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IMPACT OF DECONTAMINATION PROCESSES ON THE REDUCTION OF PESTICIDE RESIDUES IN GREEN CHILLI

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ABSTRACT

This study has been designed to determine the extent of pesticide residue removal from chilli fruits through common household practices. One time foliar application of quinalphos, profenophos, ethion, cyhalothrin, imidacloprid, and acetamiprid was done as a tank mix at recommended doses at 50% fruit formation stage. Samples were collected after 48 hr of spray, subjected to various decontamination treatments, and analysed using the validated QuEChERS method employing GC-ECD (Gas Chromatograph Electron capture detector), and Liquid Chromatograph Tandem Mass Spectrometer (LC-MS/MS). Compared to all the treatments, soaking in 5% acetic acid for one min was found to be most effective in the removal of quinalphos (23.68%), profenophos (19.47%), ethion (23.33%), and cyhalothrin (25.00%). The next best treatment was found to be soaking for one min in lukewarm water, which removed 20-30% of quinalphos, ethion, cyhalothrin, and acetamiprid residues.

Key words: Pesticide residues, chilli, household practices, QuEChERS method, GC-ECD, quinalphos, profenophos, ethion, cyhalothrin, imidacloprid, and acetamiprid

Chilli (*Capsicum annuum* L.) is one of the most important vegetable, consumed as fresh and as a processed commodity (Tiwary et al., 2005). Chilli crop is ravaged by many insect pests from seedling to harvest stage. Among these, chilli fruit borer, *Helicoverpa armigera* (Hubner), tobacco caterpillar *Spodoptera litura* (F), and sucking pests like whitefly *Bemisia tabaci* (Gennadius), thrips, *Scirtothrips dorsalis* (Hood) and mite *Polyphagotarsonemus latus* (Banks) cause substantial yield loss. Insecticides are repeatedly applied against these insect pests. Insecticides such as acetamiprid, cyhalothrin, imidacloprid, lambda-cyhalothrin, oxydemeton methyl, phorate, phosalone, quinalphos are commonly used (Kodandaram et al., 2013). Around 13-14 % of pesticides used in the country are applied on vegetables, and the maximum use is in chilli (5.13%) followed by brinjal (4.6%). Improper and indiscriminate application of pesticides without following GAP (Good Agricultural Practices) has led to pesticide residues. This makes both green and red chilli laden with pesticides (Mahapatro and Rajna, 2020). A temporary ban was imposed on Indian green chillies in May 2014, which was revoked in January 2016 (The Economic Times, 2022). In 2016, there were concerns over shipments of mangoes, chillies, and cucumbers being brought in from India by UAE, which contained pesticide residues beyond the Codex Alimentarius Commission's limits (Goyal et al., 2017). Considering the popularity of chilli in Indian cuisine and the problems associated with pesticide residues, practical solutions are to be evolved to satisfy consumer needs. Decontamination of pesticide residues by simple methods are need of the hour. In this study, decontamination techniques, such as washing under running tap water combined with soaking in lukewarm, 1% NaCl, 5%NaCl, 5% acetic acid, $NaHCo_3$, 0.1% $KMnO_4$ were evaluated to know their efficacy.

MATERIALS AND METHODS

Quinalphos 25%EC (Syngenta Pvt Ltd.), profenophos 50%EC (Syngenta Pvt Ltd.), ethion 50%EC (PI industries Ltd.), cyhalothrin 5%EC (Syngenta Pvt Ltd.), imidacloprid 17.8%SL (Sumitomo Chemical India Ltd.) and acetamiprid 20%SP (Rallis India Limited) were used. Acetonitrile (Lichrosolv ®), hexane (Lichrosolv ®), anhydrous sodium chloride and magnesium sulfate, Primary Secondary Amine (PSA), GCB (Graphitised Carbon Black) were obtained from Himedia. The study was conducted at the Pesticide Toxicology Laboratory, Department of Agricultural Entomology, Tamil Nadu Agricultural University, Coimbatore. The insecticide spraying was done at fruiting stage in farmers' field at

Madhampatti village, Coimbatore in February, 2020. Tank mix of insecticides viz. quinalphos 25%EC (500 g a.i./ ha), profenophos 50%EC (1000 g a.i./ ha), ethion 50%EC (2000 g a.i./ ha), Cyhalothrin 5%EC (30 g a.i./ ha), imidacloprid 17.8%SL (100 g a.i./ ha) and acetamiprid 20%SP (40 g a.i./ ha) was prepared and applied. About 10-12 kg of chilli fruit were collected from the pesticide-treated experiment plot after 48 hr and subjected to various treatments viz., washing with tap water, lukewarm, 1% NaCl, 5%NaCl, 5% acetic acid, $NaHCO_3$, 0.1% $KMNO_4$ and no wash treatment (control). Control plots were free of this application.

Chilli fruits (10-12 kg) were processed immediately on the sampling day itself to avoid any degradation of insecticide residues. The collected samples were brought to the laboratory and divided into eight equal parts for decontamination studies. The analytical method used was validated by assessing the parameters i.e., linearity, limit of detection (LOD), and limit of quantification (LOQ). The insecticide mix at three concentrations in the range from 0.05 – 0.50 µg mlL-1 in GC and LC-MS/MS was prepared for linearity studies. The calibration curve was drawn by plotting the peak area (x) against corresponding analyte concentrations (y). LOD and LOQ were obtained by signal to noise ratio of >3:1 and 10:1, respectively. Method accuracy was studied by spiking the insecticide mix standards in untreated samples at 0.05, 0.25, and 0.5 µg ml^{-1} levels. The spiked samples were processed according to the modified QuEChERS method along with the control sample and replicated thrice. In all the treatments, 1 kg chilli fruits were washed under running tap water for 1 min before and after decontamination treatments as follows- T1- soaking fruit in 2-4 l water for 10 min; T2- soaking fruit in 2-4 l lukewarm (45-50°C) water for 10 min; T3- soaking fruit in 2-4 l of 1% NaCl aqueous solution) for 10 min; T4- soaking fruit in 2-4 l of 5% NaCl aqueous solution) for 10 min; T5- soaking fruit in 2-4 l of 5% acetic acid aqueous solution for 10 min; T6- soaking fruit in 2-4 l of 5% $NaHCO_3$ aqueous solution for 10 min; T7- soaking fruit in 2-4 l of 0.01% $KMnO_4$ aqueous solution for 10 min; and T8- no washing/ treatment (control).

The chilli samples after decontamination (500 g) were homogenized in a Robot coupe blade homogenizer. A representative sample of 10 g was taken in 50 ml centrifuge tube and 20 ml of acetonitrile was added and vortexed for 1 minute. To this mixture, 4 g of anhydrous $MgSO_4$ and 1 g of sodium chloride were added, vortexed for one min and then centrifuged at 6,000 rpm for 10 min. Twelve ml of supernatant was transferred to a glass test tube containing 4 g anhydrous Na_2SO_4 and hand shaken for a minute, then nine ml of solvent was transferred into a 15 ml centrifuge tube containing 150 mg primary secondary amine (PSA), 25 mg of graphitized carbon black (GCB) and 800 mg of anhydrous $MgSO_4$. The mixture was shaken vigorously by hand for 1 min and then centrifuged for 10 min at 3,000 rpm. Four ml of supernatant was transferred to turbovap tube, evaporated to near dryness, and the residue was dissolved in one ml n-hexane for GC analysis. From the remaining supernatant, 2 ml was taken and evaporated to near dryness. The residue was reconstituted with one ml acetonitrile for LC-MS/MS analysis. The chromatographic separation was achieved in Schimadzu gas chromatography system equipped with DB-5,30 m x 0.25 mm x 0.25 µm column. The programmed column temperature was 150ºC, hold for 2 min; increased @ 4ºC/min to 200ºC, hold for 7 min.; increased @ 2ºC/min to 230ºC, hold for 0 min; increased @ 3.5ºC/ min to 280 ºC, hold for 11 min. Injection volume was 1µl. The injection port temperature (280 ºC); Detector temperature (300 ºC); gas flow of 0.80ml/min; split ratio (1:5). The residues of imidacloprid and acetamiprid was analyed using Waters LC-MS/MS-2695 system equipped with XTerra C-18, 4.8 x 250 mm, 5µ particle size column. The estimation of acetamiprid was performed at 292.18 positive ionization mode and imidacloprid at 250.10 positive ionization mode. The mobile phase ratio used for the analysis was water with 0.1% formic acid: acetonitrile with 0.1% formic acid (50:50 v/v). The column temperature was set at 30 ºC, and the injection volume was 20µl. The flow rate was set at 0.5 ml/ min.

RESULTS AND DISCUSSION

Calibration curve was obtained by injecting three different concentrations of selected organophosphorus compounds (quinalphos, profenophos and ethion), synthetic pyrethroid (lambda cyhalothrin), and neonicotinoids (imidacloprid and acetamiprid). The calibration was found to be linear with the coefficient of determination and RSD of 0.999 and 2.63%, respectively (Fig. 1). The LOD and LOQ determined were 0.01 and 0.05 µg g for all the studied insecticides. The % recoveries were in the range of 72.60 - 93.40 for quinalphos, 80.42 -98.40 for profenophos, 100.70 - 107.81 for ethion, 94.03 - 101.13 for lambda cyhalothrin, 104.38 - 113.64 for imidacloprid and 102.25 - 108.58 for acetamiprid (Table 1). The residues of quinalphos, profenophos, ethion and cyhalothrin, imidacloprid and acetamiprid in chilli sample showed a considerable reduction by different decontamination methods. The concentration of pesticide residues retained in green chilli fruit after various treatment methods is presented in Table 1. Washing under running tap water for one min initially and after soaking in different chemicals was maintained common for all treatments. Soaking in 2-4 l of 5% acetic acid aqueous solution for 10 min has resulted in 0.29, 1.53, and 1.61 mg/ kg of quinalphos, profenophos and ethion residues with a maximum reduction of 23.68, 19.47 and 23.33 % over treated control (0.38, 1.90 and 2.10 mg/kg, respectively). Soaking in 2-4 l sof lukewarm water (45-50°C) for 10 min removed 21.05 % (0.30 mg/ kg) of quinalphos residues and 19.52 % (1.69 mg/ kg) of ethion residues and was found to be the next best treatment. Profenophos residues were removed up to 17.89 % (1.56 mg/ kg) by soaking in 2-4 l of 5% NaCl aqueous solution for 10 min.

Soaking in 2-4 l of lukewarm water (45-50°C)/ 5% NaCl aqueous solution/ 5% acetic acid aqueous solution for 10 min had similar effect on lambda cyhalothrin residue and resulted in maximum of 25% reduction (0.06 mg/ kg) over treated control (0.08 mg/ kg). Soaking in 2-4 l of 1% NaCl aqueous solution for 10 min was the best treatment to remove maximum of 21.87% (0.25 mg/ kg) of imidacloprid residues over the treated control (0.32 mg/ kg). Soaking in 2-4 l of water/ lukewarm water (45-50°C) / 5% NaCl aqueous solution for 10 min were the treatments that resulted in 18.75 % (0.26 mg/ kg) reduction of imidacloprid residues. In the case of acetamiprid, the lowest detected residue was 0.21 mg/ kg with a 30% reduction over the treated control (0.30 mg/ kg) by soaking in 2-4 l of lukewarm water (45-50°C) for 10 min. Soaking in 2-4 l of water for 10 min removed 26.66 % (0.22 mg/ kg) of acetamiprid residues and was found to be the next best treatment. Dipping of green chillies in 2% salt solution for 10 min followed by water wash proved to be effective, facilitating the removal of 32.56 and 84.21% residues after sprays of triazophos, while acephate residues were removed to an extent of 78.95% (Kumar et al., 2000). Radwan et al. (2004) reported that acetic acid, potassium permanganate, sodium chloride and sodium hydroxide solution were effective in the removal of pirimiphos- methyl residues from sweet pepper and eggplant fruits. In hot pepper fruit, 70.16 and 76.61%

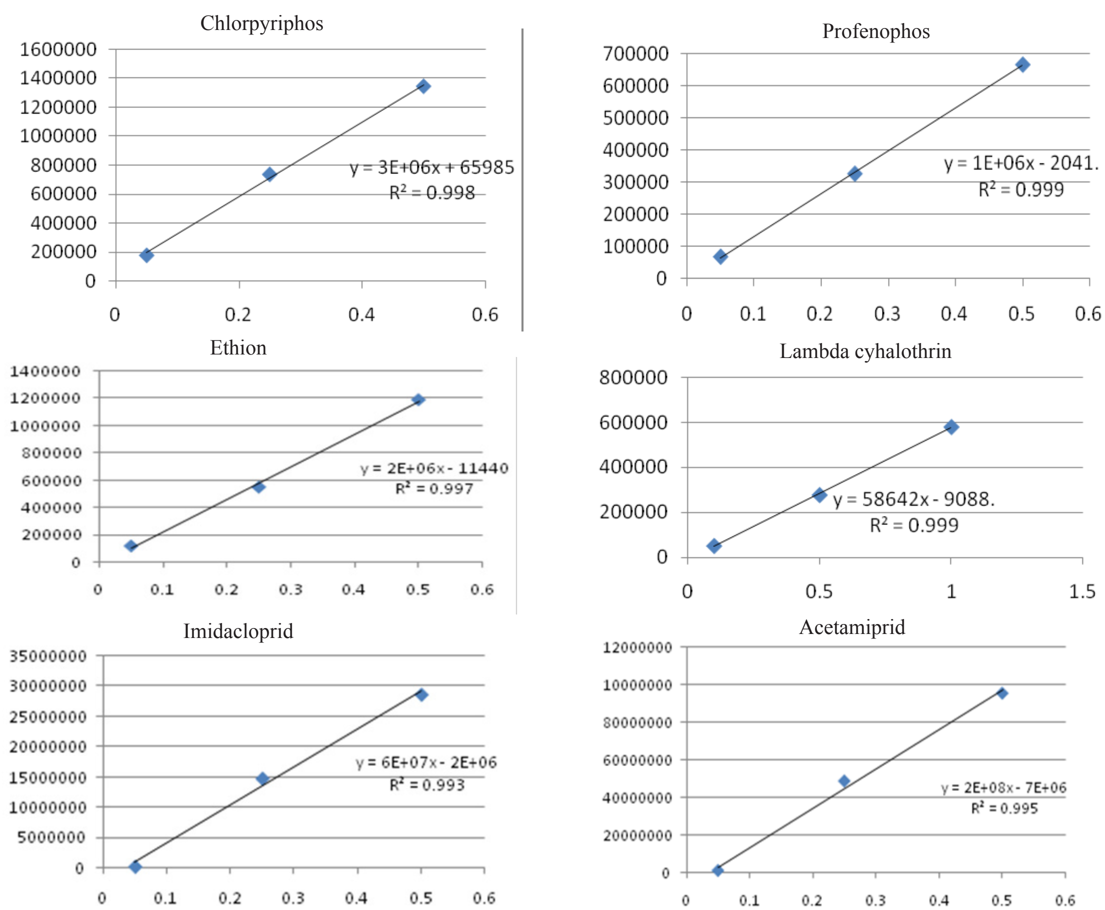

Fig. 1. Linearity of selected pesticides

Table 1. Pesticide residues and recovery of selected pesticides in chilli

Treatments	Quinalphos		Profenophos		Ethion		Cyhalothrin		Imidacloprid		Acetamiprid	
	Resdiue mg/ kg	% removal	Resdiue mg/ kg	% removal	Resdiue mg/kg	% removal	Resdiue mg/ kg	% removal	Resdiue mg/ kg	% removal	Resdiue mg/ kg	% removal
T1-Soaking water	0.33	13.15	1.66	12.63	1.88	10.47	0.07	12.50	0.26	18.75	0.22	26.66
T2-Lukewarm	0.30	21.05	1.62	14.73	1.69	19.52	0.06	25.00	0.26	18.75	0.21	30.0
T3-1% NaCl	0.31	18.42	1.70	10.52	1.87	10.95	0.08	0.0	0.25	21.87	0.24	20.0
T4-5% NaCl	0.31	18.42	1.56	17.89	1.73	17.61	0.06	25.00	0.26	18.75	0.26	13.33
T5-5% acetic acid	0.29	23.68	1.53	19.47	1.61	23.33	0.06	25.00	0.28	12.50	0.29	3.33
T6-5% NaHCO3	0.36	5.26	1.87	1.57	1.97	6.19	0.08	0.0	0.28	12.50	0.27	10.0
T7-0.01% KMnO4	0.36	5.26	1.68	11.57	1.80	14.28	0.07	12.50	0.28	12.50	0.29	3.33
T8-No washing	0.38	-	1.90	-	2.10	-	0.08	-	0.32	-	0.30	-
Recovery												
Fortification (mg/ kg)	Mean % recovery*	RSD	Mean % recovery*	RSD	Mean % recovery*	RSD	Mean % recovery*	RSD	Mean % recovery*	RSD	Mean % recovery*	RSD
0.05	93.40	0.18	98.40	3.84	107.81	7.33	100.48	3.03	104.38	2.74	104.20	3.18
0.25	75.20	1.31	81.40	1.35	100.70	8.34	95.03	0.93	105.61	7.51	108.58	5.14
0.5	72.60	0.45	80.42	0.50	106.10	2.39	101.13	1.07	113.64	1.22	102.25	1.65

*Mean of three replications

reduction in residue was reported after washing with soap and acetic acid solution, respectively. Kumari (2008) worked on effects of household processing on reduction of pesticide residues in vegetables for organochlorines, synthetic pyrethroids, organophosphate and carbamates which were determined in the three different vegetables viz., brinjal, cauliflower and okra. A maximum reduction (77%) of OP insecticides was observed in brinjal followed by in cauliflower (74%) and in okra by washing (50%).

Bhushan et al. (2012) reported that dipping of chilli fruits in 2% salt solution and water removed 78.95 and 77.36 % of acephate, 32.56 and 16.28% of triazophos, 90.56 and 28.37% of cypermethrin. Washing of brinjal and chilli with 2% salt solution was effective in removing various pesticides (Cherukuri et al., 2014; Shashi et al., 2014). Bairwa (2016) reported that dipping chilli fruits in 2% KMnO4 solution for 10 min was significantly superior in removing residues of profenophos (58.58%) and ethion (64.23%). Baby Rani et al. (2019) found the removal of 48.68% for profenophos and 42.57% for lambda cyhalothrin by washing with 2% salt solution in green chilli. Solutions of 1% and 5% NaCl and 5% CH_3COOH served as efficient decontaminants in removal of quinalphos, profenophos, ethion, and lambda-cyhalothrin residues from chili, whereas for imidacloprid and acetamiprid there was a mild decontamination only (Anjana Srivastava et al., 2021). The results obtained in the decontamination of selected organophosphate, neonicotinoids and synthetic pyrethroid in green chilli fruits showed maximum % reduction by dipping in 5% acetic acid as most effective in the removal of quinalphos (23.68%), profenophos (19.47%), ethion (23.33%), and lambda cyhalothrin (25.00%) residues. Lukewarm water was found to be effective in the removal of quinalphos (21.05%), ethion (19.52%), lambda cyhalothrin (25.00%) and acetamiprid (30.00%) residues, and 1% NaCl treatment showed removal of 21.87% of imidacloprid residues.

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AUTHOR CONTRIBUTION STATEMENT

Study planned by KB, Field experiment conducted by PK, PT & AS, Laboratory experiment and data analysis done by PK, VM, CS & EM, manuscript prepared by PK, edited by CS, reviewed and approved by KB.

CONFLICT OF INTEREST

No conflict of interest.

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