EFFECT OF DIRECT SUNLIGHT AND UV-RAYS ON DEGRADATION OF BUPIRIMATE, PENCONAZOLE AND PROFENOFOS.

Makram. A. Sayed, Ibrahim. H. Hussein and Mohammed. A. Mahfouz.
Plant Production Dept., Faculty of Agric., Fayoum Univ., Egypt

ABSTRACT

The exposure to sunlight, UV-rays led to the degradation of the pesticides formulations (Namrod 25% EC) bupirimate, (Agrozole 10% EC) penconazole and (Actacron 72% EC) profenofos. Their residues were determined by high performance liquid chromatography (HPLC). The results showed that exposure to direct sunlight in (Winter at the morning) was more effective in degradation of the tested pesticides than exposure to direct sunlight in (Winter at the evening) for 4 hours. The percentage residue of bupirimate, penconazole and profenofos were 18.24, 48.52 and 19.26 % in winter at the morning, respectively. Therefore, bupirimate was the highest affected by this treatment. Also, the data showed that exposure to direct sunlight in (Summer at the evening) was more degraded than exposure to direct sunlight in (Summer at the morning) for 4 hours. The percentage residue of bupirimate, penconazole and profenofos were 11.14, 15.45 and 7.72 % after 4 hours in (Summer at the evening), respectively. Therefore profenofos was more degraded than other pesticides. In general the degradation of the tested pesticides in summer was higher than winter. Withal, the data demonstrated that the exposure to UV-ray at distance 22.5 cm was more effective in degradation of the three tested pesticides than exposure to UV-ray at distance 45 cm for 4 hours where, the percentage residue of bupirimate, penconazole and profenofos were 17.08, 39.56 and 15.00 % after 4 hours of exposure to UV-ray at distance 22.5 cm respectively, and therefore profenofos was the highest degraded in the three pesticide in the same period of exposure to UV-ray.

Keywords: *Sunlight, UV-Rays degradation, bupirimate, penconazole, profenofos.*

INTRODUCTION

Pesticides are widely used in agriculture against insects, weeds and other agriculture pests to increase crop productivity. This pesticides use increased after World War II in order to increase world food production. Since, there has been a marked development of different types of pesticides belonging to various chemical groups **(Dipakshi *et al*., 2010).** Wide range of insecticides, including organophosphates, carbamates, pyrethroids and others, have been used on vegetable crops. In developing countries, these chemicals are too expensive for farmers and are often ineffective against sap sucking pests **(Christou and Capell 2009).** An important consideration in the choice of insecticides for crop protection is how long which the toxic residues will persist on foliage or reproductive tissue, as well as in soils **(Raha *et al*., 1993).** Also there presence in the atmosphere as a result of direct and indirect emission through dispersion during spraying operations, volatilisation from ground or leaf surfaces, and by wind erosion **(Sauret *et al*., 2000).** Therefore, there are some ways to eliminate of these chemicals: photodegradation is an abiotic process in the dissipation of pesticides where molecular excitation by absorption of light energy results in various organic reactions, or reactive oxygen species such as OH*, O_3 and $^1O_2$ specifically or none specifically oxidize the function groups in a pesticide molecule **(Katagi., 2004).**

The influence of the climatic factors on pesticides breakdown is extremely complex. This chemical process is affected by changes in heat and light. Photolysis occurs where the radiant energy in the form of photons breaks the chemical bonds of molecule. The UV component of sunlight range 240-400 nm is responsible for pesticide photolysis in the environment. Both heat and light affect the efficiency of pesticide which are measured by the duration of their residual effect **(Burrows *et al.*, 2002).**

Sunlight photo degradation is one of the most destructive pathways for pesticides after their release in to the environment **(Soliman, 2011).** All kinds of pesticide are subject to photolysis to some extent. Factors affecting pesticide photolysis are intensity of sunlight, time of exposure, the properties of the sites, the method of application, and the properties of pesticides **(Al-Mamun, 2017)**.

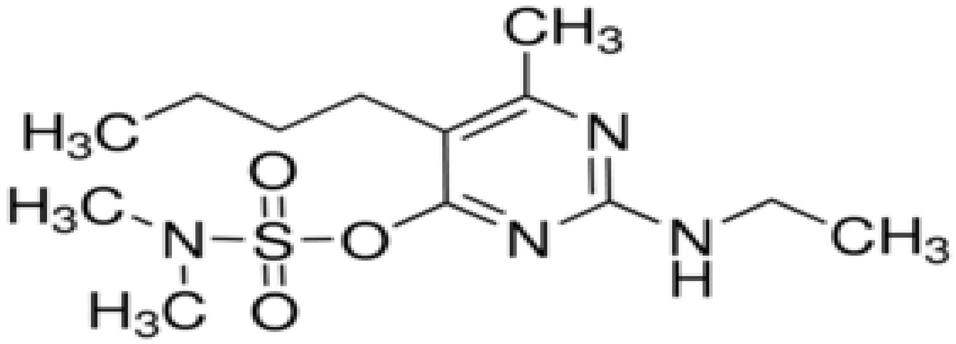
Ultraviolet light is a very high source of energy that promotes the breakdown of many chemicals. Most of the pesticides we use today are somewhat subject to photodecomposition. **(Emara and Shereen, 2010).**

This study was carried to know the effect of sunlight and UV rays on the degradation of three pesticides, bupirimate, penconazole and profenofos.

MATERIALS AND METHODES

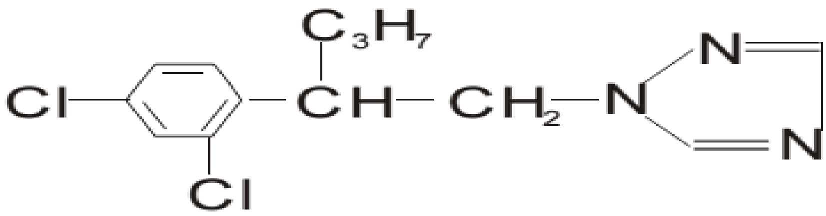
1-Pesticides used: - Three pesticides were used in the present study.

Bupirimate: - structure formula:

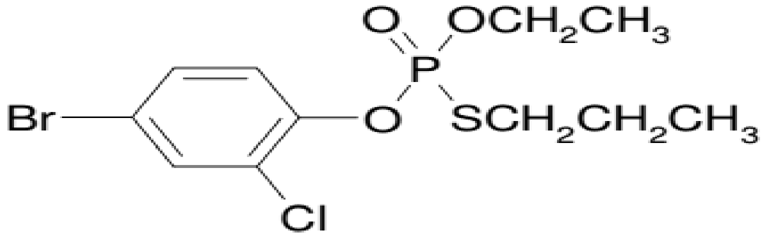


IUPIC name: 5-butyl-2-ethylamino-6-methylpyrimidin-4-yl dimethyl sulfamate
Chemical class: pyrimidine
Molecular weight: 316.4
Trade name: Nimrod 25% EC
CAS No.: 41483-43-6

penconazole:- l structure formula:



IUPIC name: 1-(2, 4-dichloro-β-propylphenethyl)-1H-1, 2, 4-triazole ()
Chemical class: Triazole
Molecular weight: 284.18
Trade name: Agrazole 10% EC
CAS No.:66246-88-6
Profenofos:- structure formula:



IUPIC name: O – 4 – bromo – 2 – chlorophenyl O – ethyl S-propyl phosphorothioate
Chemical class: organophosphate
Molecular weight: 373.6 g/mol
Trade name: Actacron 72% EC
CAS No.: 41198-08-7

2- Effect of environmental conditions on the degradation of bupirimate, penconazole and profenofos:

The concentrations were prepared in acetone as follows, 25, 50 and 100 µg/ml for bupirimate, 6.25, 12.5 and 25 µg/ml for penconazole and 684, 1368 and 2736 µg/ml for profenofos. One ml from each concentration was spreaded in petri dish surface (10 cm diameter) with three replicates. The acetone solvent was left to dry at room temperature. These groups of concentrations were repeated as needed for each experiment.

2.1. Impact of sunlight:

A group of the treated petri dishes of each pesticide is exposed to direct sunlight in the summer (August) for 4 hours at the morning and evening, with temperature averages were 39.5 and 44 ºC respectively. The same experiment repeated in the winter (December) for 4 hours at the morning and evening, with temperature averages were 30 and 29 ºC respectively. Another group was left without exposer away from a light source at ambient temperature in winter 16 ºC and in summer 28 ºC as control.

2.2. Impact of UV- ray:

A second group of the treated petri dishes of pesticides is exposed to short wave length of an ultraviolet lamp (253.7-254 nm) produced by company Philips T UV 15 W-G 15 T8, 2.8 cm diameter and 45 cm length made in Holland. The exposure to UV- ray was applied at two distances, 22.5 and 45 cm from the ultraviolet lamp.

3. Pesticides extraction:

Residues of bupirimate, penconazole and profenofos were dissolved in 1 mL hexane and repeated 3 times and quantitatively transferred to glass test tubes and the solvent was evaporated in air to dryness. The residues were transferred quantitatively by 1ml of acetonitrile into brown vials for determination by high performance liquid chromatography (HPLC).

4. Pesticide residues determination:

Determination of pesticide residues, bupirimate, penconazole and profenofos using an Agilent model 1260 HPLC system equipped with quaternary pump and UV visible detector / G 1315 D. C_{18} analytical column (100 mm ×4.6mm× particle size 3.5µm). All solvents used HPLC grade and properly degassed using sonicator and filtered through 0.45µ nylon filter medium before use. The HPLC conditions of bupirimate were according to the method of Wang *et al*., (2000) with some modifications, the mobile phase consisted of acetonitrile and water (70+30, v/v) instead of (55+45, v/v) and flow rate 1ml/min with injection volume 20 µl and a UV detector set up at 200 nm and external standard was used to identify and quantify bupirimate residues in sample. The HPLC conditions of penconazole were according to the method of Monaci *et al*., (2011) with some modifications, the mobile phase consisted of acetonitrile and water (60+40, v/v) and flow rate 1ml/min with injection volume 10 µl instead of 20 µl and a UV detector set up at 205 nm and external standard was used to identify and quantify penconazole residues in samples. The HPLC conditions of profenofos were according to the method of Habiba *et al*., (1992) with some modifications, the mobile phase consisted of acetonitrile and water (90+10, v/v) instead of (60+40, v/v) and flow rate 1ml/min instead of 0.7 ml/min with injection volume 10µl and detected by UV absorbance at 254 nm and external standard was used to identify and quantify profenofos residues in samples.

RESULTS AND DISCISSION

1. Impact of sunlight on degradation of the tested pesticides:

1.1. Impact of sunlight in winter at morning and evening:

The results in Table (1) showed that the residue of the three tested pesticides decreased greatly after 4 hours of exposure to the sun in winter-morning, The percentage of residues of bupirimate decreased 24.48, 16.72 and 13.51% from initial concentrations (0.318, 0.637 and 1.274 µg/cm^2), respectively. The percentage of residues of penconazole decreased 38.72, 45.92, and 60.91% from initial concentrations (0.080, 0.159 and 0.318 µg/cm^2), respectively. Also, the percentage of residues of profenofos was reduced 20.38, 19.49 and 17.92% from three initial concentrations (8.713, 17.427 and 34.853 µg/cm^2), respectively.

Table (1): Effect of sunlight in winter at morning and evening along 4 hours on the degradation of bupirimate, penconazole and profenofos.

Pesticides	Initial Conc. µg/cm^2	Sunlight (9-1 o'clock		Sunlight (1-5 o'clock)		Control	
		Conc. (µg/cm^2)		Conc. (µg/cm^2)		Conc. (µg/cm^2)	
		Mean±SE*	Residue (%)	Mean±SE	Residue (%)	Mean±SE	Residue (%)
Bupirimate	0.318	0.078±0.002	24.48	0.082±0.006	25.69	0.305±0.005	95.92
	0.637	0.106±0.004	16.72	0.135±0.007	21.22	0.599±0.009	94.06
	1.274	0.172±0.005	13.51	0.209±0.022	16.39	1.205±0.014	94.61
Penconazole	0.080	0.031±0.001	38.72	0.040±0.004	50.56	0.074±0.002	92.32
	0.159	0.073±0.011	45.92	0.088±0.003	54.69	0.151±0.003	95.12
	0.318	0.194±0.021	60.91	0.202±0.011	63.40	0.303±0.001	95.04
Profenofos	8.713	1.775±0.038	20.38	3.242±0.161	37.20	8.274±0.196	94.95
	17.427	3.397±0.235	19.49	7.576±0.405	43.47	16.524±0.503	94.82
	34.854	6.246±0.171	17.92	12.583±0.701	36.10	33.135±0.843	95.07

*SE= Standard error.

The data in Table (1) showed that the residues of the three tested pesticides decreased considerably after 4 hours of exposure to the sun in winter-evening. Percentage of the residues of bupirimate decreased to 25.69, 21.22 and 16.39 % from initial concentrations, respectively. The percentage of the residues of penconazole decreased 50.56, 54.96 and 63.40 % from initial concentrations, respectively. Also, percentage of the residues of profenofos decreased to 37.20, 43.47 and 36.10% from initial concentrations, respectively. While the percentage of degradation does not exceed 6% in the dishes were placed in the dark in morning or evening for the same periods. The previous results appeared that the rate of degradation in winter-morning was more effective than winter-evening for all tested pesticides. Also, the photodecomposition rate of bupirimate was more rapid than the other two tested pesticieds. These results were consistence with **(Fred, 1997, Eissa *et al*., 2006, Kralj *et al.*, 2007, Hu *et al.*, 2009, Soliman, 2011, Radwan and El-Shiekh, 2012, Cao *et al.*, 2013, Verma *et al.*, 2014, and El Boukili *et al.*, 2018),** whom reported that exposure to sunlight lead to a significant impact on pesticide degradation. Sunlight photo degradation is one of the most destructive pathways for pesticides after their release into the environment. Factors that influence pesticide photodegradation include the intensity of the sunlight; properties of the application site, the application method and the properties of the pesticide.

1.2. Impact of sunlight in summer at morning and evening:

The data in Table (2) showed that, the residues of the three tested pesticides decreased considerably after 4 hours of exposure to the sun in summer- morning. The percentage of residues of bupirimate decreased to 20.44, 14.31and 10.46% from initial concentrations, respectively. And the percentage of residues of penconazole decreased to 18.72, 18.80 and 19.28 % from initial concentrations, respectively.

Also, the percentage of the residues of profenofos decreased 12.07, 7.99 and 5.34% from initial concentrations, respectively.

The results in Table (2) showed that the residue of the three tested pesticides decreased considerably after four hours of exposure to sunlight in summer-evening. The percentage of the residues of bupirimate decreased to 16.56, 8.80 and 8.05% from initial concentrations, respectively. Also, the percentage of the residues of penconazole decreased to 14.24, 16.80 and 15.32% from initial concentrations respectively. Withal, the percentage of the residues of profenofos decreased to 11.29, 7.20 and 4.68% from initial concentrations, respectively. While the percentage of degradation of the three tested pesticides does not exceed 9.5% in the dishes that were placed in the dark in morning or evening for the same periods. The previous results appeared that the rate of degradation in summer-evening was higher than summer-morning for the three tested pesticides. The photodecomposition rate of profenofos was more rapid than the other two tested pesticides when exposed to sunlight in summer morning or evening. This finding agrees with **Ishag *et al.*, (2019) and El Boukili *et al.*, (2018).**

Table (2): Effect of sunlight in summer at morning and evening along 4 hours on the degradation of bupirimate, penconazole and profenofos.

Pesticides	Initial Conc. µg/cm^2	Sunlight (9-1 o'clock)		Sunlight (1-5 o'clock)		Control	
		Conc. (µg/cm^2)		Conc. (µg/cm^2)		Conc. (µg/cm^2)	
		Mean±SE*	Residue (%)	Mean±SE	Residue (%)	Mean±SE	Residue (%)
Bupirimate	0.318	0.065±0.003	20.44	0.053±0.003	16.56	0.290±0.009	91
	0.637	0.091±0.003	14.31	0.056±0.002	8.80	0.577±0.013	90.66
	1.274	0.133±0.013	10.46	0.103±0.004	8.05	1.146±0.019	89.79
Penconazole	0.080	0.015±0.002	18.72	0.011±0.0004	14.24	0.072±0.003	90.40
	0.159	0.030±0.0001	18.80	0.027±0.001	16.80	0.146±0.003	91.60
	0.318	0.061±0.012	19.28	0.049±0.001	15.32	0.291±0.004	91.48
Profenofos	8.713	1.051±0.089	12.7	0.984±0.104	11.29	8.002±0.328	91.84
	17.427	1.392±0.126	7.99	1.255±0.110	7.20	16.011±0.535	91.88
	34.854	1.862±0.049	5.34	1.631±0.216	4.68	31.836±0.767	91.34

*SE= Standard error.

2. Impact of UV ray:

The results in Table (3) showed that the residues of bupirimate, penconazole and profenofos decreased appreciably after 4 hours of exposure to ultraviolet radiation at distance 45cm. The percentage of residue of bupirimate decreased to 32.44, 27.92 and 21.91%, respectively. The percentage of residue of penconazole decreased to 57.12, 61.52 and 64.08%, respectively. In addition, the percentage of residue of profenofos decreased according to the three concentrations 17.42, 18.96 and 16.30%, respectively. Also, the results indicate that the residues of the three tested pesticides decreased appreciably after 4 hours of exposure to ultraviolet radiation at distance 22.5 cm, the percentage of residue of bupirimate decreased to 23.68, 16.16 and 11.39%, respectively. The percentage of residue of penconazole decreased to 32.64, 41.44 and 44.60%, respectively. In addition, the percentage of residue of profenofos decreased to

16.46, 15.48, and 13.06%, respectively. While the percentage of degradation of the three tested pesticides does not exceed 6% in the dishes that were placed in the dark for the same periods. This data in Table (3) were convenient with **Eissa *et al.*, (2006)** they showed that the rate of degradation of

two pesticides (cadusafos- carbofuran) exposed as thin film in uncovered petri dishes to irradiation of UV (254 nm) varied according to their chemical structure as well as time of exposure to UV-rays.

It can be concluded that the rate of degradation of the tested pesticides at a distance of 45 cm was less than the rate of degradation at a distance of 22.5 cm. Also, the photodegradation rate of profenofos was more rapid than the other two tested pesticides. The results were harmonious with **(Schwack and Hartmann, 1994, Bourgine *et al*., 1995, Moza *et al.*, 1998 and Santoro *et al*., 2000).**

The present results are in line with **(Raikwar and Nag, 2006, Senthilnathan and Philip, 2009, Durkic *et al.*, 2017, Nadia *et al.*, 2018 and Akbari and Shokri, 2017)** whom reported that the degradation rate of the imidacloprid rises by increasing the UV light intensity due to the decrease in the distance of light source from the surface of the solution. Could be attributed to the acceleration of electron– hole generation by increasing light intensity, which causes an increase in the amount of produced hydroxyl radicals and eventually raises the photocatalytic degradation of the pollutant.

Table (3): Effect of UV ray at wave length 254 nm at distance of 22.5 and 45 cm for 4 hours on the degradation of bupirimate, penconazole and profenofos.

Pesticides	Initial Conc. μg/cm^2	45 cm Conc. (μg/cm^2)		22.5 cm Conc. (μg/cm^2)		Control Conc. (μg/cm^2)	
		Mean±SE*	Residue (%)	Mean±SE	Residue (%)	Mean±SE	Residue (%)
Bupirimate	0.318	0.103±0.016	32.44	0.075±0.009	23.68	0.302±0.005	94.68
	0.637	0.178±0.009	27.92	0.103±0.035	16.16	0.597±0.009	93.76
	1.274	0.279±0.006	21.91	0.145±0.012	11.39	1.188±0.011	93.27
Penconazole	0.080	0.045±0.005	57.12	0.026±0.001	32.64	0.074±0.002	93.44
	0.159	0.098±0.010	61.52	0.066±0.006	41.44	0.150±0.004	94.16
	0.318	0.204±0.013	64.08	0.142±0.012	44.6	0.301±0.003	94.36
Profenofos	8.713	1.518±0.103	17.42	1.434±0.105	16.46	8.358±0.143	95.93
	17.427	3.304±0.271	18.96	2.698±0.250	15.48	16.722±0.258	95.96
	34.853	5.681±0.310	16.30	4.550±0.553	13.06	32.978±0.569	94.62

*SE= Standard error.

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تأثير ضوء الشمس والاشعة الفوق بنفسجية علي هدم الببريمات والبنكونازول والبروفينوفوس

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قسم وقاية النبات- كلية الزراعة- جامعة الفيوم

الملخص العربي

في هذه الدراسة تم اختبار تأثير التعرض لأشعة الشمس والأشعة الفوق بنفسجية على تدهور المبيدات الثلاثة وهي: نمرود ٢٥٪ مركز قابل للاستحلاب (الببريمات) و أجروزول١٠٪ مركز قابل للاستحلاب (البنكونازول) واكتاكرون٧٢٪ مركز قابل للاستحلاب (البروفينوفوس)، وتم تقدير بقاياها بواسطة جهاز الكروماتوجرافي السائل عالي الأداء. وقد أظهرت النتائج أن التعرض لأشعة الشمس المباشرة في (الشتاء صباحاً) كان أكثر فاعلية في تدهور المبيدات الثلاثة المختبرة من التعرض لأشعة الشمس المباشرة في (الشتاء مساءاً) لمدة ٤ ساعات، حيث كانت النسبة المئوية لبقايا الببريمات والبنكونازول والبروفينوفوس ١٨.٢٤ و ٤٨.٥٢ و ١٩.٢٦٪ بعد ٤ ساعات في (الشتاء صباحاً) على الترتيب، وبالتالي كان مبيد الببريمات الاعلى هدماً في المبيدات الثلاثة في نفس الفترة. كما أظهرت النتائج ايضا أن التعرض لأشعة الشمس المباشرة في (الصيف مساءاً) كان أكثر فعالية في تدهور المبيدات الثلاثة المختبرة من التعرض لأشعة الشمس المباشرة في (الصيف صباحاً) لمدة ٤ ساعات، حيث كانت النسبة المئوية لبقايا الببريمات والبنكونازول والبروفينوفوس ١١.١٤ و ١٥,٤٥ و ٧.٧٢٪ بعد ٤ ساعات في (الصيف مساءاً) على الترتيب، وبالتالي كان مبيد البروفينوفوس الاعلى تدهورا في المبيدات الثلاثة في نفس الفترة. وهكذا كان تدهور المبيدات الثلاثة في فصل الصيف أعلى من فصل الشتاء. كما أظهرت النتائج أن التعرض للأشعة الفوق بنفسجية على مسافة ٢٢.٥ سم كان أكثر فعالية في تدهور المبيدات الثلاثة المختبرة من التعرض للأشعة الفوق بنفسجية على مسافة ٤٥ سم لمدة ٤ ساعات، حيث كانت النسبة المئوية لبقايا الببريمات والبنكونازول والبروفينوفوس ١٧.٠٨ و ٣٩.٥٦ و ١٥ ٪ بعد ٤ ساعات من التعرض للأشعة الفوق بنفسجية على مسافة ٢٢.٥سم على الترتيب ، وبالتالي كان مبيد البروفينوفوس الاعلى تدهوراً في المبيدات الثلاثة في نفس الفترة من التعرض للأشعة الفوق بنفسجية.

الكلمات الدالة :اشعة الشمس، الاشعة الفوق بنفسجية، تدهور، ببريمات، بنكونازول، بروفينوفوس.