on APSP by both Spectrophotometric technique and COD

Table 5.1: Variation in the Adsorption Time

Initial concentration: 1600(Spectrophotometric)-400(COD) ppm, Agitation Time: (30-200) min, Temperature: 30°C, pH: 5 (Clp), 3(Mcp), Dose of adsorbent: 0.5 g, adsorbent: APSP, Volume of aqueous solution: 25mL, adsorbate: Chlorppyrifos and Monocrotophos

Time (min)	Percentage uptake of Pesticides			
	Spectrophotometric		COD	
	Chloropyrifos	Monocrotophos	Chloropyrifos	Monocrotophos
30	19.8286	13.0202	76.5695	59.1138
60	22.2773	15.5847	79.5952	63.1210
90	33.1215	24.2551	76.5695	63.1210
120	40.2344	41.2295	82.6209	67.1282
150	44.4321	55.5173	82.6209	71.1354
180	47.3473	64.9204	82.6209	71.1354
200	47.50000	64.9300	82.6200	71.1804

5.4.2 Effect of Adsorbent Dosage:

The effect of adsorbent dosage is an important parameter because this determines the capacity of an adsorbent for a given initial concentration of adsorbate. Variation in the dose of the adsorbent was conducted at different doses of APSP 0.1-0.7g while taking the concentration of the adsorbate for spectrophotometric technique as 1600ppm and for COD measurements as 400ppm in a total volume of 25 mL maintained at 30°C and pH5. The solutions were equilibrated for 180 min. From Figure 5.3 and Table 5.2 percent adsorption was found to be increased with increasing amount of the APSP upto certain

limit i.e. 0.6g for initial concentration of 120- 160 ppm. Further increase of adsorbent concentration does not affect adsorption, probably due to interference between binding sites of APSP doses [5.16].

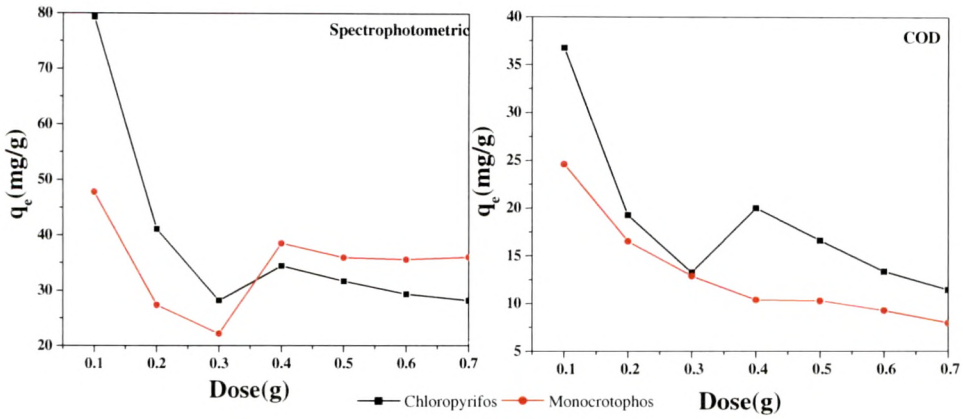


Figure 5.3: Effect of dose on amount of pesticide adsorbed on APSP by both Spectrophotometric technique and COD

5.4.3 Effect of Initial Concentration:

The adsorption of monocrotophos and chloropyrifos by APSP was studied at different initial concentrations (100 to 1200 mg/L). Table 5.3 show the results for effect of initial concentration on adsorption of both monocrotophos and chloropyrifos onto APSP by spectrophotometric and COD measurements. From Figure. 5.4 and Table 5.3 it is evident that the adsorption capacity of APSP increases with increase in equilibrium concentration and the percentage uptake was found to decrease with the increase in concentration of adsorbate suggesting limiting number of adsorption sites available for adsorption at higher concentration of adsorbate molecules which may be attributed to the increase in the concentration gradient and thus indicating the saturation of adsorption sites. At low concentrations, the ratio of surface active sites of adsorbent is more than the

total adsorbate components, and hence may interact with the adsorbent and can be removed from the solution [5.16].

Table 5.2: Variation in the Dose of the adsorbent

Initial concentration: 1600(Spectrophotometric)-400(COD) ppm Agitation Time: 180 min, Temperature: 30°C, pH: 5 (Clp), 3(Mcp), Dose of adsorbent: 0.1-0.7 g, adsorbent: APSP , Volume of aqueous solution: 25mL, adsorbate: Chlorppyrifos and Monocrotophos.

Dose (gram)	Percentage of Uptake of Pesticides			
	Spectrophotometric		COD	
	Chloropyriphos	Monocrotophos	Chloropyriphos	Monocrotophos
0.1	19.8286	20.7638	36.7606	35.0705
0.2	20.5282	35.0092	38.5404	47.0922
0.3	21.1112	47.4396	39.7269	55.1066
0.4	34.4042	56.8722	80.0699	59.1138
0.5	39.5668	89.0755	83.0362	73.1391
0.6	43.9395	93.4013	80.0699	79.1499
0.7	43.9300	95.9240	80.0699	79.1499

Table 5.3: Variation in concentration

Initial concentration: 120-1200(Spectrophotometric), 40-1000(COD) ppm, Agitation Time: 180 min, Temperature: 30°C, pH: 5 (Clp), 3(Mcp), Dose of adsorbent: 0.5 g, adsorbent: APSP, Volume of aqueous solution: 25mL, adsorbate: Chlorppyrifos and Monocrotophos.

Conc (ppm)	Percentage uptake of Pesticides					
	Spectrophotometric		COD			
	Chloropyriphos	Monocrotophos	Conc (ppm)	Chloropyriphos	Conc (ppm)	Monocrotophos
120	97.0305	97.3614	40	99.7523	40	99.9874
160	97.5397	96.1593	80	99.3376	80	95.5659
200	87.9571	92.8560	120	89.4726	120	89.6854
240	87.1657	88.2073	160	86.8095	160	64.9148
400	75.9562	86.2396	200	90.6579	200	71.9318
800	60.4594	83.2146	400	80.7825	240	70.5323
1200	71.9294	78.0103	600	54.3048	280	73.1391
-	-	-	800	36.1335	320	59.3157
-	-	-	1000	25.2306	360	57.6028
-	-	-	-	-	400	59.0375

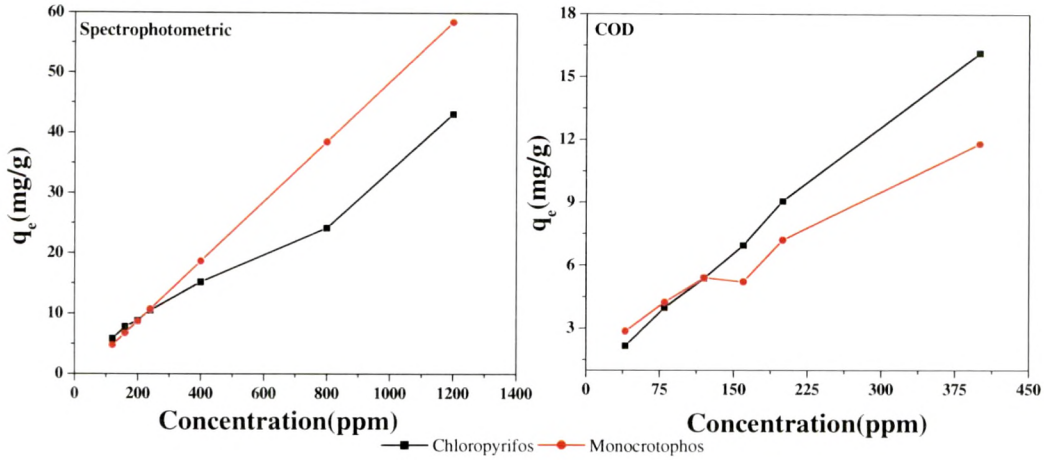


Figure 5.4: Effect of concentration of pesticide adsorbed on APSP by both Spectrophotometric technique and COD

5.4.4 Adsorption Isotherms:

The Freundlich and Langmuir isotherms were plotted for both monocrotophos and chloropyrifos on APSP by both spectrophotometric and COD measurements which are shown in Figure 5.5. To determine q_m, linear plots were made with the corresponding parameters of various models. Linear regression analysis was carried out for both monocrotophos and chloropyrifos for the two adsorption equilibrium models. The slopes of the straight lines give the values of $1/n$ (adsorption intensity), which is <1 indicating the better removal efficiency of monocrotophos at low concentrations. The slope value of <1 indicated L-type isotherms, which are characterized by the decrease in the adsorption at higher aqueous concentration of compounds, thus, adsorption of monocrotophos by APSP was concentration dependent [5.17]. These types of adsorption isotherms are observed when the molecules are adsorbed in a flat position, not suffering a strong competition from the water molecule, which explain the high affinity to adsorbent for

solute at low concentrations. However, as the concentration increases adsorption sites become limiting, leading to decrease in adsorption. Earlier researchers [5.48-5.50] have reported L-type adsorption isotherms for pesticide adsorption in fly ash–soil mixtures and fly ash. The slope value is ~1 in the case of chloropyrifos suggesting intensive adsorption process compared to monocrotophos.

The intercepts of the plots yield the value of q_m (adsorption capacity in mg/g) as given in Table 5.4. In Figure 5.5 the plot of amount adsorbed (q_e) against the equilibrium concentration (C_e) shows that adsorption obeys the Langmuir model for monocrotophos and chloropyrifos both by COD and spectrophotometric measurements demonstrating that Langmuir model is also followed by the adsorption data. The values of q_m (mg/g) are calculated from the slopes of the linear plots. The results are shown in Table 5.4. Table 5.5 shows the comparison of maximum monolayer adsorption capacity of some pesticides on various adsorbents reported in literature with APSP used in this work. The adsorbent used in this work has comparable adsorption capacity as compared to those cited in literature. The adsorption capacity of APSP used in present studies was 51.09mg/g and 52.63mg/g for batch 11.57mg/g and 14.24mg/g for COD by Langmuir isotherm and for monocrotophos and chloropyrifos respectively. The q_m values for spectrophotometric and COD measurements are different which we are not able to explain. Similar observations have been reported by Vergili and Barlas in their studies on the removal of 2,4-D, MCPA and Metalaxyl from water using Lewatit VP OC 1163 as adsorbent which was monitored spectrophotometrically and by COD measurements [5.21].

Comparison of K_f and q_m values for monocrotophos and chloropyrifos indicated that adsorption capacity of APSP for chloropyrifos is higher than monocrotophos. The

higher adsorption of chloropyrifos on APSP can be explained by its aqueous solubility as adsorption of organic compounds is generally inversely proportional to their aqueous solubilities [5.22]. Thus chloropyrifos which has low aqueous solubility was adsorbed more compared to monocrotophos.

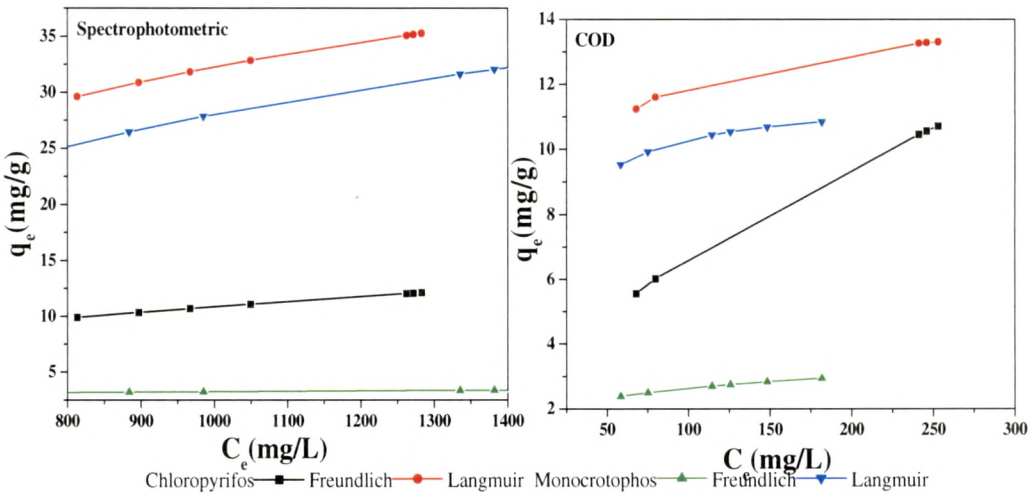


Figure 5.5: Isotherms plots of pesticides for (a) Spectrophotometric (b) COD

Table 5.4: Isotherm parameters and Thermodynamic constants

Initial concentration: 1600 ppm (spectrophotometric), 400ppm (COD), Agitation Time: 180 min, Temperature: 30°C, pH: 5 (Clp), 3(Mcp), Dose of adsorbent: 0.1-0.7 g, adsorbent: APSP, Volume of aqueous solution: 25mL

APSP	Parameters	Spectrophotometric		COD	
		Clp	Mcp	Clp	Mcp
Freundlich	K_f (mg/g)(dm^3/mg)$^{1/n}$	0.211	2.140	0.406	1.219
	N	0.980	3.676	0.869	2.304
	r^2	0.999	0.999	0.999	0.999
Langmuir	q_m (mg/g)	52.63	51.099	14.247	11.574
	K_a (L/mg)	0.002	0.001	0.0544	0.078
	r^2	0.999	0.999	0.999	0.995
Monocrotophos	Thermodynamic Parameters		303K	313K	323K
	ΔG° KJ mol^{-1}		-11.441	-12.205	-12.595
	ΔH° KJ mol^{-1}		-9.771		
	ΔS° Jmol^{-1}K^{-1}		0.057		

Table 5.5: Comparison of Adsorption capacities of agro-based adsorbents

Adsorbent	Pesticide	Adsorption Capacity	References
Water melon peel	Methyl parathion	24.3μmol g^{-1}	[5.7]
Chestnut shells	Methyl parathion	22.5 μmol g^{-1}	[5.6]
Chestnut shells	Carbofuran	10.8 μmol g^{-1}	[5.6]
Wood Charcoal	Atrazine	0.8 mg g^{-1}	[5.9]
Rubber granules	Atrazine	0.5 mg g^{-1}	[5.9]
Coal fly ash	Atrazine	3.3 mg g^{-1}	[5.9]
Coal fly ash	Metribuzin	0.6 mg g^{-1}	[5.9]
Coal Fly ash	Metolachlor	1.0 mg g^{-1}	[5.9]
Activated carbon from date stones	2,4 D	238.1 mg g^{-1}	[5.23]
Acid treated date stones	Aldrin, Dieldrin and Endrin	15.7, 14.1 and 11.7 mg g^{-1}	[5.12]
Rice bran, Rice husk	Triazophos	0.01, 0.03 mmol g^{-1}	[5.33]
Chick pea husk	Triazophos, Methyl parathion	0.01, 0.03 mmol g^{-1}	[5.16]
Bamboo canes, Date stones	Endosulfan sulphate	12.9, 13.5 mg g^{-1}	[5.31]
Olive stones, Peanut shells	Endosulfan sulphate	11.1, 9.6 mg g^{-1}	[5.31]
Avocado stones	Endosulfan sulphate	8.7 mg g^{-1}	[5.31]
Wood sawdust, Straw	Endosulfan sulphate	6.7 ,5.6 mg g^{-1}	[5.31]
Sal wood charcoal	Endosulfan	1.0 μg g^{-1}	[5.31]
APSP	Monocrotophos	51.1 mg g^{-1}	Present study
APSP	Chloropyriphos	52.6 mg g^{-1}	Present study

5.4.4 Kinetics:

The first order kinetic model depends mainly on adsorbate concentration and gives a good description of the adsorption of contaminants at very low concentrations while the second order kinetic model is derived from adsorption processes where the rate-controlling step is an exchange reaction [5.23]. The correlation efficient are closer to unity for the pseudo second order model by both COD and spectrophotometric measurements suggesting that both monocrotophos and chloropyrifos adsorption onto APSP is best described by this model. Hence this rate model was applied to understand the controlling mechanism of the adsorption process. Similar phenomena have been observed for the adsorption of phenol from aqueous solutions by activated carbon prepared from biomass material, endosulfan adsorption using acid treated agricultural stones [5.24, 25] and by Kuo et al. [5.26] for the adsorption of direct dyes by carbon nanotubes. Adsorption capacity q_e and the rate constant K_2 determined from the slope and intercept of the plot respectively are shown in Table 5.6.

To test the validity of the kinetic expression for intra-particle diffusion variations in q_t were plotted *vs* the square root of time. Figure.5.6. shows that kinetic plots obtained for Monocrotophos and Chloropyrifos by both spectrophotometric and COD measurements do not pass through origin suggesting that the intra-particle diffusion is not the only mechanism operating. The plots display more than one linear region where an initial portion is attributed to the diffusion of adsorbate through the solution to the external surface of the adsorbent or the boundary layer diffusion of solute molecules, second portion is attributed to the gradual adsorption stage, where intra-particle diffusion is the rate limiting, third portion is attributed to the final equilibrium stage where intra-

particles start to slow down due to extremely low adsorbate concentration in solution [5.27-5.30]. The slopes of the linear part corresponding to stage 2 with their correlation coefficients are given in Table 5.6 The adsorption coefficient or distribution coefficient K_d was calculated for each pesticide using the equation: $K_d = C_{s,eq}/C_{l,eq}$. Comparing average K_d values calculated for each pesticide (Table 5.6) with the corresponding pseudo second order kinetic rate constant values (k_2) revealed that chloropyrifos with higher kinetic rate constant value had higher K_d values and adsorbed faster compared to monocrotophos.

Table 5.6: Kinetic Parameters

Initial concentration: 1600 ppm (Spectrophotometric), Agitation Time: (30-240) min, Temperature: 30°C, pH: 5 (Clp), 3(Mcp), Dose of adsorbent: 0.5 g, adsorbent: APSP, Volume of aqueous solution: 25mL

Initial concentration: 400 ppm (COD), Agitation Time: (30-180) min, Temperature: 30°C, pH: 5 (Clp), 3(Mcp), Dose of adsorbent: 0.5 g, adsorbent: APSP, Volume of aqueous solution: 25mL

Kinetics	Parameters	Spectrophotometric		COD	
		Clp	Mcp	Clp	Mcp
Pseudo 1st Order	q_e (mg/g)	7.0780	12.1090	202.7550	1.4560
	K (min^{-1})	0.0240	0.0240	0.1860	0.0120
	r^2	0.9950	0.9880	0.9650	0.9990
Distribution Coefficient	K_d	44.9620	92.5330	-	-
Pseudo 2nd Order	q_e (mg/g)	62.8930	251.8890	16.940	10.5370
	K_2 (g/mgmin)	0.0001	5.710E-06	0.0130	0.0080
	r^2	0.9950	0.9980	0.9990	0.9980
Intra-particle	K_i(mg/g$min^{0.5}$)	3.5300	8.3650	0.2190	0.4060
	r^2	0.9850	0.9970	0.9950	0.9990

The same trend was observed by De Wilde et al. [5.8], which suggest that strongly adsorbing pesticides (high K_d values) exhibit a fast kinetic adsorbing process (high kinetic rate constant values). K_d values indicate that the highest adsorption is for Chloropyrifos, which has a higher hydrophobic character (log K_{ow} = 4.2).

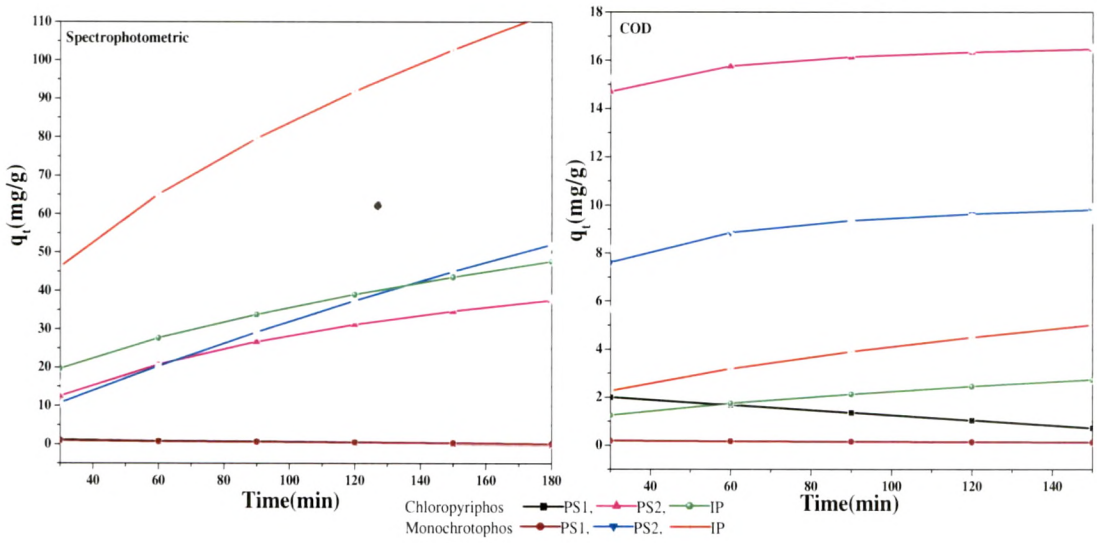


Figure 5.6: Kinetics (a) Spectrophotometric (b) COD

5.4.6 Adsorption Thermodynamics:

The studies of temperature influence on adsorption of chloropyrifos and monocrotophos revealed that chloropyrifos adsorption did not show any appreciable change with temperature while adsorption capacity of APSP for monocrotophos decreased with increasing temperature. The thermodynamic parameters of the adsorption process could be determined from the experimental data obtained at various temperatures using the equations:

$$\Delta G^{\circ} = - RT\ln K_d$$

$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$

Where, ΔG° is gibbs free energy, ΔH° is enthalpy of the reaction, ΔS° is entropy of the reaction, R is gas constant, T is temperature in $^{\circ}K$, K_d is distribution coefficient. The negative values of ΔH^0 reported in Table 5.4 indicate the exothermic nature of monocrotophos adsorption on APSP and reveal that the adsorption is physical, involving weak forces of attraction. Similar observations have been reported by Memon et al. [5.6] for the adsorption of methyl parathion onto chestnut shells and El Bakouri et al for drin pesticide on acid treated agricultural stones. The negative ΔG^0 values suggest a spontaneous pesticide adsorption process for monocrotophos.

5.4.7 Banghams equation:

The double logarithmic plot according to Bangham equation yielded non-linear curves showing that the diffusion of the adsorbate into the pores of the sorbent does not perfectly control the sorption process. From the figure 5.7 it is showing that the non-linearity of these plots confirms the non-applicability of Banghams equation and indicated that the adsorption of the Chloropyrifos and monocrotophos on APSP by both spectrophotometric and COD is not a pore diffusion controlled.

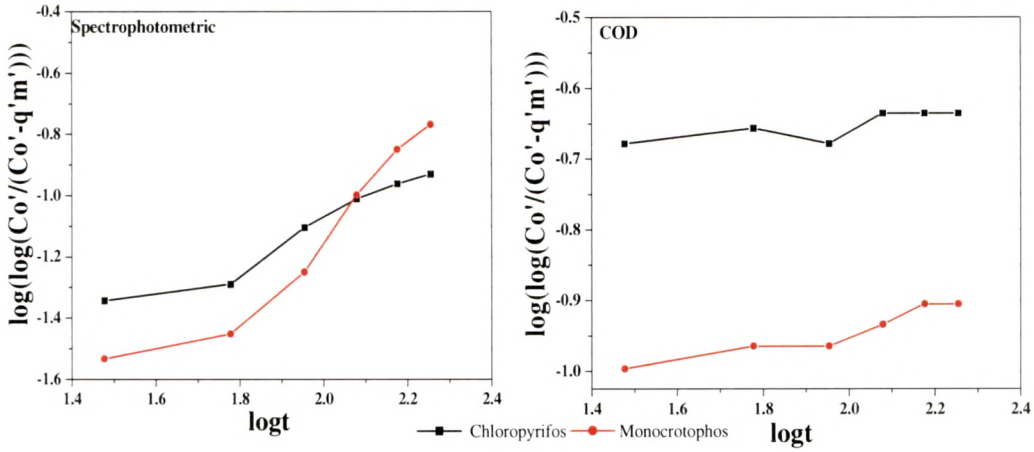


Figure 5.7: Banghams plots of pesticides from both Spectrophotometric technique and COD

5.4.8 Conclusion:

APSP is a good adsorbent for the removal of monocrotophos and chloropyrifos from water. The process reaches equilibrium within 180 min and follows both Freundlich and Langmuir isotherm model. Weak Vander Waals interaction is mainly responsible for this adsorption process. The pesticide adsorption efficiency of APSP depended on the initial concentration of pesticide in the solution and maximum removal of pesticide was observed at lower concentrations, which are generally encountered in the water samples. The negative values of the thermodynamic parameters, *i.e.* ΔH and ΔG indicate that adsorption is exothermic, feasible, and spontaneous in nature for monocrotophos. The spectrophotometric and COD data for the pesticides correlated very well suggesting that APSP has potential use as low cost adsorbent for the removal of pesticides under study from waste water and runoff water from agricultural soils. It can also find use as a material in the preparation of bio-beds to minimize environmental contamination from pesticide use.

5.5 Study of Radiolytic Degradation of Chloropyrifos and Monocrotophos

5.5.1 Introduction

Human population is constantly exposed to numerous chemical species present in the environment of which pesticides is a serious problem. Advanced Oxidation Process (AOP), using ozone, hydrogen peroxide, ultraviolet and gamma irradiation, is a promising technology for generation of OH radicals and removal of organic pollutant from the environment. The most simple and efficient method for generating OH radicals " in situ" is the interaction of ionizing radiation with water. This method was successfully applied for liquid samples containing aliphatic, aromatic hydrocarbons and pesticides [5.35-5.39, 5.41]. The use of ionizing radiation has great ecological and technological advantages, especially when compared to physical, chemical and biological methods [5.38, 5.39, and 5.41].

However there has been no published report on the radiolytic degradation of monocrotophos and the effect of irradiation at low dose rates (0.62 Gy/min) for a long period on monocrotophos and chloropyrifos. The advantage of using gamma irradiation technique is that it not only generates oxidizing radical like OH but also results in the formation of reducing radicals such as hydrated electron and H atom when water is subjected to gamma radiolysis. Therefore oxidation and reduction of solute under study takes place simultaneously that result in its decomposition. The radiolysis method also allows carrying out reaction under total oxidizing or reducing environment by appropriate choice of experimental conditions. The hydrated electron produced during the radiolysis of water is especially important in radiation- induced dechlorination of organochlorinated

pesticides. The hydrated electron reacts by dissociative attachment with these substances to generate an organic radical and a chloride anion. The organic radical scavenges a hydrogen atom from the solvent and a dechlorinated molecule is thus obtained. The use of ionizing radiation has great ecological and technological advantages, especially when compared to physical- chemical and biological methods. It degrades organic compounds, generating substances that are easily biodegraded without the necessity of adding chemical compounds [5.37, 5.38, and 5.41]

This study presents a preliminary study of chloropyrifos and monocrotophos degradation in liquid samples by exposition to ionizing radiation. The objectives of this study are i) To determine the degradation products of chloropyrifos and monocrotophos in water and acetonitrile medium by GC-MS after irradiation at low dose rates for a long period ii) Spectrophotometrically monitor the effect of different doses of gamma irradiation.

5.5.2 Experimental procedure:

Solutions of chloropyrifos were prepared in acetonitrile and subsequently diluting the stock solution with double distilled water to the required concentration. Solutions of monocrotophos were prepared in double distilled water. Samples were irradiated at low doses having a dose rate of 0.62 Gy/min and at high doses having a dose rate of 50 Gy/ minute in a BRIT make GAMMA CHAMBER 5000 determined by using Fricke's Dosimetry solution[5.40]. The degradation of monocrotophos and Chloropyrifos were observed using UV –Visible spectrophotometer by measuring the absorbance of monocrotophos and chloropyrifos before and after irradiation at the wavelengths of

absorbance maxima of individual pesticides against water blank at room temperature (30°C) using following equation:

% degradation = A_0 -A_{obs} / A_0

where A_0 is the absorbance before irradiation and A_{obs} is the absorbance after irradiation.

The degradation products for low dose irradiation of monocrotophos and chloropyrifos in aqueous media were determined using GC-MS in the electron impact mode. A TR-5MS column (15m X 0.25m i.d.) was programmed from 50 to 650°C. Injector and detector temperatures were at 30 and 50°C respectively. Helium was used as the carrier gas at 1.0 mL/min. EI spectra were obtained at 70 eV, in full scan mode m/z 50 to 650. The radiolytic products were determined by comparision of areas in the GC-MS chromatograms.

5.5.3 Results and Discussion:

Chloropyrifos and Monocrotophos (25 ppm) in water and acetonitrile medium were irradiated at low dose rate of 0.62 Gy/min to give a dose of 5-1500 Gy in a batch system for spectrophotometric and GC–MS measurements. The spectrophotometric results revealed that monocrotophos degraded by 42% even at a dose of 10 Gy but chloropyrifos did not show any appreciable change.

GC-MS measurements of samples irradiated at 895 Gy revealed that irradiation of aqueous solutions of monocrotophos gave higher degradation yields than in acetonitrile (92% in water and 84% in acetonitrile) caused by the higher concentrations of solvated electrons in irradiated polar than nonpolar solvents. In the case of chloropyrifos lower degradation yields (20% in water and 45% in acetonitrile) were obtained both in water

and acetonitrile medium due to low solubility of chloropyrifos in water resulting in reduced interaction with solvated electrons.

The extent of degradation of monocrotophos and chloropyrifos monitored spectrophotometrically at a higher dose rate of 50 Gy/ minute to give a dose of 100 to 5000 Gy was found to depend on the applied dose (Figure 5.8 and 5.9). The results show that there was 42% and 47% degradation in the case of chloropyrifos and monocrotophos respectively.

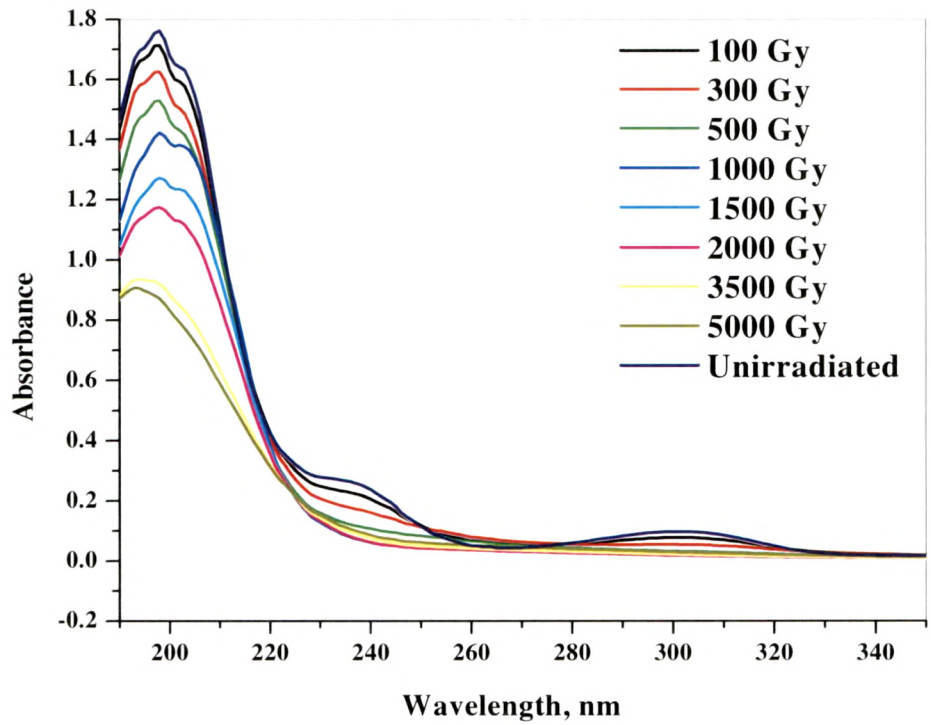


Figure 5.8: Absorption spectra of monocrotophos at different gamma doses at dose rate of 50 Gy/min

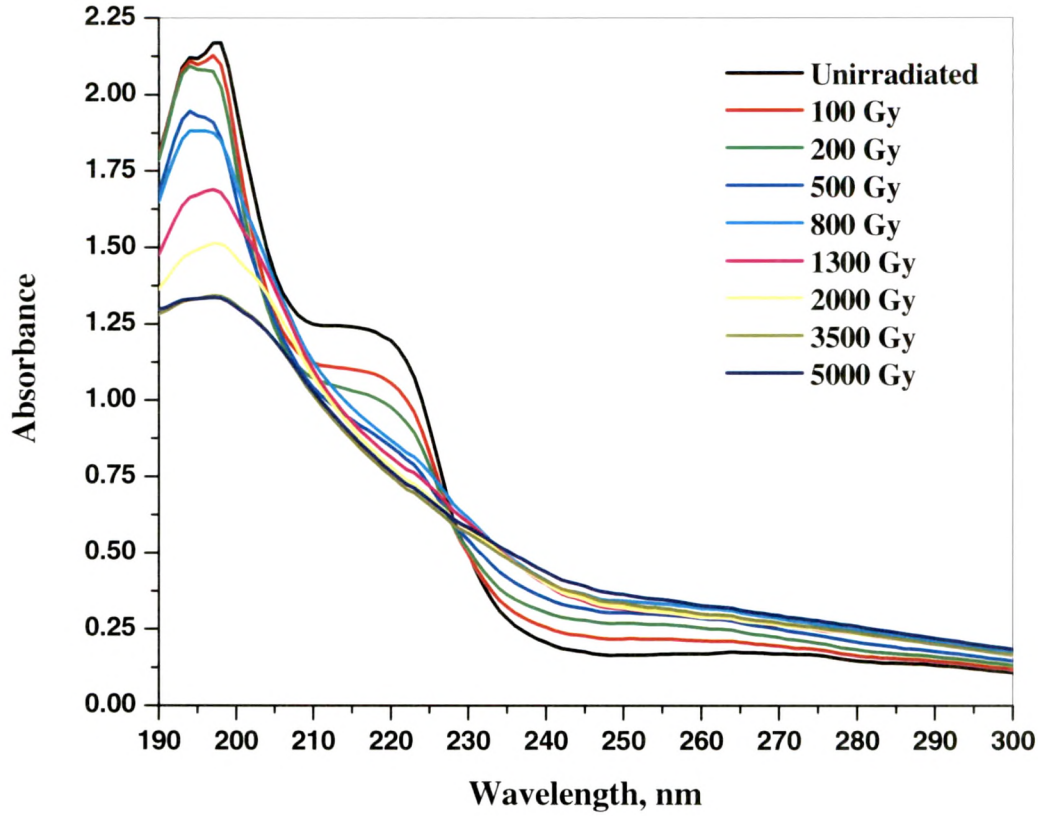


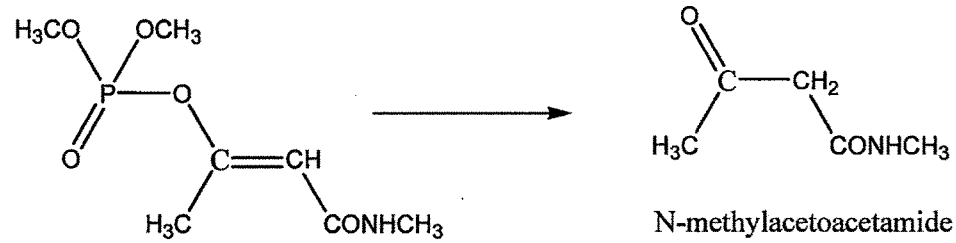
Figure 5.9: Absorption spectra of chloropyrifos at different gamma doses at dose rate of 50 Gy/min

5.5.4 Identification of Degradation Products:

The GC-MS chromatograms of the solutions irradiated at 0.62 Gy / min to give a dose of 850 Gy (Scheme 5.1) revealed that residual monocrotophos concentration was 8% and 16% while residual chloropyrifos concentration was 80% and 55% in aqueous and acetonitrile medium respectively after irradiation. Monocrotophos irradiated in aqueous and acetonitrile medium gave N-methylacetoacetamide (molecular ion peak

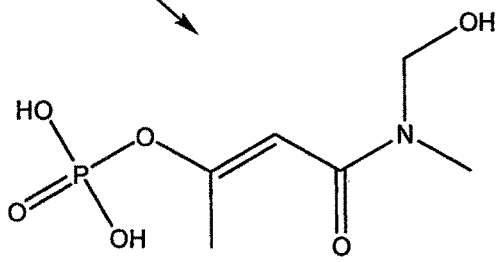
(M^+) m/z 115 (16%), fragment ion peaks m/z 84 (100%), 73/71 (18%) and 58 (40%) and N-(hydroxymethyl) monocrotophos (molecular ion peak m/z 223 (6%)), fragment ion peaks- m/z 192 (15%), 127 (100%) and 84(5%). N-Methylacetoacetamide and O-desmethylmonocrotophos have been identified as hydrolytic degradation products of monocrotophos by Lee et al. [5.43]

In the case of Chloropyrifos the degradation product identified was 3, 5, 6-trichloro-2-pyridinol (TCP) (molecular ion peak m/z 197 (100%)), fragment ion peaks - m/z 169 (14%) and 134 (8%) in acetonitrile and aqueous medium. Similar observations were made by Gustavo et al and Walia et al during photo degradation [5.44, 5.45]. This product seems to be formed directly from chloropyrifos. The formation of TCP was also reported by Mori et al when irradiated at 4.5 KGy/h. They also have observed the formation of chloropyrifos oxon which we were not able to identify in this study [5.46]. In addition signals due to monocrotophos and chloropyrifos were also observed in their respective solutions suggesting incomplete degradation of monocrotophos and chloropyrifos. It is interesting to note that gamma-radiolysis follows the same pathway as chloropyrifos and monocrotophos degradation, involving chemical and microbiological processes.

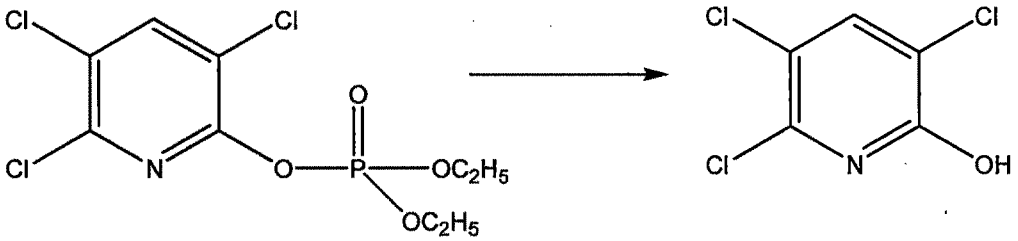


Monocrotophos

N-methylacetoacetamide



N-hydroxy-methyl monocrotophos



Chloropyriphos

3,5,6-Trichloro-pyridin-2-ol

Scheme 5.1: Degradation products of monocrotophos and chloropyrifos

5.5.5 Conclusions:

GC-MS has proved to be an advantageous and powerful technique for pesticide analysis mainly because of its high sensitivity. Using the GC-MS it was possible to evaluate the pathway and the intermediate by-products of chloropyrifos and monocrotophos radio degradation. The main intermediate by-products of incomplete chloropyrifos and monocrotophos degradation were 3, 5, 6-trichloro-2-pyridinol and N-methylacetoacetamide, N-(hydroxymethyl) monocrotophos respectively. The presence of water was fundamental in the efficiency of this process as using gamma radiation. Irradiation at lower dose rates for a longer time was as effective as irradiation at high dose rates for a short time to give the same total effective dose. The degradation of chloropyrifos was lesser than monocrotophos in both water and acetonitrile.

5.6 Low Temperature Thermoluminescence Studies of Chloropyrifos and Monocrotophos

5.6.1 Introduction

More than 700 pesticides are registered for use in the world, and many more continue to persist in the environment, even though they are no longer being applied. For the protection of human health and the environment, pesticide residues are routinely monitored in food, water, soil, and tissue samples. "Acceptable" residue limits have been set for various foods and environmental samples by agencies such as the United States Environmental Protection Agency (U.S. EPA), the Codex Alimentarius Commission, and many other governmental organizations around the world. A great many methods have been developed to screen for pesticides in food and the environment to ensure that risks associated with pesticide use are minimized.

Recently, concern has increased that certain pesticides and other synthetic chemicals may be acting as pseudo hormones which disrupt the normal function of the endocrine system in wildlife and humans. Birth defects, behavioural changes, breast cancer, lowered sperm counts, and reduced intelligence are among the many disorders that have been blamed on these "endocrine disrupting" compounds, though much research must be done to verify these assertions. In 1996, Colborn, Domanoski, and Myers brought these issues into the public spotlight with the publication of their book *Our Stolen Future*. Recently, the United States Congress passed legislation calling for increased testing of suspected endocrine disrupters and monitoring their levels in food and water supplies. Because the endocrine system can be exquisitely sensitive to

extremely low hormone concentrations, there is a need to measure concentrations of suspected endocrine disrupters (many of which are pesticides) at very low levels?[5.47]

Clearly, there is pressure to push pesticide detection limits to even lower levels than are routinely achieved today. Most residue measurements are made by gas chromatography using a variety of element-selective or mass spectral detectors (GC/MS) and HPLC. Therefore, to achieve lower detection limits, it is necessary to improve the detection limits of these GC and HPLC methods. Low temperature thermoluminescence is also a new technique to detect the pesticides even in low concentrations.

5.6.2 Thermoluminescence:

Thermally stimulated luminescence (TSL) is called Thermoluminescence (TL). Covalent solids exhibit thermoluminescence, metals do not. It's a well known phenomenon amongst the thermally stimulated processes. Its theory and application have been fully developed inter alia by Mc Keever, Chen and Visocekas and it proved to be a most interesting tool to study the structure of solids, mainly ordered crystals. To that end, the studied material is "activated" at low-temperature, usually by radiant energy (UV, X-rays, gamma rays, electron beams, alfa-particles or neutrons) which most generally creates electron-holes pairs which become separately "trapped" at different energy levels. Then, when the irradiated material is warmed up, the heating serves as a trigger to release the initially accumulated energy and the trapped electrons and holes move and recombine. A characteristic glow is emitted most often under the shape of different successive peaks according to the depths of the initial traps. As a general rule this phenomenon is observed in ordered crystals though is can be equally seen in disordered

materials such as glasses. In that mechanism, imperfections in the lattice play a major role and are considered to be the place where luminescent centres appear. Thus, thermoluminescence is a good tool to study these imperfections and understand how they appear in the crystal [5.48]. In general, crystal grown in the laboratory with strict control of impurities can only exhibit thermoluminescence, because thermoluminescence is very dependent on minute amounts (ppm) of impurity and also on thermal history of the material. A Defect due to one of the negative ions, being absent from its proper place, that is, a negative–ion vacancy acts as an electron trap because the local deficit of negative vicinity. Ionized electrons result from the action of nuclear radiation in detaching electrons from their parent nuclei. This ionizing effect of nuclear radiation, as opposed to the much less probable event of damage to the lattice, gives rise to the thermoluminescence.

In view of the high sensitivity of the low temperature thermoluminescence technique in detection of ultra low dilutions we have selected to study the two pesticides widely used in India for pest control. We could hope that the freezing process would maintain this specificity and that, accordingly, the thermoluminescence glow after irradiation would be different from one sample to the other and closely related to their individual original structure. It is reported that the high dilutions keep their original features even when they are beyond the Avogadro's number.

In recent studies on Thermoluminescence of Irradiated High Dilutions Prof. L. Rey, stated that it has often been claimed and also in the practice of classical homeopathy, that high dilutions of different products prepared by successive operations under vigorous mechanical stirring, proved to be different between themselves and with

the dilution fluid, according to careful comparative biological and clinical testing performed in double blind and multicentric conditions. It has been suggested that these effects could be related to the hydrogen bond structure [5.49-5.51, 5.52]. The purpose of the present study is to correlate the LTTL characteristics of low concentrations of pesticides and try to use this fingerprinting technique as a tool to detect the low concentrations of pesticides in water.

5.6.3 Experimental procedure:

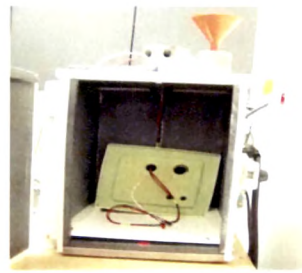
Frozen samples are "activated" by irradiation at low temperatures (mainly in liquid nitrogen at-196°C) using X-Rays which in turn create meta stable structures within the matrix by creating electron-hole pairs, free radicals which are subsequently studied in the course of re-warming. There, depending upon the depth of the different traps, these features recombine or are deactivated and emit characteristic glows which are recorded and analyzed using photomultipliers and CCD cameras coupled with spectrographs as already described in some previous publications by Prof. Rey et al,.

In the present study the Organo Phosphorous Pesticides, Chlorpyrifos 20% E.C. and Monocrotophos 25% S.L. are collected from the Baroda Agrochemicals, Baska, which are diluted to 100 ppm by using Distilled water for Chlorpyrifos and Monocrotophos.

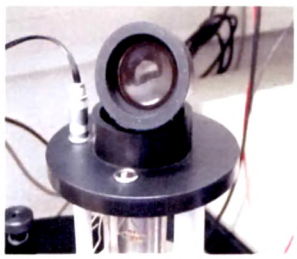
The samples of one cubic centimetre of each solution is placed in aluminium test cavities of 20mm diameter and 2mm depth and frozen to -20 °C on a cold metallic block. The frozen samples are finally immersed into liquid nitrogen and kept at -196 °C for one hour. A test dose of 0.5KGy X-ray was imparted to the specimens which are maintained

at -196°C using Philips X-ray irradiator. After irradiation, all the "activated" samples are transferred into a liquid nitrogen container and kept, there, for a week-time, to even out whatever small differences could exist between them. Finally, all samples are placed in the thermoluminescence equipment (maintained at -196°C) and their respective glow (TL) recorded with both a photo-multiplier and a CCD camera connected to a spectrograph in the course of re-warming between -196°C and -60°C (Figure 5.10). The heating rate used was 5°C per minute.

X-ray irradiator **Irradiation Chamber** **Aluminium Cavities**


Detector **CCD Camera** **Liquid nitrogen container**



TL Setup **Sample holder** **Photomultiplier**

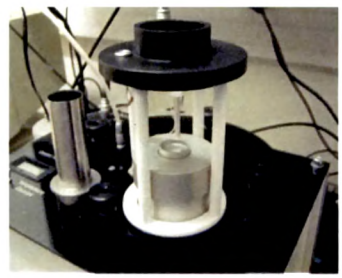
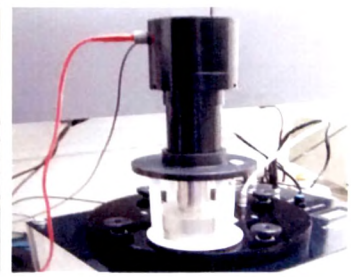




Figure 5.10: Experimental Setup

5.6.4 Result & Discussion:

Figures 5.11 and 5.12 are the LTTL of X-ray irradiated 100ppm Monocrotophos and Chlorpyrifos. The chloropyrifos samples displayed a hump around -140° C and a well resolved peak nearly at -136° C followed by a low intensity TL peak at -110°. Upon rewarming to room temperature it turned colourless again. The 100ppm Monocrotophos sample exhibited a hump nearly at -132°C and a well resolved peak at -152°C. The TL of Distilled water also recorded and the results are compared. The distilled water sample displayed a hump around -120°C and a well resolved peak at -109°C. The TL emissions of Distilled water are around 450nm and 490nm. It is interesting to note that the irradiated Monocrotophos sample turned to pale purple. The same phenomenon was observed by K.V. R Murthy et al (2007) [5.53] in low temperature irradiated rice samples.

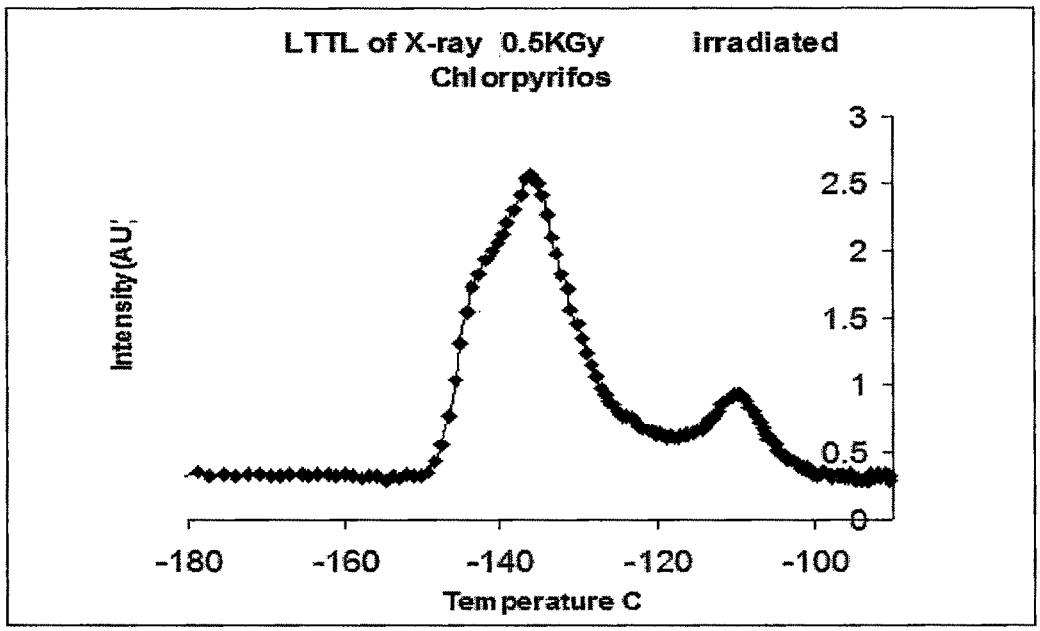


Figure 5.11: LTTL of X-ray irradiated Chloropyrifos

Figures 5.13 and 5.14 are the TL emissions of the Monocrotophos and Chlorpyrifos. It is observed that the TL emissions are around 550nm and 620nm for Chlorpyrifos while a broad emission in the visible region with a maximum at 444nm and 482nm was observed for Monocrotophos. The initial results are interesting in nature. However, to pin point which chemical constituent of the pesticide is responsible for TL and TL emissions is very difficult at this stage.

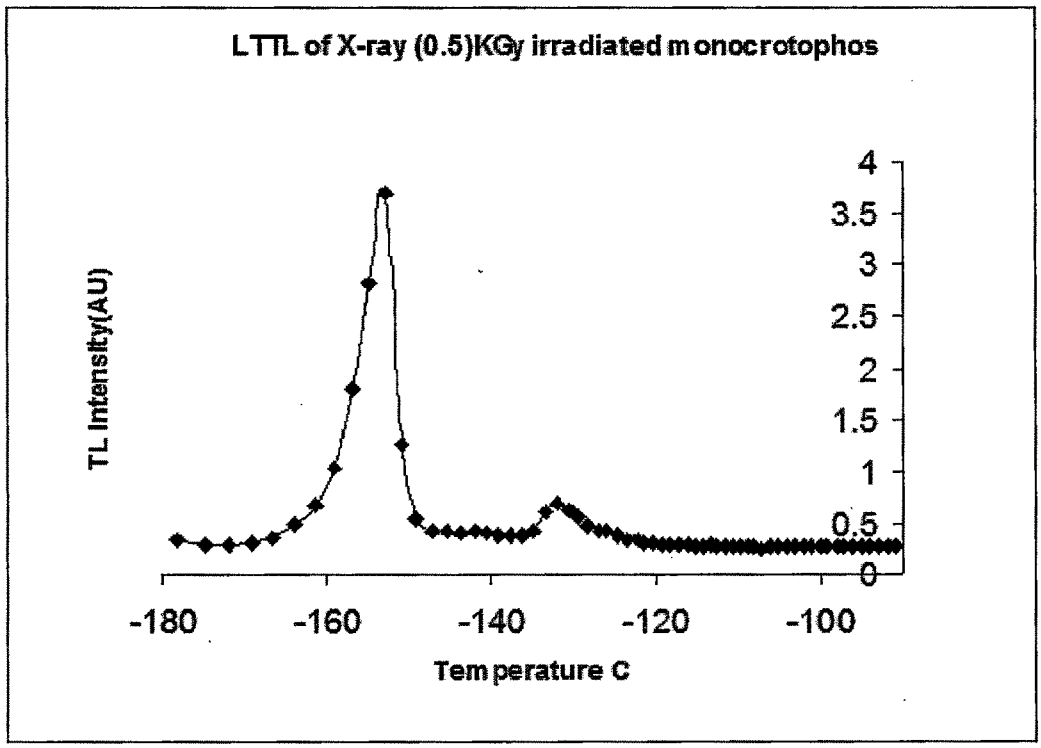


Figure 5.12: LTTL of X-ray irradiated Monocrotophos

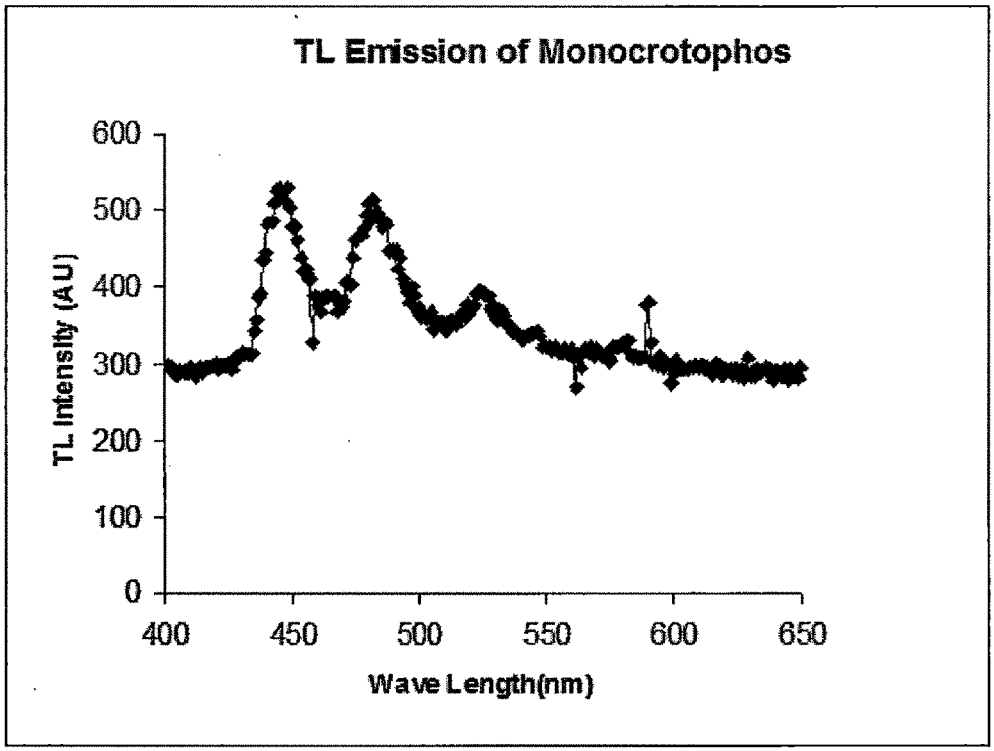


Figure 5.13: TL Emission of Monocrotophos

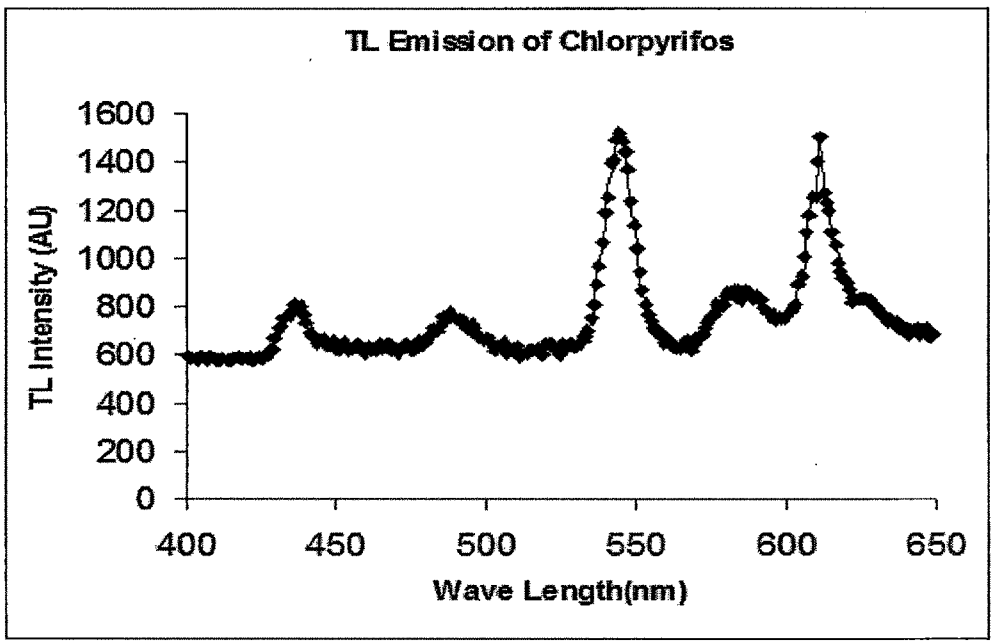
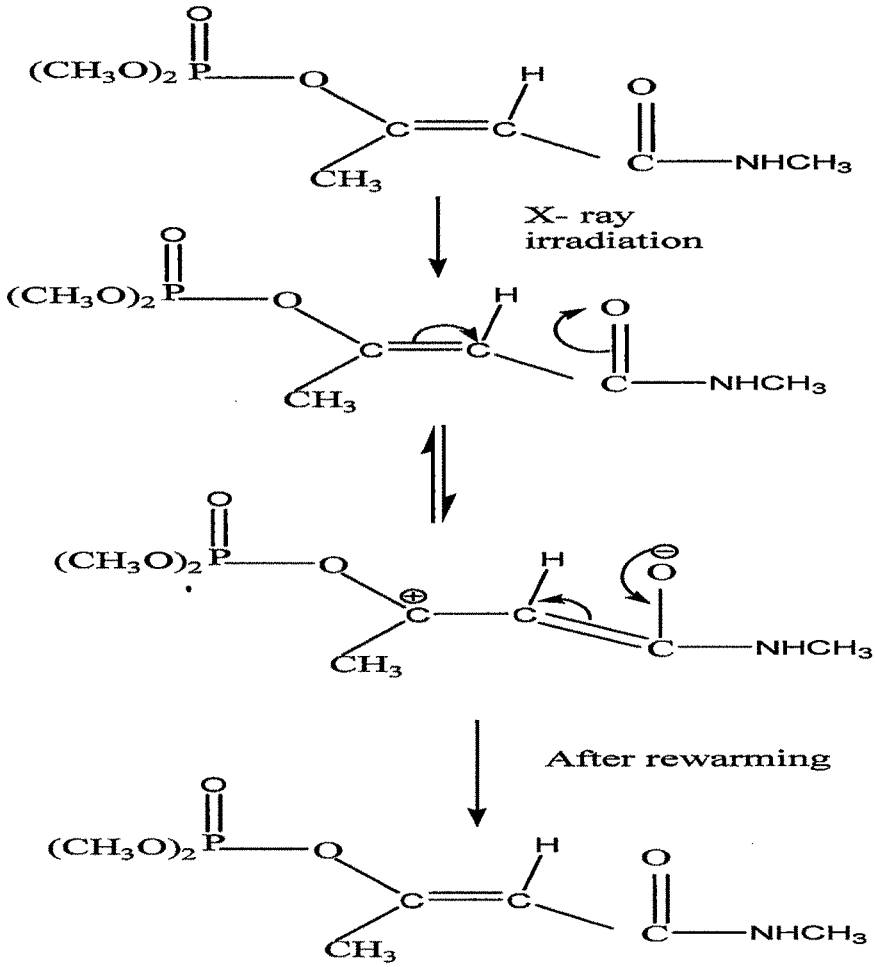


Figure 5.14: TL Emission of Chloropyrifos

Scheme 5.2 is the tentative mechanism of the bond change of Monocrotophos where the delocalization of pi-electrons leads to the formation of a new stable pi-bond at -196°C between the C-C. Due to this delocalization a colour change is observed for the X- ray irradiated Monocrotophos maintained at -196°C. These bonds are stable from -196°C to -70°C, upon re-warming to -60°C and above the specimens become colourless. [5.54]



Scheme 5.2: Mechanism of the bond change in Monocrotophos

5.6.5 Conclusion:

The TL emissions are around 550nm and 620nm for Chlorpyrifos and a broad emission in the visible region with a maximum at 444nm and 482nm for Monocrotophos which is different from water and methanol. Thus it can be concluded that the TL emissions are due to the concentrations of the pesticides but not from the water or methanol. However, to pin point which chemical bonded constituent of the pesticide is responsible for TL and TL emission is very difficult at this stage.

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