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COMPARISON BETWEEN CUSTOMS PREPARATIONS AND WORKOUT PREPARATIONS FOR PESTICIDE PROFENOFOS FROM DIFFERENT SOURCES AND UNDER SPECIFIC ENVIRONMENTAL CONDITIONS

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ABSTRACT

Four generic profenfos formulations under trade name Camkron and Tiliton 72% EC (customs, workout) for each of those, which currently applied in Egypt from different companies were studied for the effects of sunlight exposure, UV-light, PH and storage on the stability of profenofos, its respective impurity 4-bromo-2-chlorophenol content and water as a relevant impurity. Exposure to sunlight, UV-light at 16 hours and storage for 14 days at 54±2^{o}C indicated various degradation effects on profenofos content and increase the formation of its impurity 4-bromo-2-chlorophenol and the change in PH in long period cause breakdown of the active substance instability of some component. The storage of profenofos at intervals of 3, 7 and 14 days at 54 ± 2^{o}C from the results obtained showed serious effects on the rate of degradation of profenofos and the increase in the rate of formation of 4-bromo-2-chlorophenol, as well as on sunlight, UV-light exposure, for all of the profenofos formulations under study. It found that the Camkron (workout) is invalid for use it may be due to several factors affecting the consistency of the formulation of profenofos in the manufacturing process, the origins of technical materials, the use of various forms of adjuvants and the long storage time in poor conditions. Analysis before and after storage, sunlight exposure, UV-light using GC-MS identified four degradation products: 4-bromo-2-chlorophenol, O-(4-bromophenyl) O-ethyl S-propyl phosphorothioate, O-(2-chlorophenyl) O-ethyl S-propyl phosphorothioate and O-(4-bromo-2-chlorophenyl) S-propyl hydrogen phosphorothioate and also used IR spectra.

Keywords: profenofos, 4-Bromo-2-Chlorophenol, Impurities, IR, GC/MS and Degradation.

INTRODUCTION

profenofos organophosphates (OP) pesticide is widely used in agriculture for crop protection and pest control (Radwan *et al.,* 2005; Firestone *et al*., 2005).

Long-term exposure to polluted water with profenofos is harmful to people's health because it is considering a neurotoxic pesticide action as chlinesterase inhibitor in nerve and instability erythrocyte membrane (Shi *et al*., 2012; Kushwaha *et al.,* 2016).

Profenofos degrade rapidly due to exposure to sunlight, UV light radiation as a result of the generation of free radicals' species oxidized profenofos to 4-bromo-2-chlorophenyl O, S- dihydrogen phosphorothioate by de ethylation and depropylation. Successive oxidation, cleavage of the C-O bond give rise to the release of orthophosphate and generation of 4-bomo-2-chlorophenol (Rodrigues *et al*., 2020; Amin *et al*., 2014).

4-bromo-2-chlorophenol is one of the metabolites of profenofos due to breaking ester bond linkage of the parent by bacteruin. Further hydrolysis, is found that 4-bromo-2-chlorophenol decomposed to samples products identified in soil, irradiated with sunlight on UV light (Jabee *et al*., 2015; Malghani *et al*., 2009a).

The use of profenofos (PFF) has increased because of its efficacy against pests' resistant to other organophosphates (OP). Its presence in the environment may lead to acute or chronic poisoning for people who use it for daily farming activities and for people who come into contact with polluted soil, water, air or food (Gonzales-Condori *et al*., 2020).

This investigation aims to study comparison of products customs and workout products for profenofos from different sources and its impurity 4-bromo-2-chlorophenol and water in terms of the effect of storage, UV-light, Sunlight, PH and effect of stability of the degradation produced by IR and GC-MS spectroscopy.

MATERIAL AND METHODS

Chemical reagents

Analytical standard of profenofos (72% EC) under trade name Camkron and Tiliton (customs, workout) were obtained from three different companies for three groups. The first group Camkron (workout) from Kam Agrochemical, the second group Camkron (customs) from the cam factory and the third group Tiliton (customs, workout) from Agrochemical.

Accelerated storage procedures (CIPAC MT 46, 1995)

Formulations of emulsifiable concentrate of profenofos 720 g/l were placed in bottles (about 50 ml). These bottles were classified into three groups and subjected to different treatments as follows: The first group was exposed to storage at 54 ±2^{o}C for different intervals 0, 3, 7, and 14 days, while the second group and third group were exposed to sunlight and UV-light for the different intervals for in 0, 2, 4, 8 and 16 hours.

Samples from the three tested groups were subjected to evaluate the stability of each formulation.

Preparation of samples

Profenofos Standard Preparation

Weight 10 mg of profenofos of known purity analytical content in 25 ml grade (A) flask measurement, dissolved and finished methanol.

Sample Preparation

From each formulation, a particular weight equal to 10 mg of profenofos analytical norm was obtained and transferred to a 25 ml grade (A) measuring flask, complete with methanol.

(4-bromo-2-chlorophenol)

Standard Preparation

Ten mg of the 4-bromo-2-chlorophenol analytical standard was weighed, dissolved and completed with methanol for volume in a 25 ml grade (A) measuring flask.

Sample Preparation

From the formulation sample, one gm of profenofos was weighed into a 25 ml grade(A) measuring flask, dissolved and methanol-completed to volume.

pH Measurement

The pH value of profenofos 72% EC formulation and its impurity 4-bromo-2-chlorophenol was measured by using a PH meter Jen way instruments PH 3510 PH meter it was recalibrated before testing **CIPAC MT 75.3 (2000)**.

Emulation stability [MT 36.3]

Formulation, if diluted with CIPAC normal waters A and D at 30±2°C **CIPAC MT 18 (1995)** in the emulsion characteristics experiment 5 ml of formulation sample were separately mixed with standard water (CIPAC A. 20 PPM hardness, PH 5.00 – 6.00, Ca^{+}: Mg^{2+}=1:1 and CIPAC D, 342 ppm hardness PH 6.00 -7.00 Ca^{2+}: Mg^{2+} = 4:1 a100 ml) measurement cylinder to produce 100 ml of an aqueous emulsion.

The stopper was mounted on the cylinder, which was turned 10 times upside down afterwards. Subsequently, the amount of free oil or cream separated at the top of the emulsion was observed after the emulsion had been allowed to stand undisturbed for 30 minutes.

Exposure under sun and UV-light

The effect of sunlight and UV-light on samples, UV Japan lamp with specifications (G13T8 tube, 30 W, 254 nm) put in a tightly locked wooden box and connected to an electrical source, then placed the samples directly with distance about 10 centimetres below the source of light inside the box and outdoor to sunlight for in 0, 2, 4, 8 and 16 hours.

Water measurement

Water % of profenosfos 72% EC formulation was measured by using METTLER TOlEDO C_2OS coulometric KF Titrator.

Gas Chromatography Determination analysis of Profenofos 72% EC (customs, workout)

Identification and determination of profenofos and its impurity 4-bromo-2-chlorophenol by GLC instrument Hewlett– Packard G.C (Model 6890 instrument) equipped with a flame ionization detector (FID), capillary column 15 m × 0.55 mm. Nitrogen was used as a carrier gas at a flow rate of 40 ml/min in Jector temperature 250°C.

Temperature detector: 300°C and temperature of the oven: 200°C and 140°C, respectively (Mann 1981). At these conditions, the retention time (RT) of Profenofos and its 4-bromo-2-chlorophenol were 3.408 and 3.695 minutes, respectively.

The results of the above samples were quantitative determination by comparison with the standard of known purity under the identical GLC condition.

Gas-Chromatography- Mass spectrometry analysis of Profenofos 72% EC (customs, workout)

Apparatus Agilent 7890 B, 5977 A MSD gas chromatography equipped with an Agilent mass spectrometric detector, with a direct capillary interface and fused silica capillary column (30 m × 0.025 mm HP-5-0.25 micron -60 to 325/325ºC) was used.

Samples were injected under the following conditions: Helium was used as carrier gas at approximately 1 ml/min, pulsed split mode, split ratio (10:1), split flow 10 mL/min. The solvent delay was 4 min and the injection size was 1 µL. oven temperature program, 50°C for 0.5 min, then 10°C/min ramp to 190°C followed by a 10°C/min ramp to 210°C for 1 min followed by a 10°C/min ramp to 300°C and held for 2 min (total run time: 29.5 min) the injector temperature was set at 280°C.

In the identification of the separated peaks, a Wiley mass spectral database was used.

The absorbance of Profenofos 72% EC (customs, workout) in infrared (IR spectra)

The Fourier transform infrared (Avtra 330 Thermo Nicolet) was used to analyze, with some alteration, the effect of storage on the absorption of feature groups and the fingerprint of formulations of Organophosphorus insecticide according to (Barbara 1985).

The samples were prepared by homogenising 0.01 gm of the sample with 0.1 gm of dry potassium bromide (KBr) using an agate mortar and pestle, and then 0.03 gm of the above mixture was transferred with forceps to a clean stainless steel slide and put in the piston to form a clear and thin film of a sample.

RESULTS AND DISCUSSION

Effect of storage on the stability of profenofos 72%EC (customs, workout) and their impurities.

Table (1, 2) showed the effect of storage at 54±2°C for different intervals 0, 3, 7, and 14 days on the stability of the commercial profenfos formulation under trade name

Table (1): Effect of storage of Tiliton 72%EC (customs, workout) and their impurities.

Storage Periods (Days)	Tiliton (customs)				Tiliton (workout)			
	#Profenfos % w/v	Loss%	#4-bromo-2-chlorophenol	Increase %	#Profenfos % w/v	Loss%	#4-bromo-2-chlorophenol	Increase %
0	71.98	0.00	0.69	0.00	71.78	0.00	0.83	0.00
3	71.64	0.47	0.73	5.79	71.57	0.29	0.84	1.2
7	71.46	0.72	0.75	8.69	70.1	2.34	0.91	9.64
14	70.03	2.71	0.79	14.49	68.5	4.57	0.95	12.00

Zero: one hour before storage Average, three injections

Table (2): Effect of storage of Camkron 72%EC (customs, workout) and their impurities.

Storage Periods (Days)	Camkron (customs)				Camkron (workout)			
	#Profenfos % w/v	Loss%	#4-bromo-2-chlorophenol	Increase %	#Profenfos % w/v	Loss%	#4-bromo-2-chlorophenol	Increase %
0	71.82	0.00	0.83	0.00	66.80	0.00	5.69	0.00
3	71.59	0.32	0.89	7.22	65.83	1.45	6.01	5.62
7	70.25	2.19	1.1	32.53	59.64	10.7	6.696	17.68
14	69.53	3.19	1.2	44.57	48.63	27.2	8.23	44.64

Zero: one hour before storage Average, three injections

Table (3): photolysis of Tiliton 72%EC (customs, workout) and their impurities exposed to sunlight for 16 hours.

Storage Periods (Days)	Tiliton (customs)				Tiliton (workout)			
	#Profenfos % w/v	Loss%	#4-bromo-2-chlorophenol	Increase %	#Profenfos % w/v	Loss%	#4-bromo-2-chlorophenol	Increase %
0	71.98	0.00	0.69	0.00	71.78	0.00	0.83	0.00
2	71.49	0.68	0.799	15.79	71.24	0.75	0.84	1.21
4	70.60	1.92	0.871	26.23	70.33	2.02	0.85	2.41
8	69.87	2.93	0.893	29.42	69.65	2.99	0.86	3.61
16	65.62	8.84	0.981	42.17	65.03	9.4	1.197	44.22

Zero: one hour before storage Average, three injections

Table (4): photolysis of Camkron 72%EC (customs, workout) and their impurities exposed to sunlight for 16 hours.

Storage Periods (Days)	Camkron (customs)				Camkron (workout)			
	#Profenfos % w/v	Loss%	#4-bromo-2-chlorophenol	Increase %	#Profenfos % w/v	Loss%	#4-bromo-2-chlorophenol	Increase %
0	71.82	0.00	0.83	0.00	66.80	0.00	5.69	0.00
2	70. 96	1.41	0.88	6.02	65.63	1.75	6.09	7.03
4	70.62	1.67	0.91	9.64	55.39	17.08	7.38	29.70
8	70.1	2. 39	1.28	54.21	49.1	26.49	8.70	52.89
16	64.5	10.3	1.58	90.36	42.007	37.11	10.35	81.89

Zero: one hour before storage Average, three injections

Table (5): photolysis of Tiliton 72%EC (customs, workout) and their impurities exposed to UV-light for 16 hours.

Storage Periods (Days)	Tiliton (customs)				Tiliton (workout)			
	#Profenfos % w/v	Loss%	#4-bromo-2-chlorophenol	Increase %	#Profenfos % w/v	Loss%	#4-bromo-2-chlorophenol	Increase %
0	71.98	0.00	0.69	0.00	71.78	0.00	0.83	0.00
2	71.62	0.50	0.77	11.59	71.29	0.68	0.833	0.361
4	70.99	1.38	0.85	23.19	70.46	1.84	0.85	2.41
8	70.78	1.68	0.877	27.10	70.2	2.20	0.853	2.77
16	67.68	5.97	0.94	36.23	65.52	8.72	1.18	42.19

Zero: one hour before storage Average, three injections

Table (6): photolysis of Camkron 72% EC (customs, workout) and their impurities exposed to UV for 16 hours.

Storage Periods (Days)	Camkron (customs)				Camkron (workout)			
	#Profenfos % w/v	Loss%	#4-bromo-2-chlorophenol	Increase %	#Profenfos % w/v	Loss%	#4-bromo-2-chlorophenol	Increase %
0	71.82	0.00	0.83	0.00	66.80	0.00	5.69	0.00
2	71.15	0.93	0.87	4.82	66.0	1.2	6.02	5.79
4	70.67	1.60	0.913	10	59.6	10.78	6.741	18.45
8	69.5	3.2	0.978	17.83	49.03	26.6	8.17	43.59
16	66.27	7.73	1.043	25.66	42.81	35.91	9.42	65.5

Zero: one hour before storage
Average, three injections

Table (7): identification of profenofos (Tiliton) by using the IR spectrum.

groups	TC (custom)				TW (workout)			
	Before storage	After storage	Sun	UV	Before storage	After storage	Sun	UV
O-H	3443	3428	3415	3422	3446	3462	3449	3448
C-H	2963	2965	2955	2957	2964	2964	2966	2265
	2931	2933	2929	2930	2932	2934	2938	2936
	2874	2876	2875	2877	2875	2877	2876	2879
C=C	1473	1474	1470	1471	1474	1474	1475	1475
P-O	1253	1254	1255	1254	1253	1254	1255	1254
C-Cl	684	684	683	683	685	684	686	686
C-Br	630	629	628	628	629	629	630	631
P-S	923	924	925	924	923	924	925	924
R-OR	1026	1027	1028	1027	1029	1028	1029	1028

Table (8): identification of profenofos (Camkron) by using the IR spectrum

groups	KC (custom)				KW (workout)			
	Before storage	After storage	Sun	UV	Before storage	After storage	Sun	UV
O-H	3469	3425	3422	3423	3649	3559	3228	3228
C-H	2962	2965	2966	2965	2963	2963	2964	2963
	2930	2932	2929	2925	2931	2932	2931	2932
	2873	2875	2876	2875	2873	2874	2875	2874
C=C	1473	1474	1475	1474	1473	1472	1473	1473
P-O	1253	1254	1254	1254	-	-	-	-
C-Cl	685	685	685	685	683	684	686	685
C-Br	630	629	630	629	626	626	626	626
P-S	923	924	925	924	923	925	927	927
R-OR	1026	1027	1027	1027	1028	1029	1033	1027

Figure 1: illustrates the chemical structure of profenofos.

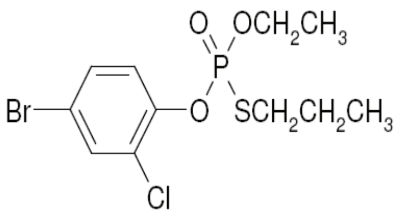


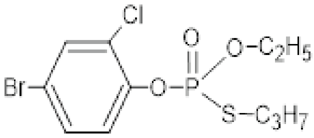
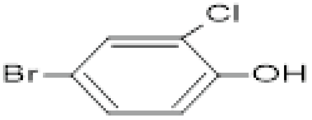
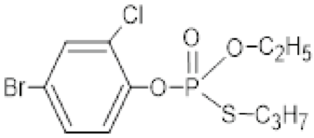
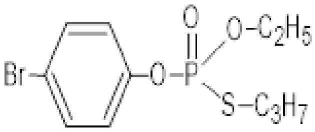
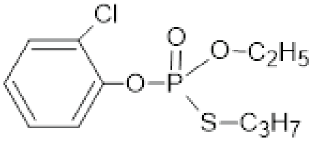
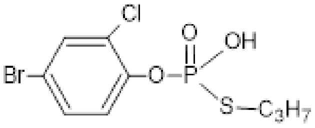
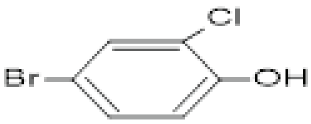
Figure. 1. profenofos (IUPAC Name: O-(4-bromo-2-chlorophenyl)- O-ethyl-S-propyl phosphorothioate: formula $C_{11}H_{15}BrClO_3PS$).

Camkron and Tiliton 72% EC (customs, workout).

The data of the four samples showed that no significant differences in profenofos and its impurity content before and after storage for 14 days at 54±2ºC, suggesting that the formulation is stable at 54±2ºC for 14 days where a percentage of active ingredient were within recommended specifications. Increase period of storage showed a significant increase in the rate of degradation for all sources and the loss percentages increased to reach 2.71, 4.57, 3.19 and 27.2 % for Tiliton (customs, workout) and Camkron (customs, workout), respectively.

The data in table 1 showed the effect of storage on

Table (9): Table (3). Identification of the degradation products of profenofos by GC-MS

storages periods	Characteristic ions (m/z)	Retention time(min)	Structure and Formula
Initial	Profenofos m/z=373.6	23.79	M.F: $C_{11}H_{15}BrClO_3PS$ 
	4-bromo-2- chlorophenol m/z=207.4	12.77	M.F: C_6H_4BrClO 
After Storage	Profenofos m/z=373.6	21.59	M.F: $C_{11}H_{15}BrClO_3PS$ 
	O-(4-bromophenyl) O-ethyl S-propyl phosphorothioate m/z=339	19.91	M.F: $C_{11}H_{16}BrO_3PS$ 
	O-(2-chlorophenyl) O-ethyl S-propyl phosphorothioate m/z=294.7	19.51	M.F: $C_{11}H_{16}ClO_3PS$ 
	O-(4-bromo-2-chlorophenyl) S-propyl hydrogen phosphorothioate m/z=345.5	13.36	M.F: $C_9H_{11}BrClO_3PS$ 
	4-bromo-2-chlorophenol m/z=207.4	10.51	M.F:C_6H_4BrClO 

M.F: Molecular Formula

Initial: One hour before storage

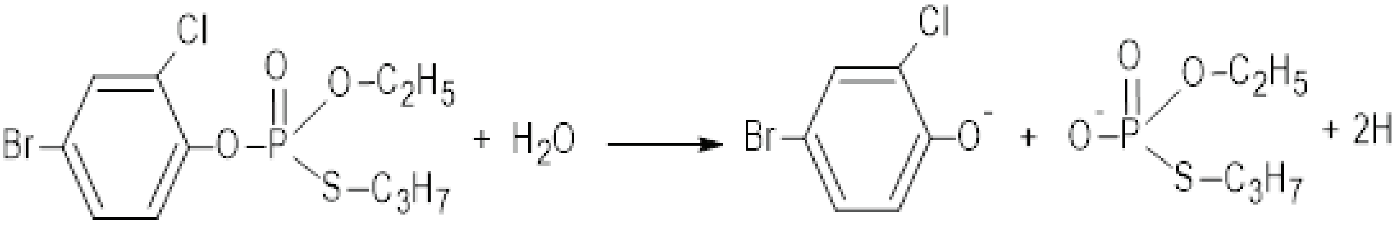


Figure. 2. hydrolysis of profenofos.

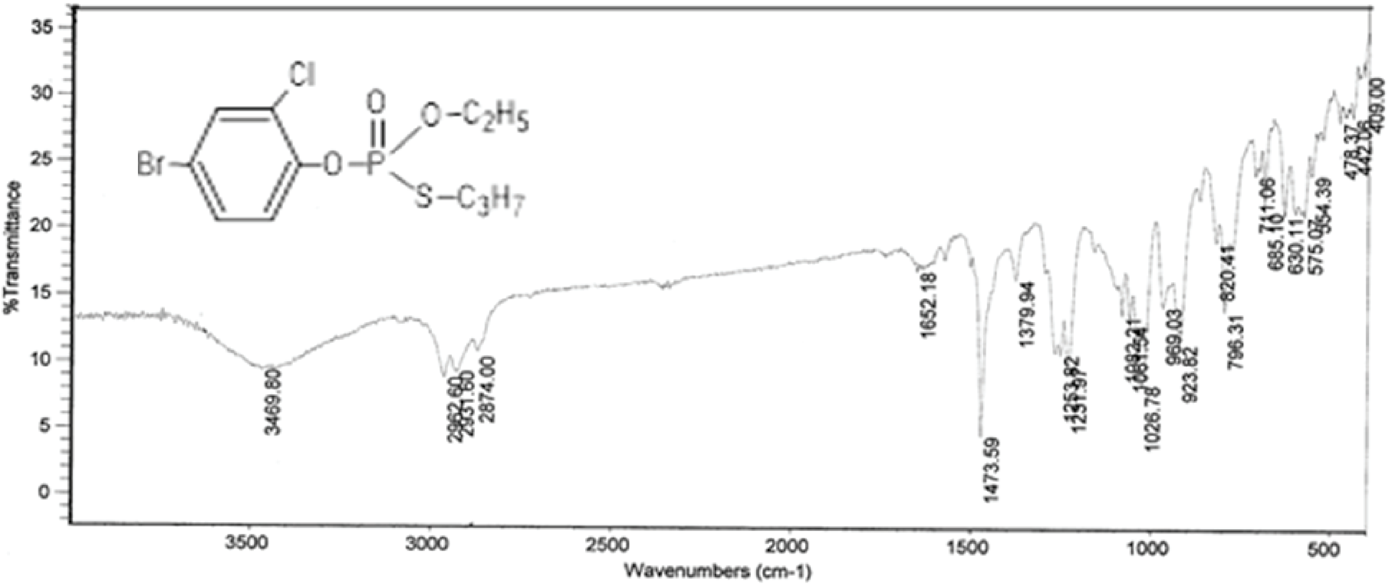


Figure (3) infrared spectrum of the produced during profenofos degradation.

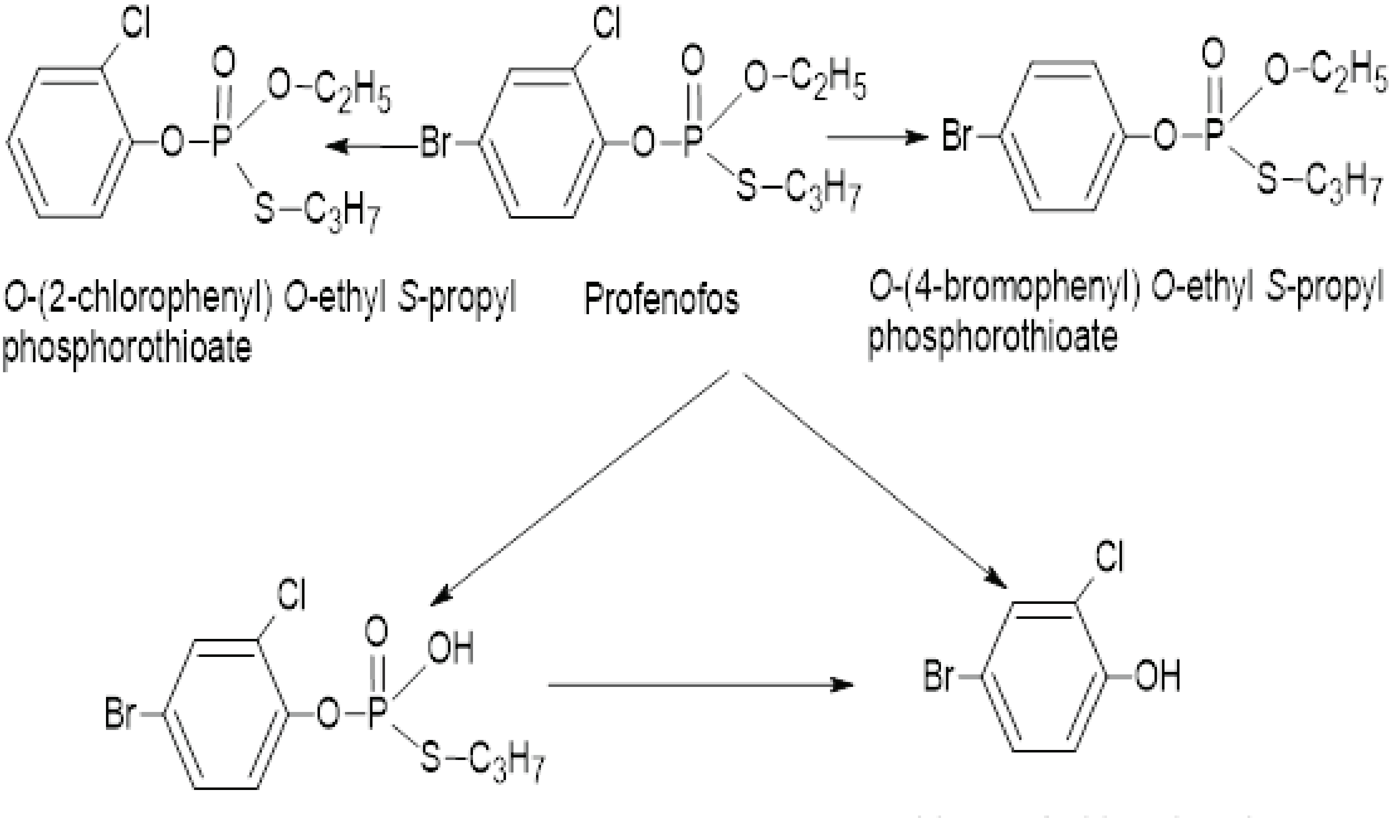


Figure (4). The degradation pathways of profenofos.

the amount of 4-bromo-2-chlorophenol at 54±2°C for the various study intervals. The amount of 4-bromo2-chlorophenol was within the FAO limits for all sources before storage except Camkron (workout), where the maximum level of 4-bromo-2-chlorophenol in profenofos samples is 1% of profenofos content, and the results showed that the amount of 4-bromo-2-chlorophenol before storage was 0.69, 0.83, 0.83 and 5.69 % for Tiliton (customs, workout) and Camkron (customs, workout), respectively, and there was a significant increase in the amount of 4-bromo-2-chlorophenol after storage after 14 days and the amount of 4-bromo-2-chlorophenol increased to 0.79, 0.95, 1.2 and 8.23 % for Tiliton (customs, workout) and Camkron (customs, workout), respectively as these values higher than the maximum allowed limits after storage for Camkron (customs, workout).

Effect of sunlight on profenofos 72%EC (customs, workout) and their impurities.

The data in Table (3, 4) showed the effect of the sunlight in 0, 2, 4, 8 and 16 hours of the commercial profenfos formulation under trade name Camkron and Tiliton 72%

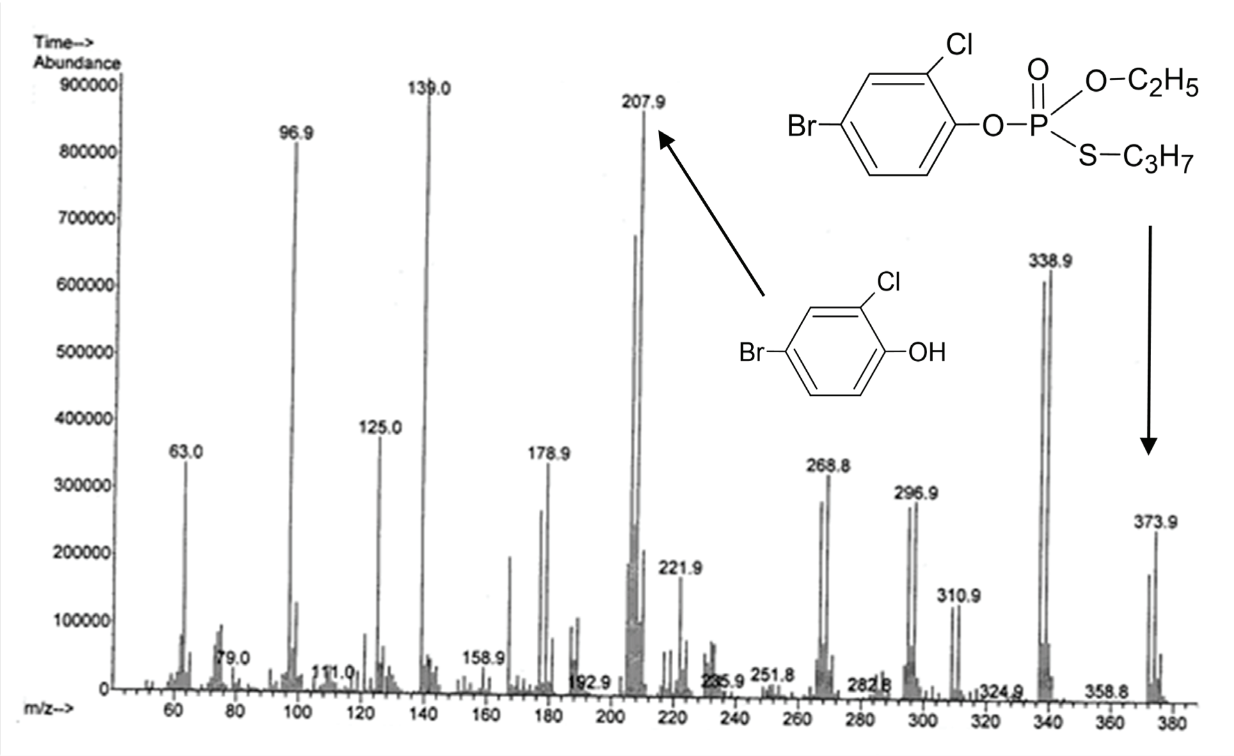


Figure (5) The possible degradation pathways of profenofos of storage, UV and sunlight.

EC (customs, workout) and the amount of 4-bromo-2-chlorophenol after exposure to sunlight.

The results indicated that the loss percentages at 16 hours were found to be 8.84, 9.4, 10.35 and 37.11 % for Tiliton (customs, workout) and Camkron (customs, workout), respectively.

From the data, we observed that Camkron (workout) was less stable. After 16 hours of exposure to sunlight, the amount of 4-bromo-2-chlorophenol increased to 0.981, 1.197, 1.58, and 10.35 percent for Tiliton (customs, workout) and Camkron (customs, workout), respectively.

The obtained results showed that the amount of 4-bromo-2-chlorophenol was more than the maximum allowed limits after storage for all sources except Tiliton (customs).

The previously mentioned results clearly showed that the rate of degradation of the profenofos [Tiliton and Camkron (customs, workout)] formulations under investigation and the amount of impurity were influenced by a long period of storage at 54±2°C as well as exposure to sunlight.

There is no significant difference in the rate of degradation for all profenofos formulations and the amount of 4-bromo-2-chlorophenol except profenofos from Camkron (workout), as it was observed that the rate of degradation was faster, and its stability was less than other sources of profenofos and the amount of 4-bromo-2-chlorophenol was greater than other sources, however, many factors influence these results, including the manufacturing process, starting material sources, adjuvants, chemical composition, exposure to air, light, and elevated temperature, as well as hydrolysis.

All these factors can also be affected by the degradation of profenofos, which increases the 4-bromo-2-chlorophenol content.

It was interesting to note that storing profenofos at 54±2°C for 14 days had a significant impact on the degradation rate of profenofos and increased the rate of formation of 4-bromo-2-chlorophenol as compared to exposure to sunlight.

Our findings are following (Ali and Lamia 2018) they stated that after exposure to heat and sunlight, profenofos degraded quickly than chlorpyrifos, even the results obtained consistent with several investigators (Burkhard and Guth 1979) and (Liu *et al*., 2019) reported that 4-bromo-2-chlorophenol is the main degradation product of profenofos and it can be formed via photolysis and hydrolysis (Capps *et al.,* 1996).

Effect of UV-light on profenofos 72%EC (customs, workout) and their impurities.

The effect of UV-light in 0, 2, 4, 8 and 16 hours on profenofos formulation under trade name Camkron and Tiliton 72% EC (customs, workout) and the amount of 4-bromo-2-chlorophenol were tabulated in the table (5, 6). The results indicated that the loss percentages at 16 hours were found to be 5.97, 8.72, 7.73 and 35.91 % for Tiliton (customs, workout) and Camkron (customs, workout), respectively. From the data, we observed that Camkron (workout) was degraded faster in this respect.

There was also an increase of 4-bromo-2-chlorophenol after exposure to UV-light for 16 hours and an increase of 4-bromo-2-chlorophenol to 0.94, 1.18, 0.913 and 1.18 % for Tiliton (customs, workout) and Camkron (customs, workout) respectively.

The obtained results showed that the amount of 4-bromo-2-chlorophenol was more than the maximum allowed limits after 16 hours for Tiliton and Camkron (workout).

Photodegradation with UV-rays was generally positively correlated with the exposure period. These results are those obtained by (El-Sayed *et al*., 1980; Abdel-Razik *et al*., 1982b; Abu-Zahw *et al*., 1988; Abdel-Baki *et al*., 1999 and Hegazy *et al*., 2001).

Effect of storage on the emulsion stability.

The result showed that emulsion stability of the commercial profenfos formulation under trade name Camkron and Tiliton (customs, workout) were obtained from three different companies for three groups. The first group Camkron (workout) from Kam Agrochemical, the second group Camkron (customs) from cam factory and the third group Tiliton (customs, workout) from Agrochemical after 14 days of storage at 54±2°C.

The formulation, when diluted at 30±2°C with CIPAC standards A and D shell comply with the specification of profenofos emulsifiable concentrate. Results indicated that profenofos formulation passed successfully through emulsion stability before and 14 days. Except for camkron (workout) manufacture from cam Agrochemical, it is found that level of cream and precipitate layer exceed 2 ml at the bottom cylinder after 30 minutes. The maximum level of cream and precipitate layer after 30 minutes of dilution does not exceed around 2ml, according to JMPS FAO/WHO definition (2010).

Effect of storage at 54 ±2°C on PH value for profenofos 72% EC formulation.

It is found that PH of Tiliton 72% EC (customs, workout) and Camkron 72% EC customs were 3.82, 3.75 and 3.76, respectively before storage and change to 3.80, 3.72, 3.75 after 14 days of storage.

According to FAO specification (1997) which reported that PH range for profenofos 72% EC from 3 to 7 the tested profenofos 72% EC formulation pass successfully. Except for PH of camkron (workout) from Kam Agrochemical was 2.27 and changed to 2.22 after 14 days of storage.

The potential of hydrogen (PH) can show the stability of the emulation concentration (EC) during the storage period. The change in PH in long period cause breakdown of the active substance instability of some component. When the formulation is exposed to high temperature may exhibit accelerated degradation, change in physical, chemical properties and it also affects emulsification capacity (i.e emulsion concentrate) this result is in harmony with Lawrence and Ree (2012); Khalifa *et al*., (2017).

Finally, from the results obtained from the effects of exposure to sunlight, UV-light, PH and storage on the stability of profenofos [Tiliton and Camkron (custom, workout)], Camkron (workout) was found to be invalid for use because of the manufacturing process, the source of technical materials, the use of various types of adjuvants and the extended storage time in poor conditions.

Other impurities consisted primarily of profenofos analogues produced from other 4-bromo-2-chlorophenol ring-halogenated phenols used as the starting material for the development of profenofos (Al Deen *et al*., 2002).

Effect of storage at 54 ±2°C on the water as relevant impurities for profenfos 72%EC.

Water content was undetectable for Tiliton 72% EC (custom, workout) and camkron 72% EC (custom), while camkron (workout) was 0.683%. the presence of water in the formulation change of surfactant during the storage period, wherein part of surfactant distributes from interference to aqueous phase leading to decrease in the correlation of the essential oil, surfactant and solvent cause an increase in the particles.

The more amount of the water finds that degradation of the profenofos into 4-bromo-2-chlorophenol is the main degradation in Fig. 2 and it can be formed from the results found the Camkron (workout) is invalid for use this is agreed with (Ali and Lamia 2018) and biodegradation (Talwar and Ninnekar 2015).

Identification of profenofos in infrared.

Table (7, 8) and Fig. 3 found Broad strong bands at 3228-3649 cm^{-1} are due to O-H stretching vibration for profenofos [Tiliton and Camkron (custom, workout)]. Also it clear that C-H aliphatic and aromatic appeared are three strong bands one for methyl at 2955-2966 cm^{-1}, second for methylene at 2925-2938 cm^{-1} and third for methane at 2873-2879 cm^{-1} corresponding to asymmetrical and symmetrical banding vibration of methylene group for propenofos.

The C=C stretching vibration heteroaromatic compound was observed in the region 1470-1475 cm^{-1} and C-Br at 623-627 cm^{-1}. On the other hand, it was noticed from these findings that the P-O bond appears at 1253-1255 cm^{-1} in the [Tiliton (custom, workout) and Camkron (custom) but in Camkron (workout) was broken due to the presence of excess water in this pesticide from Fig. 2 found 4-bromo-2-chlorophenol is the main degradation of the profenofos and it can be formed by photolysis are in agreement with (Ali and Lamia 2018) and biodegradation (Talwar and Ninnekar 2015).

Identification of profenofos by chemical ionization GC/MS spectroscopy.

Results from the GC-MS study are shown in Table 9 and Fig. (4,5) to classify the degradation products of profenofos before and after the effect of storage, UV-light and sunlight and We found all give the same degradation. The following degradation products were observed i.e, profenofos m/z=373.9, found was identified as O-(2-chlorophenyl) O-ethyl S-propyl phosphorothioate m/z=294.7, formed by reductive debromination, O-(4-bromophenyl) O-ethyl S-propyl phosphorothioate m/z=339 formed by reductive dechlorination, O-(4-bromo-2-chlorophenyl) S-propyl hydrogen phosphorothioate m/z=345.5 and 4-bromo-2-chlorophenol m/z=207.4. All the previous reactions can be explained in Fig. 2 where shows the possible degradation pathways of profenofos.

Data also in Table (9) show that Rt of a breakdown product of profenofos was before storage 23.79 minutes and after 14 days of storage was 21.59 minutes was easily degradation into 4-bromo-2-chlorophenol that Rt was before storage 12.77 minutes and after 14 days of storage was 10.51 minutes.

This bond quickly cleavage contributes to the formation of 4-bromo-2-chlorophenol, depending on the type of the chemical structure of profenofos it contains an O-P bond. Hydrolysis and photolysis and cleavage of the phosphorothioate ester bond will easily degrade Profenofos to 4-bromo-2-chlorophenol this result is in harmony with (Capps *et al*., 1996; Zamy *et al*., 2004, Ma *et al*., 2019 and Liu *et al*., 2019). 4-bromo-2-chlorophenol is the main degradation of the profenofos and it can be formed by photolysis (Ali and Lamia 2018) and biodegradation (Talwar and Ninnekar 2015).

CONCLUSIONS

Compared to exposure to UV-light, sunlight and PH, Profenofos was affected by storage at 54±2^{o}C for 14 days, which caused an increase in the rate of degradation and the amount of its impurity of 4-bromo-2-chlrophenol. Profenofos can be degraded into some degradation products by hydrolysis and photolysis and 4-bromo-2-chlrophenol is the key degradation product of profenofos. It was found that Camkron (workout) is invalid for use because it may be due to several factors affecting the consistency of the formulation of profenofos in the manufacturing process, the origins of technical materials, the use of various forms of adjuvants and the long storage time in poor conditions.

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