BEHAVIOR OF INSECTICIDES LAMBDA-CYHALOTHRIN, CHLORANTRANILIPROLE AND THIAMETHOXAM IN BRINJAL *SOLANUM MELONGENA* LINN.

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Abstract. The behavior of lambda-cyhalothrin, thiamethoxam and chlorantraniliprole residues in brinjal crop was examined with Reverse Phase- High Performance Liquid Chromatography (RP-HPLC) using the modified QuEChERS method. As brinjal is consumed without peeling, it is important to study the pesticide residue and an effective procedure is needed to eliminate the residue before consumption. Decontamination methods were studied, in which treatment with (2%) brine solution was found to be the most effective decontamination method. The initial deposits of chlorantraniliprole, lambda-cyhalothrin and thiamethoxam sample treated with warm (2%) brine solution were 0.33 mg kg^{-1}, 0.20 mg kg^{-1} and 0.35 mg kg^{-1}. Results revealed that the half-life of chlorantraniliprole, thiamethoxam and lambda-cyhalothrin was found to be 1.30, 1.30 and 1.02 days. Tsi of chlorantraniliprole, thiamethoxam and lambda-cyhalothrin were 5.29, 0.94 and 1.32 days which proves the highest decontaminating method in brinjal.
Keywords: *HPLC, brinjal, decontamination, QuEChERS, half-life, Tsi*

Introduction

Brinjal (*Solanum melongena* L.) is attacked by several insect pests throughout the crop period, which damage both shoot and fruit. In India, brinjal is the most popular vegetable, which is consumed raw as salad; it is a favorite cuisine consumed by both vegetarians as well as non-vegetarians without peeling, so it is important to check the pesticide residues. Several conventional insecticides have been deployed for the control of brinjal pests leading to health hazards, problems of pesticide residues, resistance development and resurgence of secondary pests. In India, most of the farmers do not follow the recommended doses, so it is important to study the persistence behavior of insecticides. In case farmers applied them without following the recommendations, we can eliminate the pesticide residues by household-level decontamination methods. The shoot and fruit borer is the major pest of brinjal. Controlling this pest is difficult once it enters the fruit, so mostly the insecticides are sprayed starting from vegetative stage. Because of this, there will be residual effect on soil, water and plant system which leads to harmful effects. In developing countries like India, food safety is the major responsibility as majority of the population is below poverty line and for that effective procedures should be deployed to reduce the load of pesticide contaminants. Chlorantraniliprole has been recommended for spraying as broad-spectrum insecticide to several insect pests of brinjal like coleoptera, diptera, in cultivated vegetables, and in greenhouses (Malhat et al., 2012; Ambujakshi et al., 2018). It is chemically known as

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3-Bromo-4'-Chloro-1-(3-chloro-2-pyridyl)-2'- methyl-6'-(methyl carbamoyl) pyrazole-5-carboxanilide belonging to the anthranilicdiamide group. It affects the Ryanodine receptor (RyR) which leads to dysfunction of muscle and paralysis (Cordova et al., 2007). It is considered non carcinogenic to humans with no short-term effects, and shows low toxicity to two stingless bees, *Partamona helleri* and *Scaptotrigona xanthotrica* (US EPA, 2012; Tome et al., 2015). It is likely to transport to groundwater and surface water where soils are poorly drained with shallow water table (DuPont, 2014). Lambda-cyhalothrin is a pyrethroid insecticide which is chemically called as (*R*,*S*)-α-cyano-3-cyano-3-phenoxybenzyl(1S)-cis-3-[(Z)-2-chloro-3,3,3-trifluoropropenyl]-2,2-dimethylcyclopropanecarboxylate. It has been recommended to monitor chewing and sucking pests like lepidopteran and coleopteran in brinjal, cereals, cotton, wheat, and oilseed (Lina et al., 2010). In humans, lambda-cyhalothrin poisoning leads to vomiting, nausea, mouth ulcer, abdominal pain and diarrhea (Hossain et al., 2005). The improper use and continuous exposure to lambda-cyhalothrin in the farming area leads to resistance development of *Anopheles gambiae* (WHO, 2012). Thiamethoxam is a second-generation broad-spectrum neonicotinoid insecticide chemically called as (3-[(2-Chloro-1,3-thiazol-5-yl)methyl]-5-methyl-N-nitro-1,3,5-oxadiazinan-4-imine). It binds to the post-synaptic nicotinic acetylcholine receptors (nAChR) in the central nervous system and belongs to thianicotinyl subclass (Maienfisch et al., 2001). It has been recommended to monitor whiteflies, aphids, certain beetles as foliar, soil, and seed treatment (Rancan et al., 2006; Pandey et al., 2009). It is entered into the environment through spraying, coated seeds, soil erosion and transport to surface water by water runoff and it further breaks down into clothianidin which is another pesticide and needs years to break down in plants and soil (US National Library of Medicine, 2022). However, when these pesticides were not properly used they will cause havoc to the environment and their toxicity is prone to humans and animals. Researchers have found effective culinary processes which could degrade pesticide residues using household level decontamination methods (Bhilwadikar et al., 2019). Good monitoring of pesticide residues in plants, soil, and water is required as well as their production and distribution, strict tailing of the banned insecticides and finding out the pesticides which remain longest. The study of decontamination method like peeling, washing, cooking, juicing, frying and freezing in sweet pepper, orange and strawberry helps in the removal of residue by 19%-100% (El-Saeid et al., 2016; Ahlawat et al., 2019; Solanki et al., 2019; Paramasivam, 2020; Kansara et al., 2021). Washing with normal water is the preliminary step in removing pesticide residues and treating with 2% salt solution shows a promising effect by 98%-100% which makes it below MRL level (Shashi et al., 2015). Some studies reported that using H_2O_2 and NaCl strikes the chemical bonds between crops and pesticides (Fatih et al., 2012). Hence, this study is about the persistence behavior of insecticides and an effective decontamination method to eliminate the pesticide residue on this crop before consumption.

Materials and methods

Chemicals and reagents

The standard compounds of thiamethoxam (99.75%), chlorantraniliprole (98.0%), and lambda-cyhalothrin (98.8%) were purchased from Sigma- Aldrich, Kolkata, India. The HPLC grade water, HPLC grade acetonitrile, Primary secondary amine (PSA), activated charcoal, anhydrous sodium sulfate (Na_2SO_4), sodium chloride and activated anhydrous magnesium sulfate ($MgSO_4$) were purchased from E. Merck (India) Ltd, Mumbai, India. Reagent blanks run were done before analysis of a sample to see the accuracy of the chemicals and standards.

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Details of layout

The experiment was performed at ICAR, Research Complex for North Eastern Hill region Manipur Centre, Lamphelpat, India during 2020-21 on the brinjal variety "Noori". The study was done in randomized block design with four treatments and four replications with plot size of 2 x 1.5 m by following recommended dose of *i.e.* thiamethoxam 25 WG @ 50 g a. i.ha^{-1} (Actara), chlorantraniliprole 18.5 SC @ 40 g a. i.ha^{-1} (Coragen), lambda-cyhalothrin 5 EC @ 15 g a. i.ha^{-1} (Karate) given by Central Insecticide Board and registration Committee (CIB&RC) which also included control at 28.5ºC with 82.5% RH (*Figure 1*). The climate of the study area is warm during summer and dry and cool in winter. The soil type of the study area is acidic (*Figure 2*). Fertilizer was applied @ 50:50:50 NPK kgha^{-1} and the crop were sown during 10th October, 2020 and transplanted during 25th November, 2020. The fruiting stage was observed on 2nd December, 2020 and insecticides were sprayed when the insect population reached Economic Threshold Level (ETL) during evening hours with one time spraying as brinjal is consumed without peeling. Brinjal planting was done where there was no history of those insecticides sprayed. The insecticidal treatments were applied with the help of a knapsack sprayer with hollow cone nozzle as a foliar spray. About 300-350 g of brinjal crop was harvested at 50% fruiting stage in order to study the recovery and after that the crops were further sprayed with pesticides. After spraying, samples of brinjal were assembled from each insecticidal treatment plots and control plots on 0 (1 hour), 1, 3, 5, 7, and 9 days and put inside the sampling bags and brought to the laboratory for further analysis. The MRLs were taken based on the Food Safety & Standard Authority of India (FSSAI).

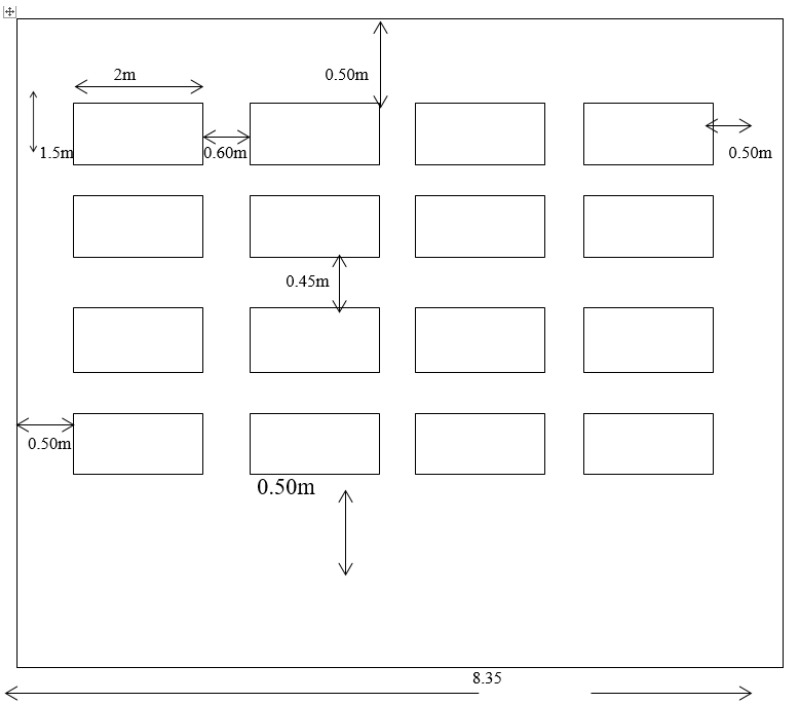

Figure 1. *Experimental Design*

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Figure 2. *Overview of the experimental site*

Extraction and clean up

Thiamethoxam, chlorantraniliprole, and lambda-cyhalothrin standard stock solution (1 mg/ml) was prepared in HPLC grade acetonitrile and stored at -4ºC. Fortification of brinjal samples was done at several levels of 1.00, 0.50, 0.25, and 0.1 mg kg^{-1} with five replications for each standard. The QuEChERS method is based on work done and introduced by Anastassiades and Lehotay (2003). The method was performed by taking a fresh sample of brinjal as substrate; cutting it into pieces, putting inside the Waring commercial blender (Model: 8011ES) for blending and homogenized by using a homogenizer (Heidolph Robot coupe Blixer). The blended substrate 15 gm was taken into a 50 ml centrifuge tube in three replications. Later, 30 ml HPLC grade acetonitrile was added into blended samples and mixed by handshaking vigorously for 5 mins. The samples were homogenized at 1500 rpm for 5 mins. 10 gm of NaCl was added to each of the samples and centrifuged by using Centrifuge (Model: 5810 R, Germany) for 10 mins at 2500 rpm. The top 15 ml supernatant was removed and put into a 15 ml centrifuge tube containing 5 mg of Na_2SO_4 and shaken using rotospin for 3 mins. The 6 ml supernatant was again taken out and poured into another 15 ml centrifuge tube containing 900 mg activated anhydrous magnesium sulfate, 150 mg PSA sorbent and 15 mg activated charcoal and was tightly capped and shaken for 1 min. The mixture was centrifuged again at 2500 rpm for 6 mins. The extracted sample (4 ml) was taken out into a glass vial for HPLC analysis.

Culinary process

Brinjal sample treated in 2% warm brine solution

The brinjal samples collected from field application were collected at 0 (1 hour after application), 1, 3, 5, 7 and 9 days and were dipped in 2% warm brine solution and kept there for 10 minutes. After that the samples were dried by clean cloth and the solution was drained off. The samples were chopped and blended for further QuEChERS method.

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Brinjal sample treated with normal water

The brinjal samples collected from field application were collected at 0 (1 hour after application), 1, 3, 5, 7 and 9 days and were washed with normal water for 2 minutes by gentle rubbing with hands. After that the samples were dried with clean cloth and were chopped into pieces and blended for further QuEChERS method.

Analytical method of HPLC analysis

RP- HPLC assembled with detector (UV- VIS) with C18 column, dual pumps provided by M/S Perkin Elmer, United States and Brownlee Analytical (250 mm column length, 5 µl particle sizes and 4.6 mm inside diameter) was used for determination of chlorantraniliprole, thiamethoxam, and lambda-cyhalothrin residues without the derivatisation step (*Figure 3*). TC Nav software obtained from Perkin Elmer was used for data acquisition and processing. The C18 column provides an acceptable result which separates the peak separately without any nosiness. For quantification of chlorantraniliprole, the mobile phase involving acetonitrile: water (90: 10, v/v) with a flow rate of 0.5 ml/min with detection at 225 nm gives acceptable chromatograms with a retention time of 5.3 min. The peaks of thiamethoxam and lambda-cyhalothrin were detected at 4.5 min and 4.3 min with the wavelength of 230 nm with mobile phase consisting of acetonitrile only (100 v/v) at a flow rate of 0.7 ml/min and mobile phase involving acetonitrile: water (95: 5 v/v) at a flow rate of 0.7 ml/min, respectively. The insecticides in the sample were identified by checking the retention times of the sample run with those of peak heights of standards run with the same functioning procedures.

Figure 3. *RP-HPLC equipment*

Statistical data analysis

Chlorantraniliprole, lambda-cyhalothrin, and thiamethoxam residues (mg kg^{-1}) were analyzed by calculating standard deviation and mean with three replications each. The degradation kinetics of chlorantraniliprole, lambda-cyhalothrin, and thiamethoxam were studied by plotting residue concentration against time and the highest squares of correlation coefficient formed were used to decide the equations of best-fit curves.

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Exponential relations were used for all the samples studied corresponding to the first-order rate equation. The first-order kinetics were drawn graphically from the linearity of the plots of log *C* against time where *C*= residue x 100 (*Figure 4*). The half-life ($T_{1/2}$) and safety interval were calculated by following Hoskins (1961).

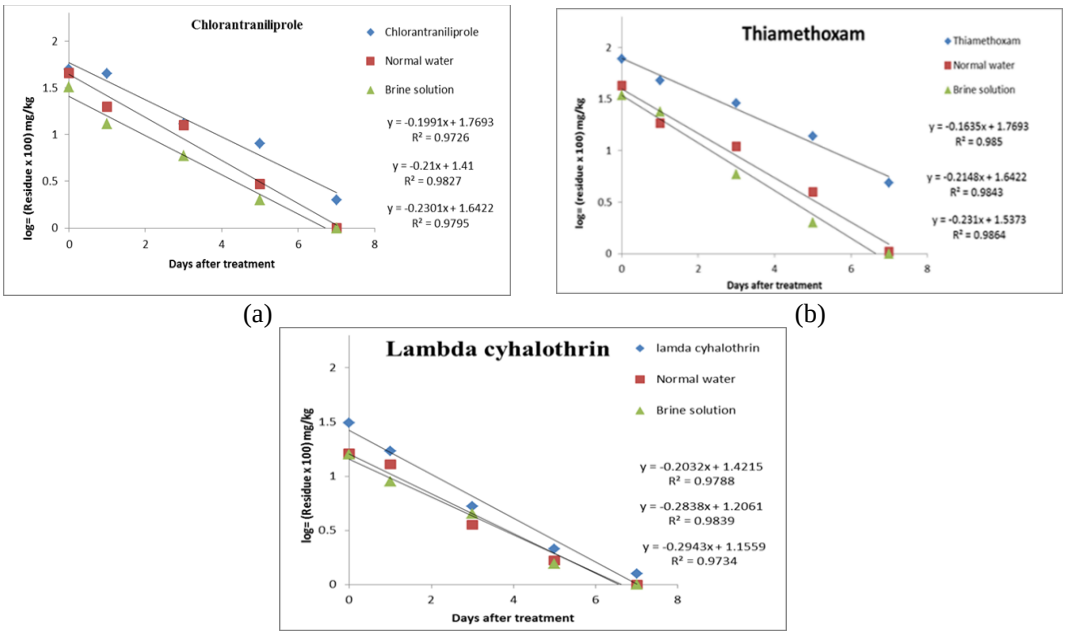

Figure 4. *Graphs in semi-logarithm presenting degradation kinetics of a) chlorantraniliprole b) thiamethoxam c) lambda-cyhalothrin residues on brinjal fruits*

Results and Discussion

Recovery method for estimation of chlorantraniliprole, lambda-cyhalothrin and thiamethoxam

RP-HPLC assembled with UV- VIS detector with C18 column was used for the determination of chlorantraniliprole, thiamethoxam, and lambda-cyhalothrin residues. The mean percent recoveries were carried out for thiamethoxam, chlorantraniliprole and lambda cyhalothrin which was spiked at 0.10, 0.25, 0.50, and 1.00 mg kg^{-1} with three replications to know the efficiency of extraction and clean-up procedures. The control samples of brinjal and reagent blanks were also run in the same process to find out the nosiness. The mean percent recoveries were shown to have found 83.67 percent to 96.67 percent range for chlorantraniliprole, 86.33 percent to 94.00 percent for thiamethoxam and 81.67 percent to 98.00 percent for lambda-cyhalothrin (*Table 1*).

Table 1. *Recovery (%) of chlorantraniliprole, thiamethoxam and lambda cyhalothrin*

Fortified (mg kg^{-1})	Chlorantraniliprole	RSD (%)	Thiamethoxam	RSD (%)	Lambda cyhalothrin	[b]RSD (%)
0.1	[a]83.67± 0.21	0.25	87.00± 0.36	0.41	93.67± 1.16	1.23
0.25	92.33± 2.52	2.72	86.33± 0.98	1.13	81.67± 1.53	1.87
0.50	85.67± 0.89	1.03	92.33± 1.93	2.09	92.00± 1.02	1.10
1.00	96.67± 1.04	1.07	94.00± 1.00	1.06	98.00± 1.73	1.76

[b]RSD= Relative Standard Deviation: [a]Mean± Standard deviation of 5 replicates

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Limit of quantitation (LOQ) and Limit of detection (LOD)

Half-scale deflection of 1.0 ng was attained for each chlorantraniliprole, lambda-cyhalothrin, and thiamethoxam which can be seen from the baseline. 15 g of brinjal sample was extracted and made up to a final volume of 4 mL, and samples were injected finally at 20 µL which did not produce any background interference. For chlorantraniliprole maximum residue limit (MRL) in brinjal is 0.03 mg kg^{-1}, for lambda-cyhalothrin 0.2 mg kg^{-1} and for thiamethoxam 0.3 mg kg^{-1} for the FSSAI. The lowest concentrations of all the method validation are within the acceptable range 0.02 mg kg^{-1} in chlorantraniliprole, 0.01 mg kg^{-1} and 0.05 mg kg^{-1} in lambda- cyhalothrin and thiamethoxam was found to be below MRL according to our study. Thus, LOQ was calculated 0.02 mg kg^{-1} and LOD 0.006 mg kg^{-1} for chlorantraniliprole, LOQ was 0.01 mg kg^{-1} and LOD 0.003 mg kg^{-1} for lambda-cyhalothrin and thiamethoxam was observed to have LOQ 0.05 mg kg^{-1} and LOD 0.016 mg kg^{-1}.

Residues of chlorantraniliprole without treatment, treatment with normal water and 2% brine solution

The initial deposit of chlorantraniliprole @40 g a. $i.ha^{-1}$ on brinjal was 0.51 mg kg^{-1} collected on 0 days (1 h after spraying) after first application. It was further decreased to 0.45, 0.13, 0.08, and 0.02 mg kg^{-1} afterward at 1, 3, 5, 7 days, respectively and no residues were detected after 9 days. The dissipation percentage gradually increased to 11.76, 74.50, 84.31 and 96.07 percent after 1, 3, 5 and 7 days, respectively. After 9 days, it became to 100 percent which became undetectable (*Table 2*). Pathipati et al. (2017) and Kansara et al. (2021) also reported that initial deposit of 0.36 mg kg^{-1} in capsicum when applied chlorantraniliprole @60 g $a.i.ha^{-1}$ and dissipated in 7 days, and 1.31 mg kg^{-1} initial deposit in poly house which dissipated to BDL in 15 days. The initial deposit of chlorantraniliprole treated with normal water was shown to have the highest 0.46 mg kg^{-1} on 0 days (1 h after application). It further declined to 0.20, 0.10, 0.03, and 0.01 mg kg^{-1} after 1, 3, 5, and 7 days of treatment, respectively. No detection of residues was observed after 9 days of treatment. The percent dissipation was 56.22, 78.26 percent after 1 and 3 days, which increased to 93.47 percent after 5 days, respectively. It was further attended to 97.82 percent and 100 percent after 7 and 9 days, respectively (*Table 2*). Aktar et al. (2010) reported that washing with tap water reduces the pesticide residue in brinjal and other vegetables. Washing, peeling, and different chemical solutions help in the removal of pesticides (El-Saeid et al., 2016). The initial deposit of chlorantraniliprole sample treated with warm (2%) brine solution was 0.33 mg kg^{-1} on 0 days (1 h after spraying). The residues were decreased to 0.13, 0.06, 0.02, and 0.01 mg kg^{-1} after 1, 3, 5, and 7 days of treatment, respectively. The percent dissipation after 1 day was 60.60 percent which again increased to 81.81% and 93.93% after 5 days and 7 days, respectively. After 9 days, it raised to 100 percent which shows that there is no residue of chlorantraniliprole (*Table 2*). Bhilwadikar et al. (2019) reported that dipping (0.9%) of NaCl for 15 mins helps in reducing pesticides in brinjal and other vegetables. Various foods processing like acetic acid, brine solution, peeling, washing leads to removal of pesticides (Toker and Bayindirli, 2003). According to the MRL (0.03 mg kg^{-1}), the residues of untreated sample were less by 7 days whereas the treatment with normal water and treatment with (2%) brine solution resulted in decrease within 5 days which means that decontamination method is effective in pesticide residue removal. The residue does not follow the first-order kinetics with R^2 values of 0.9726, 0.9827 and 0.9795 in untreated, normal water

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treated and (2%) brine solution treated samples. Half-life ($T_{1/2}$) of chlorantraniliprole sample calculated as per Hoskins was 1.51 days. The half-life of sample treated with normal water was shown to have 1.43 days and sample treated with (2%) brine solution was 1.30 days (*Table 2*). Malhat et al. (2012) reported the half-life ($T_{1/2}$) of chlorantraniliprole residue was 3.30 days in tomato fruit, 1.26 days in green chilli (Paramasivam, 2020). Therefore, Tsi (Safety interval) of the untreated sample was 6.18 days and sample treated with normal water, the Tsi was shown to have 5.80 days. The sample treated with (2%) brine solution was 5.29 days (*Table 2*). Malhat et al. (2012) reported pre-harvest interval of 8 days of chlorantraniliprole according to the maximum residue limit in tomato fruit.

Table 2. *Residues of chlorantraniliprole in untreated, normal water treated and 2% brine solution treated samples*

Days after treatment	Chlorantraniliprole (mg kg^{-1})	Percent dissipation	Chlorantraniliprole treated with Normal water (mg kg^{-1})	Percent dissipation	Chlorantraniliprole treated with warm Brine solution (2%) (mg kg^{-1})	Percent dissipation	MRL (mg kg^{-1})
0 day (1 hr after application)	*0.51± 0.25		0.46±0.60		0.33±0.13		0.03
1 day	0.45± 0.19	11.76	0.20±0.14	56.52	0.13±0.06	60.60	
3 day	0.13± 0.08	74.50	0.10±0.06	78.26	0.06±0.08	81.81	
5 day	0.08± 0.05	84.31	0.03±0.00	93.47	0.02±0.00	93.93	
7 day	0.02± 0.00	96.07	0.01±0.00	97.82	BDL	100	
9 day	BDL	100	BDL	100			
R^2	0.9726	-	0.9827	-	0.9795	-	
a + bx	-0.1991x + 1.7693	-	-0.21x + 1.41	-	-0.2301x + 1.6422	-	
$T_{1/2}$ (days)	1.51	-	1.43	-	1.30	-	
T_{si} (Safety interval)	6.18	-	5.80	-	5.29	-	

[a] Mean± Standard deviation of 4 replicates; [b]BDL= Below Determination Limit of 0.01 mg kg^{-1}; Normal water treated (already insecticides were present); ** 2% warm brine water treated on brinjal sample (already insecticides were present) ;$T_{1/2=}$ half-life, Tsi= safety interval

Residues of thiamethoxam treatment, treatment with normal water and 2% brine solution

Thiamethoxam residues were shown to have a maximum which is 0.78 mg kg^{-1} collected on 0 days (1 hr after spraying) after the first application of thiamethoxam @50 g a.i.ha^{-1}. These residues were found to be diminishing to 0.48 and 0.29 mg kg^{-1} in the brinjal fruit sample which was collected after 1 and 3 days, respectively. The residues were further decreased to 0.14 and 0.05 mg kg^{-1} after 5 and 7 days of application. After 9 days, the samples were detected to undergo below the determination limit of 0.01 mg kg^{-1}. The percent dissipation after 1 day was 38.46 percent which increased gradually with time. It was further increased to 62.82 percent after 3 days, 82.05 percent after 5 days and 93.58 percent after 7 days. After 9 days, it reached 100 percent which shows no detection of residue (*Table 3*). Allam and Singh (2016) studied the persistence behavior of thiamethoxam in the brinjal crop @50 g a.i.ha^{-1}. The residue was 0.20 mg kg^{-1} which was high on 0 days (1 hr after spraying) and decreases by 10 days.

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Table 3. *Residues of thiamethoxam in untreated, normal water treated and 2% brine solution treated samples*

Days after treatment	Thiamethoxam (mg kg^{-1})	Percent dissipation	Thiamethoxam treated with Normal water (mg kg^{-1})	Percent dissipation	Thiamethoxam treated with warm Brine solution (2%) (mg kg^{-1})	Percent dissipation	MRL (mg kg^{-1})
0 day (1 hr after application)	*0.78± 0.63		0.43± 0.11		0.35± 0.16		0.3
1 day	0.48± 0.14	38.46	0.19± 0.10	55.81	0.24± 0.05	31.42	
3 day	0.29± 0.21	62.82	0.11± 0.05	74.41	0.06± 0.08	82.85	
5 day	0.14± 0.32	82.05	0.05± 0.02	88.37	0.02±0.00	94.28	
7 day	0.05± 0.18	93.58	0.02± 0.01	95.34	BDL	100	
9 day	BDL	100	BDL	100			
R^2	0.985	-	0.9843	-	0.9864	-	
a + bx	-0.1635x + 1.7693	-	-0.2148x + 1.6422	-	-0.231x + 1.5373		
$T_{1/2}$ (days)	1.84	-	1.40	-	1.30	-	
T_{si}	1.33	-	1.01	-	0.94	-	

[a] Mean± Standard deviation of 4 replicates; [b]BDL= Below Determination Limit of 0.01 mg kg^{-1}; Normal water treated (already insecticides were present); ** 2% warm brine water treated on brinjal sample (already insecticides were present); $T_{1/2=}$ half-life, Tsi= safety interval

Rabea et al. (2018) studied that thiamethoxam residue was high in pepper fruit at the initial deposit of 1.38 mg kg^{-1} collected at 2 hours of application and dissipated by 15 days. The degradation process of thiamethoxam showed a similar way in the present investigation and became non-detectable at 9 days. The initial deposit of thiamethoxam treated with normal water was 0.43 mg kg^{-1} on 0 day (1hr after spraying). These residues were declined to 0.19, 0.11, 0.05, and 0.02 mg kg^{-1} after 1, 3, 5 and 7 days respectively. The residues were observed to have gone below the determination level after 9 days of treatment. The dissipation percent was 30.23 percent after 1 day which rises to 65.11 percent and 76.74 percent after 3 and 5 days respectively. It was further shoot up to 95.34 percent after 7days and became 100 percent after 9 days of treatment (*Table 3*). Begum et al. (2016) reported that brinjal fruit when washed with running water reduces the pesticide by 9 percent. The studies are in harmony with the reports of (Awasthi, 1993; Zohair, 2001). Similarly, the residues of thiamethoxam treated with warm (2%) brine solution was 0.35 mg kg^{-1} which is lesser compared to thiamethoxam untreated and thiamethoxam treated with normal water after 0 days (1hr after spraying). The levels of residues were 0.24, 0.06, and 0.02 mg kg^{-1} in the brinjal sample collected after 1, 3, 5, and 7 days of treatment. The residues started declining gradually. The dissipation percent after 1, 3, and 5 days were 31.42%, 82.85%, and 94.28% respectively. No residues of thiamethoxam were traced in the brinjal samples collected at 7 days of treatment. Thiamethoxam residues were shown to have decreased by the different treatments and it did not persist after 9 days of application (*Table 3*). Shashi et al. (2015) reported that when brinjal fruit were washed with (2%) salt water then pesticide was reduced to 78 percent. Based on the MRL of thiamethoxam in brinjal (0.3 mg kg^{-1}), the residues of untreated sample and sample treated with normal water were found to be less by 5 days whereas those treated with (2%) brine solution were found to be less by 3 days which

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means that 2% brine solution is effective method for eliminating pesticide residue. The first-order kinetics were not followed in untreated sample, and in those treated with normal water and treated with 2% brine solution with R^2 values of 0.985, 0.9843 and 0.9864. The half-life of the thiamethoxam untreated sample was observed 1.84 days. Whereas the sample treated with normal water was noticed to have 1.40 days and sample treated with (2%) brine solution was 1.30 days (*Table 3*). Allam and Singh (2016) found that the half-life period of thiamethoxam was 2.57 days when applied at the recommended dose in brinjal. Tsi (safety interval) of thiamethoxam in untreated sample was 1.33 days. Whereas Tsi of treated sample washed with normal water was noticed to have 1.01 days and sample treated with (2%) brine solution was 0.94 days (*Table 3*). Karmakar and Kulshrestha (2009) reported pre-harvest interval of thiamethoxam was 8 days in the tomato crop.

Residues of lambda- cyhalothrin treatment, treatment with normal water and 2% brine solution

The residues of lambda-cyhalothrin were also found to have decreased the concentration and increased dissipation rate with time. The initial deposit of brinjal sample on 0 days (1 hr after spraying) after first application of lambda-cyhalothrin @ 15 g a.i.ha^{-1} was shown to have a maximum which was 0.31 mg kg^{-1}. After 1 day, it became to 0.17 mg kg^{-1} and reduced to 0.05 mg kg^{-1} after 3 days. It further decreased to 0.02 and 0.01 mg kg^{-1} after 5 and 7 days. No residues of lambda- cyhalothrin were traced in the sample collected at 9 days. The dissipation percentage was fairly less after 1 day but increased gradually. It was found to have 45.16 percent after 1 day and 83.87 percent after 3 days. Simultaneously, it increased to 93.54 and 96.77 percent after 5 and 7 days which further increased to 100 percent after 9 days (*Table 4*). Reddy et al. (2017) observed the dissipation pattern of lambda- cyhalothrin on chili in which the initial deposit was 1.20 g a.iha^{-1} which was found to be high collected at 2 hours after spray. Gupta et al. (2015) observed that when applied lambda-cyhalothrin @ 15 g a.i.ha^{-1} the initial deposit was 0.138 g a.iha^{-1} and dissipated to 92.75 percent after 10 days. In present investigation also the residue of lambda-cyhalothrin reached below detectable level after 9 days. The residues of lambda-cyhalothrin sample treated with normal water were shown to have quite different and reducing results compared to lambda-cyhalothrin untreated. On 0 day, the residue was 0.23 mg kg^{-1}, followed by 0.13 mg kg^{-1} after 1 day. It was further declined to 0.03 and 0.01 mg kg^{-1} after 3 and 5 days. Thereafter, the residue became below the determination limit of 0.01 mg kg^{-1}. The percent dissipation attained to 43.47 percent by 1 day which further increased to 78.26 percent and 95.65 percent after 3 and 5 days. The dissipation attained to 100 percent after 7 days (*Table 4*). Dhiman et al. (2006) also reported that the pesticide on brinjal fruit can be reduced by washing it under tap water. The residues of lambda-cyhalothrin sample treated with (2%) brine solution were shown to have reduced compared to other treatments. The residue was 0.20 mg kg^{-1} on 0 day (1 hr after spraying) which is the maximum. Thereafter, it decreased to 0.10, 0.02 and 0.01 mg kg^{-1} after 1, 3 and 5 days, respectively. After 7 days, the residue was not detectable which has reached the determination limit of 0.01 mg kg^{-1}. The percent dissipation was attained to 65%, 90%, and 95% after 1, 3, and 5 days. After 7 days, it was obtained to 100 percent (*Table 4*). Bhilwadikar et al. (2019) reported that (2%) NaCl for 15 mins helps in reducing pesticides in brinjal and other vegetables. Srivastava et al. (2021) reported that 1% and 5% brine solution helps in the removal of pesticides in okra. Pseudo-first-order kinetics were followed and the R^2 values were shown to be 0.9788, 0.9839 and 0.9734 in

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untreated, treated with normal water and treated with 2% brine solution samples. The half-life of lambda-cyhalothrin untreated sample was seen to have 1.48 days and 1.06 days in sample treated with normal water. Whereas the half-life of the sample treated with (2%) brine solution was 1.02 days (*Table 4*). Gupta et al. (2015) studied that when lambda-cyhalothrin @ 15 g a.i.ha^{-1} was applied, the half- life in brinjal was 2.67 days, 1.58–1.80 days in green chilli (Ahlawat et al., 2019). Tsi of lambda-cyhalothrin untreated sample, and those treated with normal water and treated with (2%) brine solution was 1.91, 1.37 and 1.32 days, respectively (*Table 4*). Sharma et al. (2018) found that the safety interval of lambda-cyhalothrin was 1.03 days in tomato.

Table 4. *Residues of lambda- cyhalothrin in untreated, normal water treated and 2% brine solution treated samples*

Days after treatment	**Lambda-cyhalothrin (mg kg^{-1})**	**Percent dissipation**	**Lambda-cyhalothrin treated with Normal water (mg kg^{-1})**	**Percent dissipation**	**Lambda-cyhalothrin treated with warm Brine solution (2%) (mg kg^{-1})**	**Percent dissipation**	**MRL (mg kg^{-1})**
0 day (1 hr after application)	*0.31± 0.29		0.23± 0.03		0.20± 0.26		0.2
1 day	0.17± 0.07	45.16	0.13± 0.18	43.47	0.10± 0.02	50	
3 day	0.05± 0.00	83.87	0.03± 0.06	86.95	0.02± 0.00	90	
5 day	0.02± 0.00	93.54	0.01± 0.00	95.65	0.01± 0.00	95	
7 day	0.01± 0.00	96.77	BDL	100	BDL	100	
9 day	BDL	100					
R^2	0.9788	-	0.9839	-	0.9734	-	
a + bx	-0.2032x + 1.4215	-	-0.2838x + 1.2061	-	-0.2943x + 1.1559	-	
$T_{1/2}$ (days)	1.48	-	1.06	-	1.02	-	
T_{si} (Safety interval)	1.91	-	1.37	-	1.32	-	

[a] Mean± Standard deviation of 4 replicates; [b]BDL= Below Determination Limit of 0.01 mg kg^{-1}; Normal water treated (already insecticides were present); ** 2% warm brine water treated on brinjal sample (already insecticides were present); $T_{1/2=}$ half-life, Tsi= safety interval

Conclusion

All the recovery percentages were in the range between 81.67- 98.00% which proves that QuEChERS method was found to be efficient in estimation of thiamethoxam, lambda-cyhalothrin and chlorantraniliprole by RP-HPLC with UV-VIS detector. It is evident from the study that the initial deposit of the three insecticides were found to be lower in (2%) brine solution treatment as compared to untreated samples and those treated with normal water. The initial deposits of chlorantraniliprole, lambda-cyhalothrin and thiamethoxam sample treated with warm (2%) brine solution were 0.33 mg kg^{-1}, 0.20 mg kg^{-1} and 0.35 mg kg^{-1}. Results revealed that the half-life of chlorantraniliprole, thiamethoxam and lambda-cyhalothrin were 1.30, 1.30 and 1.02 days, respectively. Tsi of chlorantraniliprole, thiamethoxam and lambda-cyhalothrin were 5.29, 0.94 and 1.32 days, respectively, which proves the effective decontaminating method in brinjal. Based on the MRL, the chlorantraniliprole (0.03 mg kg^{-1}), thiamethoxam (0.3 mg kg^{-1}) and lambda-cyhalothrin (0.2 mg kg^{-1}), sample treated with (2%) brine solution was found to

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be safe after 5, 3 and 1 days, respectively, which means that 2% brine solution is effective in eliminating pesticide residue. In our study, the pesticide residue can be reduced by adopting household level processing like washing with normal and treating with (2%) brine solution. Hence, it is apparent that the brinjal applied with the recommended dose of insecticides and treated with (2%) brine solution was determined to be safe from the pesticide residues point of view. The study standardized humble cost effective tactics to eliminate harmful pesticide residues from brinjal.

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