RESIDUES OF FENOBUCARB INSECTICIDE ON AND IN TOMATO FRUITS WITH FOCUSING ON ITS PHOTO AND THERMAL DEGRADATION

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Abstract

The present investigation was carried out to determine the residues of the insecticide fenobucarb on and in tomato fruits with referring to the effect of washing process in eliminating residues from fruit surface. Photo and thermal degradation with some environmental factors namely UV-rays, direct sunlight and different temperature degrees was performed. Recovery rate of fenobucarb residues was carried out on tomato fruits at the level of 1ppm and the rate of recovery average was 95.5%.

Tomatoes were planted and treated with fenobucarb at the recommended rate 312cm^3 per feddan under the normal Egyptian field conditions

The initial deposit of fenobucarb on and in tomato fruits was 8.07ppm and the obtained residue half-life value ($t_{1/2}$) was 24 hours. Washing process removed 67.70% of the initial deposit remained on tomato fruits. The calculated half-life periods were 4 and 3.8 hours when exposed to UV-rays and sunlight, respectively. The results showed that fenobucarb was degraded more rapidly at high temperature degrees than the lower degrees. The half-life periods were 37, 24, 17 and 5 hours at 30, 35, 45 and 50ºC, respectively.

INTRODUCTION

Pesticides remain the most important means used in controlling the majority of the agriculture pests which attacks vegetables and fruits. The potential risks from pesticides use and abuse are of importance to be under focus to protect human health and environment. Pesticides are belonging to many different chemical groups, Fenobucarb is an insecticide of the common carabamate group which plays a vital role in controlling insect pests in Egypt. Tomato (*Lycopersicon esculentum*) is one of the most important vegetable crops in Egypt even for nutrition or industry.

The present investigation aimed to determine the persistence of Fenobucarb residues on and in tomato fruits with regarding to the effect of washing process with tap water in removing residues remained on fruits, also through a beam of light on the photo and thermal degradation behaviour with some of the environmental factors, namely UV-rays, direct sunlight and different temperature degrees.

MATERIALS AND METHODS

1- Insecticide used

Fenobucarb (osbac50% EC)

Chemical name: 2-(1-methyl propyl) phenyl methyl carbamate).

2-Field experiments

Tomatos were planted at Kafr Shokr, El-Kalyoubia Governorate, Egypt on june 5, 2007 in plots of 0.01 feddan. Tomato plants were treated with fenobucarb (Osbac 50%) 40 days after planting. Untreated plot was left as control check.

1- Sampling

Three replicate samples of treated and untreated tomato fruits were randomly picked up one hour after pesticide treatment and then after 1,3,5,7,14,21 and 28 days for residues estimation. Samples of zero time, one day and three days were divided into two parts, one part was washed thoroughly by running tap water to study the effect of washing on the percentages loss of insecticide residues. The other part was kept unwashed for normal residue analysis and the all samples of washed, unwashed and control check were kept in polyethylene bags at -20ºC until time of residues analysis.

4-Residue analysis techniques

4-1-Extraction

Samples were left out to reach room temperature then macerated using warning blender. Hundred grams of each sample were placed in the blender, then 200 ml of methylene chloride and 20 gram anhydrous sodium sulfate were added to the blender and mixed thoroughly for 3 min., then filtered through a dry pad of cotton and anhydrous sodium sulfate into a graduated cylinder. The filtrates were concentrated to dryness at 40ºC using a rotary evaporator. (Anonymous, 2002).

4-2- Clean up

The residues were dissolved in 5 ml methanol and cleaned up according to the technique of (Johnson, 1963) using Co- agulation solution (0.5 gm ammonium chloride and 1 ml 85% orthophosphoric acid dissolved in 400 ml distilled water). The residues were dissolved in 5ml methanol thoroughly and mixed with 10 ml of cooled freshly prepared co-agulating solution and the contents were quantitively transferred and filtered through a chromatographic column of 2-5 cm diameter packed with a 5 cm of hyflo super cell was repeated three times using 5 ml methanol and 10 ml co-agulating solution in each. The filtrate was then collected together in 250 ml separatory funnel and extracted 3x 50 ml chloroform. The extracts were collected in a round bottom flask and then evaporated under vacuum to dryness. The residues were dissolved in the 1cm of methanol (HPLC grade) prior to HPLC determination.

4-3- Effect of environmental conditions

To study the effect of the environmental conditions i.e.- temperature, UV-rays and sunlight on the persistence of fenobucarb, one ml of ethyl acetate solution containing 100ug a.i. was spread on the surface of each uncovered Petri- dishes (5Cm i.d.) then ethyl acetate was left to dry. The treated Petri- dishes were exposed to 30, 35, 45, and 50^{o}C for different periods of exposure from 0 to 144 hours inside a dark electric oven to study the effect of temperature.

Another group of treated Petri dishes were exposed to short UV-rays 254nm at the distance of 12 Cm for 0, 1, 3, 6, 12, 24 and 48 hours, respectively.

4-4 HPLC determination

The residues were dissolved in methanol and estimated using HPLC with UV/Vis detector and the operating conditions were as follows: flow rate: 1 ml/min., mobile phase: methanol/ H_2O (90/10), UV detector wavelength 254 nm. The column was C18 (125mmx 4 mm i.d.).

4-5 Recovery efficiency studies

The reliability of the analytical method was examined by fortifying untreated tomato samples with a known quantity of the insecticide. Fortified tomato samples were subjected to the aforementioned procedures of extraction, cleanup and HPLC determination. Recovery of fenobucarb insecticide was performed at the level of 1ppm on and in tomato fruits and the resulted average rate of recovery was 95.5% .The data of tested insecticide on and in tomato fruits were adjusted by recovery percentage.

RESULTS AND DISCUSSION

Data in Table (1) indicate the residues of fenobucarb on and in tomato fruits at different intervals. The initial deposit was 8.07 ppm. This amount was decreased to 4.12 ppm after one day from application. These residues were decreased to 2.11, 1.50 and 0.84 after 3, 5 and 7 days after insecticides application, respectively. No detectable residue of fenobucarb was observed after 14 days. The percent loss rate amounted to 48.94, 73.94, 81.41 and 89.59%. The half- life value was 24 hours. These results are in agreement with Mohamed and Ismail (1995) who reported that methomyl disappeared more slowly than expected. Similar results of fast initial disappearance of methomyl, followed by a slower decline have been reported after the application of methomyl on lettuce El-Sayed *et al.,* (1976). According to the Codex Alientarius Commission (2005), the maximum residue is 1 ppm.

From the above results, the short persistence of fenobucarb on tomato fruits could be due to a variety of environmental factors. Growth also may be responsible to

a certain extent for decreasing the pesticide residue concentrations due to growth dilution effect. Walgenbach *et al.*, 1991

Generally, these findings are similar to those obtained by Yossef *et al.*,(1995)., Al-Khalaf *et al.*,(1995).

The effect of washing with tap water on the residue levels is shown in Table (1). Washing with tap water removed 67.70% of the initial residues. This rate of removal recorded 81.90 and 89.83% after one and two days, respectively.

Galoux *et al.*, (1992) observed the present of aldicarb residues in potato tubers from the 7^{th} week after planting to the harvest 20^{th} week. The residues of aldicarb and its metabolites in potatoe tubers were found in rang from 0.2 to 0.3ppm befor cooking and from 0.1 to 0.2ppm after cooking, these concentration are higher than maxium residue limits authorized in Belgium (0.05ppm).

According to the data of table (1) and remarks of El- Kins (1989) removal of pesticide residues depending on several factors: Character of the surface the plant food (smooth or rough, waxy or non waxy) surface to volume ratio (washing is more effective for bigger fruits). Also those obtained results are in agreement with those finding of Nasr and Abdel- Aziz, Shereen (2005) .

-The effect of environmental factors

The present study also investigated the effect of temperature, UV-rays (short wave, 254nm) and direct sunlight on the stability of fenobucarb

1- Effect of direct sunlight

The data present in Table (2) show that the rate of photo decomposition is positively correlated with the exposure period. The results show that the amount of fenobucarb continuously decreased as the exposure period to sunlight increased. The compound lost 13.91 and 99.54% after one and 24 hours of exposure, respectively, while it was completely disappeared after 48hours of exposure. The calculated half-life value is 3,8 hours for fenobucarb.

2-Effect of ultraviolet rays

The results showed that the percent loss of fenobucarb when exposd to UV rays for 12 and 24 hours were 89.81 and 95.94%, respectively. Hence the half-life value ($t_{1/2}$) of fenobucarb is 4 hours. The data (table 2) show that fenobucarb was more stable under exposure to ultraviolet rays than exposure to direct sunlight. This is in agreement with the findings outlined by Rosen and Margulis, (1991). From the above results, it was clearly shown that the direct sunlight is more effective than uv-rays in acceleration the photodecomposition of fenobucarb insecticide, and this may be due to thermal, evaporational and light intensity consideration. These findings are similar to those obtained by Abdel-Razik (2001) and Plimmer (1970).

3-Effect of different temperatures

The results in table (3) summarize the effect of four different temperature levels (30, 35, 45 and 50^{o}C) on the stability and degradation of fenobucarb. The results indicated that the persistence of fenobucarb was influenced by increasing the temperature degrees and period of exposure. It is evident that there is positively relationship between the increasing in the degree of temperature and the rate of degradation. The data presented in table (3) demonstrated that the percentages of loss were 14.1, 17.24, 21.49 and 59.9% after 6 hours of exposure to temperatures of 30, 35. 45 and 50^{o}C respectively. The results also revealed that the percentage losses of fenobucarb after 48 hours of exposure for temperatures 30, 35, 45, 50^{o}C were 58.1, 69.47, 85.69 and 88.94% respectively. The half- life values of fenobucarb were 37, 24, 17 and 5 hours at 30, 35, 45, and 50C, respectively. The obtained results are in agreement with the findings of Barakat *et al.*, (1999). Fenobucarb showed a high degradation rate when exposed to high temperature degrees (50^{o}C) within the period of experiment, So it is recommended for the use in area with dominated low temperature 25-35^{o}C.

Table 1. residues of fenobucarb on and in tomato fruits .

Time after application (days)	Fenobucarb				MRL Codex*** (ppm)
	Unwashed samples		Washed samples		
	ppm	%loss	ppm	%loss	
Initial*	٨.٠٧	0.00	2.59	٦٧.٧٠	١
١	٤.١٢	48.94	١.٤٦	٨١.٩٠	
٣	2.11	73.94	٠.٨٢	٨٩.٨٣	
٥	1.50	81.41			
٧	0.84	89.59			
١٤	ND	100			
t1/2**	24 hours				

*: One hour after treatment.
**: Half life value (hours).
***: Maximum residue limit.
Each residue value represents the mean of three replicates.
ND: Not detected

Table 2. Effect of ultraviolet rays and direct sunlight on fenobucarb.

Exposure time	Ultra-violet rays (254nm)		Direct sun light	
(hours)	ug	%loss	ug	% loss
0	500.00	0.00	500.00	00.00
1	٤٤٦.١٨	10.76	٤٣٠.٤٥	١٣.٩١
3	٣٣٠.٣٠	٣٣.٩٤	٣٠١.٠٦	٣٩.٧٩
٦	١١٧.٢٦	٧٦.٥٥	١٠١.٧٣	٧٩.٦٥
12	٥٠.٩٣	٨٩.٨١	٤٠.٨١	٩١.٨٤
٢٤	٢٠.٢٨	٩٥.٩٤	٢.٣٢	٩٩.٥٤
٤٨	--	--	ND	100
$t_{1/2}$(hours)*	4 hours		3.8 hours	

*Half life values (hours)

Table 3. Effect of different degrees of temperature on degradation of fenobucarb.

Exposure	30 °C		35°C		45°C		50°C	
(time hours)	ug	%Loss	ug	% Loss	ug	% Loss	ug	% Loss
0	500.00	0.00	500.00	0.00	500.00	0.00	500.00	0.00
6	٤٢٩.٥٠	١٤.١	٤١٣.٨٠	١٧.٢٤	٣٩٢.٥٦	٢١.٤٩	٢٠٠.٥١	٥٩.٩٠
24	٣١٥.٧٦	٣٦.٨٥	٢٥٣.٣٢	٤٩.٣٤	١٨٣.٤٧	٦٣.٣١	٨١.٧٣	٨٣.٦٥
48	٢٩.٥٤	٥٨.١٠	١٦٢.٦٧	٦٩.٤٧	٧١.٥٣	٨٥.٦٩	٠.٣٢	٨٨.٩٤
96	١١٢.٩٧	٧٧.٤١	٣٧.٢١	٩٢.٥٦	٢.٤٦	٩٩.٥١	ND	100
144	٤٠.٩١	٩١.٨٢	ND	100	ND	100	–	–
$t_{1/2}$* hours	37 hours		24 hours		17 hours		5 hours	

*Half life values (hours).

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متبقيات مبيد الفينوبيوكارب على ثمار الطماطم مع دراسة التدهور الحرارى والضوئى

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المعمل المر كزى للمبيدات– مركز البحوث الزراعية– الدقي– جيزة

اجريت تجربة لدراسة مدى ثبات مبيد الفينوبيكارب الحشرى على وفى ثمار الطماطم تحت الظروف البيئية واستخدم الكروماتوجرافى السائل عالى الاداء المتصل بكاشف الاشعة الفوق بنفسيجية المتغير الموجه فى تقدير متبقيات المبيد المتدهورة. وسجلت متبقيات المبيد على ثمار الطماطم بعد ساعة واحدة من الرش ٨.٠٧ جزء فى المليون. تدهورت هذه الكمية الى ٤.١٢، ٢.١١، ١.٥٠، ٠.٨٤ جزء فى المليون بعد ١، ٣، ٥، ٧ يوما من الرش بنسب تدهور ٤٨.٩٤، ٧٣.٨٥، ٨١.٤١و ٨٩.٥٩% عند نفس الفترات السابقة على التوالى. كانت فترة نصف العمر للفينوبيكارب على الطماطم حوالى يوم واحد تحت ظروف التجربة. ونظرا لان الحد المسموح به من المبيد على الطماطم ١جزء فى المليون فان فترة السماح بعد الرش حوالى ٧ ايام ولعملية غسيل الطماطم المعاملة بماء الصنبور بعد الرش بساعة واحدة دورا اساسيا فى ازالة ٦٧.٧% من متبقى المبيد كما تلعب العوامل البيئية من حرارة واشعة الشمس المباشرة والاشعة فوق البنفسيجة دورا هاما متباينا فى سرعة تدهور الفينوبيكارب حيث تتناسب سرعة تدهور المبيد طرديا مع ارتفاع درجة الحرارة وطول فترة التعريض وكانت فترة نصف العمر ٣٧، ٢٤، ١٧ و ٥ساعات عند درجات حرارة ٣٠، ٣٥، ٤٥و ٥٠م كما تتناسب الفقد فى المبيد طرديا مع زيادة طول فترة التعريض للضوء الا ان تحلل المبيد ضوئيا بالتعرض لاشعة الشمس المباشرة كان اسرع كثيرا عن تحلله بالاشعة الفوق البنفسيجية.