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ORIGINAL ARTICLE

Efficacy and Residual Persistence of Organophosphate Pesticides against Thrips on Okra (*Abelmoschus esculentus L.*,)

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ABSTRACT
The research was carried out to determinie the efficacy and residual persistence of synthetic pesticides Dimethoate, Profenopfos, Chlorpyrifos and Trichlorfon. The crop was sprayed four times during the experiment period and an untreated plot was managed for observing the differences. The pest population was observed before application and after 1,2,3,4,5,6 and 7 days after the treatments. Residual persistence studies were also conducted on 1, 7 and 30 days of pesticides spray. The efficacy results showed that dimethoate was the best one against thrips by providing maximum reduction up to 92.3% in thrips population after first day, 100.0% after third day and start losing its efficacy after seventh day by providing 87.7% reduction in thrips population. Profenofos followed the dimethoate by providing 38.7% reduction after first day, 63.2% after third day, 60.1% on fourth day and 50.4% reduction in thrips population after seventh day of its application. Chlorpyrifos provided 5.4% reduction on first day, 0.1% on fifth day, 1.2% on sixth day and 2.0% on seventh day after the treatment. Trichlorfon could not found effective enough against thrips by providing 2.5% reduction in thrips population only after first day of application and after that it was unable to reduce the thrips population, but it was found still better as compared to the untreated control plot. Residual studies showed that dimethoate was the best with minimum residual persistence of 0.000274µg/kg followed by trichlorfon 0.146409 µg/kg, chloropyrifos 0.32552 µg/kg and profenofos 2.817133 µg/kg zero day after treatment (after one hour of treatment), which reduced to 0.000235µg/kg, 0.126131 µg/kg, 0.24052 µg/kg and 2.389208 µg/kg, respectively.. After one week, the residues further decreased to 2.35505µg/kg, 0.121102 µg/kg, 0.074746 µg/kg and 0.220191 µg/kg, respectively. The residual persistence of the tested pesticides after one month was observed 0.000µg/kg, 0.004928µg/kg, 0.000873µg/kg and 0.019594µg/kg respectively.
Key words: organophosphate, thrips,efficacyand residual persistence, okra

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INTRODUCTION

The agriculture sector continues to be an vital component of Pakistan's economy. It currently contributes 21 percent to GDP. Agriculture also generates productive employment opportunities for 45 percent of the country's labour force and almost 60 percent of the rural population depends upon this sector for their livelihood. It has a vital role in ensuring food security, generating overall economic growth, reducing poverty and the transforming towards industrialization[1]. Okra, *Abelmoschus* esculentus L.,is important summer vegetable belonging to family Malvaceae.The plant is cultivated intropical to subtropical and warm temperate regions around the worldJacquelyn, 1999, Henry, 2001[2,3].he loamy soil and warm climate is favorable for cultivation of okra vegetable.Okra *Abelmoschus* esculentus L.,) is very sensitive to frost and grows best in hot summer with minimum and maximum mean temperature of 18°C (65°F) and 35°C (95°F) respectively. If planted in late spring may remain vegetative until late summer or early fall [4].Its tender green fruits are used as a vegetable and a good source of iron, minerals, iodine, carbohydrates, protein and vitamins[5]. In Pakistan okra (*Abelmoschus esculentus L.)*the total a cultivation area in Pakistan is about 15.081 thousand ha with total production of 114.657 thousand tones in which Sindh contributes an area 36.2 hectares with 220 thousand tonesper year [6]. Like other plants,

okra has to suffer huge losses in production due to numerous biotic and a biotic factors. In biotic factors, there are many pathogens and insects, which destroy the quality and quantity of okra production. Most destructive insect pests of okra are jassids, whitefly, thrips, spotted bollworm, American bollworm and aphids [7].

MATERIAL AND MEHODS

Chemicals and reagents

High purity pesticide-scan grade solvents (n-hexane, dichloromethane, dithyl ether, sodium chloride,sodium sulphate) and ACS reagents were used.Hexane was double disilled and evaluated by GC analysis for purity before use. The distilled water was purified with Millipore Milli-Q water purifier, Germany. Individual pesticide standards were purchased from Accu Stanadard, USA and Dr.Ehresnstorfer's laboratory, Germany and stock solution were prepared using chromatographic grade solvent. Florisil absorbent was also purified and activatedfor 02 h at 130^{0}C before use.

All glassware were cleaned with detergent, washed with water, dipped in acid overnight and washed with distilled water again and kept in oven at 200°C for 4h. All the glassware was washed with hexane before use.

Field study

For the experiment purposes four organophosphate chemical pesticides were selected for their efficacy against thrips infestation on okra alongwith their residual persistence. Present studies were carried out in experimental fieldof Department of Agriculture and Agribusiness Management, University of Karachi. The seeds of okra were sown in a randomized complete block design (RCBD) with three replicates. Each plot had a deminsion of 4×3 meters while an untreated controlled plot was managed for observing the differences. Plant to plant distance was 22 cm while row to row distance manintained at 60 cm. The plot to plot distance was managed with 3 meters .The plants of Pigeon pea *(Cajanuscajan L.)* were sown in between all plots for differentiation.5ml of each selected pesticides were diluted in 1 liter of water and the okra crop of experimental field was sprayed with the diluted chemical pesticides. Separate sprayers were used for every plot for avoiding the intermixing of pesticides. The pest population data was taken at early morning from 5 randomly selected okra plants from each experimental plots on daily basis. The selected okra plants were observed visually from top, mid and bottom for estimating the thrips populations. The data was analyzed by using the Handerson-Tilton formula for measuring the efficacy of different pesticides against thrips.Okra fruit sample were analyzed through gas chromatography for the determination of residual persistence of chemical pesticides.

Extraction

Approximately 100 g of pooled sample was collected from the experimental fields chopped and macerated.The okra furit sample was extracted by addition of 200 mlof acetonitrile and50 mL of H_20 (4:1 v/v) homogenized at 3000 rpm for 3 minutes. The homogenate was filtered through Buckner funnel with the help of a suction pump and the residues were washed with the same solvent twice. The final volume was transferred to a separatory funnel with the addition of 100 mL petroleum ether shaken vigorously for 1-2 minutes. This was followed by addition of 50 mL of saturated sodium chloride (NaCl) solution and 500mL of water, partitioned twice with petroleum ether.The combined organic layer was collected carefully and dehydrated by passing through funnel containing 15g anhydrous Na_2SO_4. The organic layer was concentrated in arotary evaporator to 5 mL and applied to the pre-activated florisil column for further clean up. The column was washed small protions of 6, 15 and 50% diethyl etherat a rate of 2mL/min.The combine extract were concentrate on vacuum evaporator and final volume was made to 1mL in n-hexane, sealed, labled for GC analysis.

RESULTS

Table-1:Efficacy of chemical pesticides againstThrips after spray 1

Treatment	Day#1	Day#2	Day#3	Day#4	Day#5	Day#6	Day#7	Mean
Chlorpyrifos	5.4±1.75	2.3±1.74	1.5±1.90	0.6±1.86	0.1±0.05	1.2±0.27	2.0±0.47	1.9±2.01
Profenofos	38.7±4.80	51.0±1.38	63.2±0.86	60.1±0.79	58.0±1.37	54.3±2.05	50.4±2.13	53.7±7.90
Dimetoate	92.3±4.05	99.3±1.22	100.0±0.00	100.0±0.00	100.0±0.00	96.3±1.17	87.7±0.96	96.5±4.79
Trichlorfon	2.5±2.95	-0.3±4.64	-0.5±4.75	-1.6±3.99	-2.8±4.36	-3.4±2.34	-4.5±4.74	-1.5±4.06

Table-2: Efficacy of chemical pesticides against Thrips after spray 2

Treatment	Day#1	Day#2	Day#3	Day#4	Day#5	Day#6	Day#7	Mean
Chlorpyrifos	7.6±0.32	7.2±2.04	6.2±2.14	5.0±1.86	4.1±1.89	4.9±3.74	5.3±3.80	5.8±2.43
Profenofos	40.1±0.32	52.3±0.17	64.1±0.19	61.7±0.66	59.8±0.11	58.8±1.16	58.6±1.71	56.5±7.69
Dimetoate	93.1±2.37	100.0±0.00	100.0±0.00	100.0±0.00	100.0±0.00	98.8±1.12	94.3±1.46	98.0±3.03
Trichlorfon	6.6±0.54	5.6±0.72	4.3±0.49	3.0±1.50	1.6±1.48	0.9±2.34	0.6±3.05	3.2±2.64

Table-3: Efficacy of chemical pesticides againstThrips after spray 3

Treatment	Day#1	Day#2	Day#3	Day#4	Day#5	Day#6	Day#7	Mean
Chlorpyrifos	13.8±3.49	10.8±0.84	8.5±1.62	6.8±0.67	6.0±2.01	7.3±0.50	7.4±1.78	8.7±3.02
Profenofos	44.0±1.43	56.1±0.58	67.1±0.13	64.7±0.57	62.6±0.00	60.9±0.40	60.7±0.95	59.4±7.26
Dimetoate	94.8±2.91	100.0±0.00	100.0±0.00	100.0±0.00	100.0±0.00	100.0±0.00	98.4±0.44	99.0±2.06
Trichlorfon	12.1±2.05	9.3±1.72	6.7±1.34	5.9±0.84	5.7±1.07	5.3±1.02	4.8±0.92	7.1±2.76

Table-4:Efficacy of chemical pesticides against Thrips after spray 4

Treatment	Day#1	Day#2	Day#3	Day#4	Day#5	Day#6	Day#7	Mean
Chlorpyrifos	14.4±0.82	19.7±0.50	22.7±1.76	29.0±0.73	31.3±1.30	33.1±1.35	37.4±0.74	26.8±7.78
Profenofos	46.2±3.34	57.4±0.62	68.5±3.11	65.6±0.45	65.2±1.90	64.2±1.10	64.2±1.66	61.6±7.38
Dimetoate	90.0±4.27	97.6±1.43	100.0±0.00	100.0±0.00	100.0±0.00	100.0±0.00	98.2±0.30	98.0±3.75
Trichlorfon	13.0±0.86	11.5±1.69	10.3±1.92	9.7±2.89	9.6±0.44	31.8±0.86	34.1±1.55	17.1±10.40

Evaluation of pesticides for their efficacy against thrips population on okra after their 1st spray (Table-1) depicted that the highest efficacy against thrips on average was noted in plots sprayed with Dimethoate with an average efficacy of 96.5±4.79%, followed by Profenopfos (53.7±7.90%), Chlorpyrifos (1.9±2.01%), while the Trichlorfon could not provide control against the targeted insect pest in okra crop. Table-1 showed that the tested chemicalpesticides provided better results against thrips during the second spray. Maximum efficacy against thrips on average was observed in the plots treated with Dimethoate having an average efficacy of 98.0±3.03% followd by Profenopfos (56.5±7.69%) and Chlorpyrifos (5.8±2.43%). Trichlorfon provided very poor results (3.2±2.64%) but it was foung better as compare to the first spray. The data of table-3 showed that the tested pesticides were found better enough against thrip infesting okra crop as compare to the first and second spray of these pesticides. Similar to the first and second spray, the highest average efficacy against thrips (99.0±2.06%) was observed through the dimethoated treated plot of okra, followed by Profenopfos (59.4±7.26%), Chlorpyrifos (8.7±3.02%) and Trichlorfon (7.1±2.76%). In order to combat with the thrips population on okra, the thrips control on the crop followed the similar pattern of previous three sprays by showing the (Table-4) maximum average efficacy of Dimethoate (98.0±3.75%) but it was found less effective than the previous effeicacy of dimethoate. Profenopfos followed the dimethoated by providing average efficacy of 61.6 ±7.38% against okra thrips which were better as compare to its all previous results. Chlorpyrifos was found better during the fourth spray by providing 26.8±7.78% efficacy and Trichlorfon was the least effective in all the tested chemical pesticides by providing average control of 17.1±10.40% against thrips infestation on okra crop. Statistically, the difference in the efficacy of different synthetic pesticides against thrips after their first spray were significant (P<0.05).

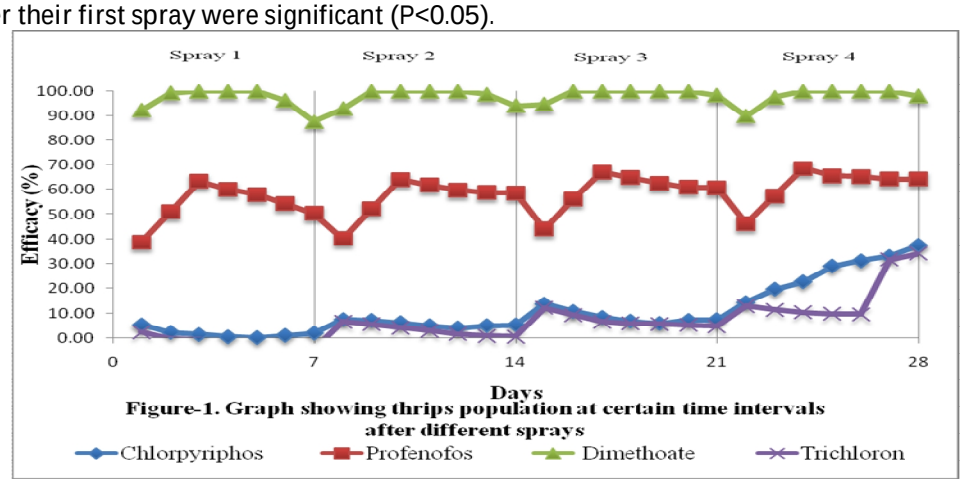


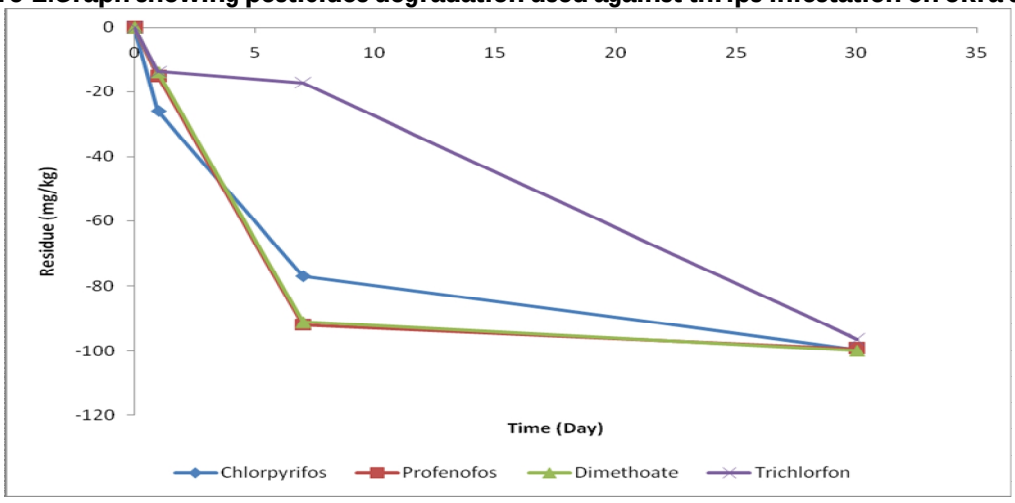
Figure-1. Graph showing thrips population at certain time intervals after different sprays

Table-5: Residues and degradation kinetics of organophosphate pesticides

Time(Days)	Residues(mg/kg^{-1})			
	Chlorpyrifos	Profenofos	Dimethoate	Trichlorfon
0	0.325523±0.01366	2.817133±0.299657	0.000274±3.41E-05	0.146409±0.01598
1	0.24052±0.014908	2.389208±0.44648	0.000235±1.69E-05	0.126131±0.018581
7	0.07476±0.015522	0.22019±0.146731	2.35E-05±9.15E-06	0.121102±0.004257
30	0.000873±0.000117	0.019594±0.007597	0±0	0.004928±0.000297
Λ	.220±0.018	.292±0.055	.335±0.87	.060±0.014
Halflife	3.14791	2.965472	1	10.89129
R^2	0.989	0.956	0.931	0.879
EU-MRLs	0.5	0.05	0.02	0.05
PHI-EU	-2.07104	13.89496	-12.71	-20.4063

Results regarding the residual persistence of tested chemical pesticides (Table-5) showed that the minimum residues were traced in the dimethoate treated field followed by trichlorfon and chlorpyrifos while the maximum residues were traced in the profenofos treated field of okra. The initial deposits of dimethoate detected were under maximum residual limits settled by the European Union (0.02mg/kg). Dimethoate deposits were 0.00027mg/kg at zero day, 0.00023mg/kg after one day, 2.35E after seven day and 0.000 after 30 days of its application. Half life of dimethoate was found 1 day. Trichlorfon initial deposits were observed 0.146mg/kg at zero day intervals, 0.126mg/kg after one day, 0.121mg/kg after seven day and 0.0049mg/kg after 30 days of its treatment while the half life of trichlorfon was found 10.892 days. The initial deposits of chlorpyrifos at zero day interval were found 0.325mg/kg, which decreased to 0.240mg/kg after one day, 0.074mg/kg after 7 day and 0.0008mg/kg after 30 days of treatment. Degradation kinetics of chlorpyrifos indicated that residues of chlorpyrifos decreased to 26.11% after one day, 77.03% after 7 days and 99.73 % degradation was observe dafter 30 day of its treatment. The half life of chlorpyrifos was found 3.147 days and was calculated on the basis of Maximum Residual Limits settled by the European Union. Initial deposits of profenofos were observed 2.817mg/kg at zero day, 2.389mg/kg after one day interval, 0.220mg/kg after 7 days and it decreased to below maximum residual limits settled by European Union after 30 days of its treatment. 30 days after applicaton tested samples of Profenofos showed 0.0195mg/kg. Half life of profenofos was calculated 2.965 days. Degradation kinetics of profenofos showed 15.19% degradation after first day, 92.18% after 7th day and 99.30% after 30 days of treatment.

Figure-2.Graph showing pesticides degradation used against thrips infestation on okra crop.



DISCUSSION

Our results were in conformity with the results reported earlier depicted that dimethoate was more effective in controlling thrips feeding on okra [8]. It was also reported that dimethoate was also effective against okra pests including aphids.Dimethoate was also found useful to control thrips, white fly, mites, plant hoppers, aphids and bollworms on different crops [9,10].According to Pareeket al[11] depicted dimethoate effective for controlling okra pests including aphids, leaf hoppers and fruit borers. Misra et al [12] depicted dimethoate effective for managing okra fruit borer. According to Shivanna et al[13]Dimethoate was most effective synthetic pesticides to control thrips while

and Kooner et al[14] suggested Dimethoate for effective control of okra insect pests in the field. Findings of prsenet studies are being supported by Ullah etal [15]reported that Profenofos was moderately effective to control thrips on okra.Prasadet al[16], depicted chlorpyrifos effective against okra fruit borer. Similar results were also reported by Sahoo et al[17] when chlorpyrifos was used in combination with carbofuran, while Sinha et al[18] depicted chlorpyrifos effectinness against okra fruit borer *E.vittella* when it was applied in combination with cypermethrin. Boopathi et al [9] depicted chlorpyrifos effecteive against okra pests including aphids. However in the present studies chlorpyrifos wasn't able to provide sufficient efficacy against thrips infestation on okra crop. This difference may be observed either due to the difference in the targeted pest or due to the change in climatical conditions during the experiment. In the present study the effectiveness of trichlorfon against jassid, A. bigutella bigutella (Ishida) whitefly, B. tabacci (G), thrips, T. tabaci (S.) and mites, T. cinnabarinus (Boisd.) and spotted bollworm was not upto the desired level and even it was least effective against thrips.

Residual persistence studies table-5. showed initial deposits of dimethoate detected were under Maximum Residual Limits settled by the European Union (0.02mg/kg). dimethoate deposits were 0.00027mg/kg at zero day, 0.00023mg/kg after one day, 2.35E after seven day and 0.000 after 30 days of its application. Dimethoate followed first order kinetics by showing 14% degradation after first day, 91.40% after 7th day and 100% degradation in dimethoae residues afrer 30 days of its application. The correlation coefficient was observed 0.931 with a half life of 1 day. Results of our present studies are in conformity with the Kumari et al [19] who reported dimethoate residues in okra fruits in the similar ranges of 0.002mg/kg. Our present findings are in conformity with Zine etal [20] who depicted that dimethoate was traced in only 4% samples when 83 samples were tested more over the dimethoate residues degraded below the acceptable levels. Present findings are in contrast with the Zhang etal [21] who depicted a half life of 5.3 days with a correlation coefficient of 0.933 while residual persistence were 3.91mg/kg at zero day, 2.65mg/kg after 2 day and 1.76mg/kg after 8th day the differences in Zhang findings might be because of the difference in applied doses during the experiment.

Table-5 shows the initial deposits of trichlorfon observed were 0.146mg/kg at zero day intervals, 0.126mg/kg after one day, 0.121mg/kg after seven day and 0.0049mg/kg after 30 days of its treatment while the half life of trichlorfon was found 10.892 days. The kinetics degradation followed by trichlorfon showed that 13.85% degradation after 1st day, 17.28% after 7th day and 99.74% degradation was observed after 30 days of its application. Our present findings regarding trichlorfon are being supported by Cavanna et.al,.[22] who depicted that a period of minimum 10 days be kept in between the pesticide's application and crop harvesting in olive crop. The differences in dissipation rates and half life might be observed either because of difference in plant or the climatic conditions and tested doses of pesticides Li et al.,[23]. Moreover certain parameters including time of illumination, photo catalysts' amount, electron acceptors, temperature, anions, metal ions and pH value could have affected the dissipation rates Weiet al.,[24].

Table-5. showed that the initial deposits of chlorpyrifos at zero day intervals were found 0.325mg/kg, which decreased to 0.240mg/kg after one day, 0.074mg/kg after 7 day and 0.0008mg/kg after 30 days of treatment. Degradation kinetics of chlorpyrifos indicated that residues of chlorpyrifos decreased to 26.11% after one day, 77.03% after 7 days and 99.73 % degradation was observe dafter 30 day of its treatment. The half life of chlorpyrifos was found 3.147 days and was calculated on the basis of Maximum Residual Limits settled by the European Union. Chai et al., [25] depicted a rapid degradation of chlorpyrifos following the first order degradation kinetics with a 57 to 70% decline in chlorpyrifos residues during 48 hours and further declined to below MRL (1.0 mg/kg) at 4th day of last application. Half life of chlorpyrifos was depicted 1.1-1.5 days with a correlation coeffiecient of 0.99. Chaiet al [25] findings slightly differ with our present results, the differences might be due to the difference in plant/leaf sizes, the bigger plants having large surface area of leaf trap more pesticides and degrade faster than the small leaf plantsZhang et al [21] depicted similar kinetics degradation of chlorpyrifos having residues 5.41 mg/kg at zero day, 3.05 mg/kg after 2 days, 1.76 mg/kg after 8 days and 0.98 mg/kg after 10 days along with the respective degradation of 0%, 35%, 76% and 87%.while it was applied at 400g/liter. More over the difference in residual levels might be found due to the different application doses but the degradation kinetics showed a similar decreasing trend whichis in conformity with our results.Moreover the half life 4.7 days reported in earlier studies is also suported to our present findings [21]. Gupta et al [26] who depicted that chlorpyriphos disspated from the tested tomato fruit samples with 7 days of application with a half-life values of 2.5–4.8 days supported our present finding for chlorpyrifos.

Table-5. showed that initial deposits of profenofos were observed 2.817mg/kg at zero day, 2.389mg/kg after one day interval,0.220mg/kg after 7 days and it decreased to below maximum residual limits settled by European Union after 30 days of its treatment. 30 days after applicaton tested samples of Profenofos showed 0.0195mg/kg. Half life of profenofos was calculated 2.965 days. The degradation followed the first order kinetics showing 15.19% after one day, 92.18% after one week and 99.30% after 30 days of profenofos applications with a correlation coefficient of 0.956. Our present studies are being supported by Gupta et al[27] who depicted a half life of 2.9-3.3 days of profenofos with a correlation coefficient of 0.996 and 0.91 while it was used at 40 and 80 g/ha against cauliflower pest. The residues deposits depicted by Gupta et al[27]were 0.390 and 0.692 mg/kg at zero day interval, 0.291 and 0.583mg/kg after one day and 0.062 and 0.114 mg/kg after 8 days of treatment by showing 70.6-71.0% degradation after fifth day of treatment. Results of our present studies are being supported by Nath etal [28] who depicted that the profenofos dissipated at the highest rate of 98.4% on 7th day of its application. Our findings are in the agreement of Gupta et al[27] who depicted that profenofos applied on tomato crop followed the first order kinetics degradation and dissipated almost after the 7th day of treatment. The depicted half life for profenofos was 2.2–5.4 days which is in conformity with our present studies. Similar findings were reported by Renuka et al[29] who depicted that initial deposits of profenofos were traced in the ranges of 2.00 and 2.76 ppm and dissipated below the detectable limits of 0.0625ppm before 30 days of its application in green cardamom. Similar trend in dissipation of profenofos were

reported by Dharmaet al[30] depicted that 92-94% profenofos was dissipated with the 30 days of last treatment in red and green chilies. Our present results are in conformity with Manjunath et al [31] who reported the of profenofos in the ranges of 2.9-3.3 days in fruits.

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