International Journal of Forestry and Horticulture (IJFH)
Volume 2, Issue 1, 2016, PP 19-24
ISSN 2454-9487
www.arcjournals.org

Risk Mitigation Methods for Removal of Pesticide Residues in Tomato for Food Safety

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Abstract: *The commercial production of highly cultivated and consumed tomato is highly dependent on regular usage of insecticides to protect the crop from insect pests. The increased consumer awareness and legal issues on food safety, with special reference to insecticide residues in foods, led us to attempt for cheap and effective methods for removal of pesticide residues to address the issues of consumer and food safety, as the farmers are not following the Good Agricultural Practices i.e pre-harvest intervals. The most commonly used pesticides such as profenophos, chlorpyriphos, dimethoate, malathion, phosalone, quinalphos, triazophos and λ-cyhalothrin were sprayed at recommended doses at fruit formation stage, samples were collected at 2 hours after treatment to quantify the deposits. The samples were subjected to various household treatments (tap water wash, lemon water wash, dipping in 2% salt water for 15 min, dipping in 2% tamarind water for 10 min, washing with 0.1% sodium bicarbonate solution, washing with 4% acetic acid solution, biowash, cooking), each in three replications, and analysed for residues using validated QuEChERS method and GC-ECD, FPD and GC-MS, so as to estimate the % removal and their effectiveness. Out of all treatments, dipping in 2% salt solution for 10 minutes is very effective in removing 45%, 43%, 52%, 50%, 54%, 48% and 76% of dimethoate, chlorpyriphos, quinalphos, profenophos, phosalone, □-cyhalothrin and malathion, respectively, and cooking removed insecticides in the range 55-80%. Dipping fruits and vegetables in 2% salt solution for 15 minutes is the best household method for removal of pesticide residues, and also the method is effective in reducing the residues below MRL (Maximum Residue Limits).*

Keywords: *Pesticide Residues, Tomato, Food Safety, Risk Mitigation, 2% salt solution.*

1. INTRODUCTION

Tomato is the most popular vegetable in India, and state of Andhra Pradesh is third most important growing Tomato producing 1.615 M mt with a share of 12% (NHB, 2013) during 2012-13. In India, about 13-14% of the total pesticides used in agriculture are used for fruits and vegetables covering only 3% of the cropped area (Arora and Singh, 2004). Repeated application of pesticides on vegetables often results in the build up of their residues (Handa, 1992). Surveys carried out in the country indicated that 50-70% of vegetables are contaminated with insecticide residues (Karanth, 2000). Studies on farm gate monitoring of vegetables carried out in different places revealed contamination mostly with organo phosphorous and synthetic pyrethroids insecticides, indicating clearly the changes in the usage pattern from organo chlorine to other groups of pesticides.

Maximum Residue Limits (MRLs) are set by Codex Alimentarius Commission (CAC) at international level and as on date, MRLs are set for 17 pesticides on tomato, and by Food Safety and Standards Authority of India (FSSAI) of Ministry of Health and Family Welfare, Government of India, as per Food Safety and Standards Act, 2006 (Food Safety and Standards Regulation, 2011) at national level based on the Good Agricultural Practices. The major insect pest of tomato is fruit and shoot borer for which farmers apply insecticides at almost weekly interval, and hence the risk of pesticide residues in foods need to be addressed as per FSSAI (Food Safety and Standards Authority of India) for the protection of consumer health and interests. In this context, household risk mitigation methods for removal of pesticide residues in tomato are to be recommended based on the scientific evaluation, as the food habits are changing enormously.

2. MATERIALS AND METHODS

Field Trial Protocol

A supervised field trial was conducted during Rabi 2012-13 in order to study the effect of house hold processing methods in the removal of certain pesticides in tomato resulting from spray application of most commonly used insecticides *viz.*, Profenophos 50EC@ 2ml/lit, Chlorpyrifos 20EC @ 2ml/lit, Dimethoate 30EC @ 4ml/lit, Malathion 50EC @ 3ml/lit, Phosalone 35EC@3ml/lit, Quinalphos 25EC@ 2ml/lit, Triazophos 40EC @ 2.5ml/lit, Lamda cyhalothrin 5EC@ 0.6ml/lit. Single spray was given at fruiting stage and tomato fruit samples were collected after 2 hours and brought to the laboratory for further analysis. The field trail was conducted in randomized block design, and all the treatments were replicated thrice.

Residue Analysis Method Validation

Prior to sample collection, AOAC official method 2007.01 (QuEChERS) for residue analysis of dimethoate, profenophos, chlorpyrifos, malathion, phosalone, quinalphos, triazophos, λ–cyhalothrin was validated by fortifying control samples at 0.50 mg/kg level, and the results indicated that the method was good as the recovery per cent was 97, 119, 96, 103, 114, 93, 99 and 97, respectively, and hence the method is used for analysis. The details of the method are as follows

- Tomato samples were homogenized with robot coupe blixer (high volume homogenizer). 15±0.1g sample was taken in 50ml centrifuge tube, and 30±0.1 ml acetonitrile was added.
- The sample was homogenized (low volume homogenizer) at 14000-15000 rpm for 2-3 min using Heidolph silent crusher, then added with 3±0.1g sodium chloride, mixed by shaking gently followed by centrifugation for 3 min at 2500-3000 rpm to separate the organic layer.
- The top organic layer of about 16 ml was taken into the 50 ml centrifuge tube and added with 9±0.1g anhydrous sodium sulphate to remove the moisture content.
- 8 ml of extract was taken in to 15 ml tube, containing 0.4±0.01gr PSA sorbent (for dispersive solid phase d-SPE cleanup) and 1.2±0.01gr anhydrous magnesium sulphate. The sample tube was vortexed for 30sec then followed by centrifugation for 5min at 2500-3000rpm.
- The extract of about 2ml was transferred into test tubes and evaporated to dryness using turbovap with nitrogen gas and reconstituted with 1ml n-Hexane for GC analysis with ECD and FPD detector. The GC column end at detector was fitted with Universal "Y" splitter for simultaneous analysis of insecticides on both detectors for confirmatory analysis. All pesticides could be detected and quantified on both ECD and FPD, except for triazophos and λ–cyhalothrin which could be detected only on ECD and FPD, respectively. The samples were also analysed on GC-MS/MS (triple quadrupole) for confirmatory analysis.

Decontamination Methods

After spray of pesticide, about 15 kgs of tomato fruits were collected randomly in polythene bags from each plot to avoid cross contamination. Each lot from treatment plot was divided in to 8 sub-lots, where one lot was analysed for initial deposits, and remaining lots were subjected to various rick mitigation methods prior to analysis. All samples were replicated thrice. The decontamination methods used in the study are presented in Table 1.

Table1. *Decontamination methods used in the study*

T1	Dipping in tap water for 10 minutes and washing under tap water for 30 sec
T2	Dipping in 2% salt solution for 10 min: 80 grams of table salt is added to 4 lts of water, and 1 kg tomato sample dipped in salt water for 10 min.
T3	Dipping in 2% tamarind Solution for 10 min: 80 grams of tamarind is added to 4 lts of water, and 1 kg tomato sample dipped in salt water for 10 min.
T4	Dipping in Lemon water (1Lemon/1lit) for 10min: Juice of 4 lemons is added to 4 lts of water, and 1 kg tomato samples is dipped in lemon water for 10 min.
T5	Dipping in 0.1% Sodium Bicarbonate solution for 10min: 4 grams of sodium bicarbonate is added to 4 lts of water; 1 kg tomato sample is dipped in solution for 10 min.
T6	Dipping in 4% Acetic acid solution for 1min: 160 ml of acetic acid is added to 4 lts of water; 1 kg tomato samples dipped in the solution for 10 min.
T7	Dipping in Formula 1 (4% Acetic acid+ 0.1%NAHCO3+ 1Lemon (1Lemon/1lit): 160 ml of acetic acid, 4 gms of sodium bicarbonate, lemon juice of 4 lemons added to 4 lts of water; 1 kg tomato samples dipping in solution for 10 min.
T8	Cooking in Pressure cooker: 1 kg tomato sample is cooked in pressure cooker for 5min.
T9	Washing with Bio wash keep it for 10min: 8 ml of commercial formula Biowash is added to 4 lts of water and 1 kg tomato samples is dipped in solution for 10 min.

After treatment, tomato samples were taken out and air dried for 5 min and analysed for residues after treatment as per validated AOAC official method 2007.01 (QuEChERS).

GC operating parameters for Profenophos, Chlorpyrifos, Dimethoate, Malathion, Phosalone, Quinalphos, Triazophos, Lamda cyhalothrin analysis

Gas Chromatograph	SHIMADZU – 2010
Detector	Electron Capture Detector and Flame photometric detecteor
Column	GC Capillary Column, MR 1 30 mts, 0.25 mm ID, 0.25mm Film Thickness
Injector Temp	260^{o}C
Injector Status	Split 10
Carrier Gas	Nitrogen (Prox Air)
Carrier Gas Flow	1.0 ml/min
Column Oven	150 ^{o}C-5 min hold up to 200 ^{o}C and then 5min hold and increase 2 ^{o}C/min – up to 280^{o}Chold it for 10 min. TOTAL 60.00 min
ECD Temp	300^{o}C
Makeup Flow	25 ml/min
Retention Time (min)	**ECD** **FPD** Dimethoate - 15.3 min 15.19 min Malathion - 21.8min 21.73 min Chlorpyrifos - 22.2 min 22.11min Quinalphos - 26.7 min 26.58 min Profenophos - 30.7 min 30.60 min Phosalone - 47.7 min 34.43 min Triazophos - - 37.40 min Lamda cyhalothrin - 48.4 min -

Results of Fortification and Recovery Studies in Tomato

The control / Tomato samples were fortified at 0.50 mg/kg levels adding required quantity of Profenophos, Chlorpyrifos, Dimethoate, Malathion, Phosalone, Quinalphos, Triazophos, Lamda cyhalothrin standards and replicated thrice.The following are the recoveries of Profenophos, Chlorpyrifos, Dimethoate, Malathion, Phosalone, Quinalphos, Triazophos, Lamda cyhalothrin at three different fortification levels.

Recoveries of Profenophos,Chlorpyrifos, Dimethoate, at various fortification levels in Tomato samples

Av.of three Replications	**Profenophos**		**Chlorpyrifos**		**Dimethoate**	
	0.5 mg/kg		**0.5 mg/kg**		**0.5 mg/kg**	
	Calculated Level (ppm)	**% Recovery**	**Calculated Level (ppm)**	**% Recovery**	**Calculated Level (ppm)**	**% Recovery**
Average/	**0.59**	**119**	**0.48**	**96**	**0.48**	**97**

The recovery of Profenophos was 119 %, Chlorpyrifos 96 %, and Dimethoate was 97% from the Tomato samples fortified at 0.50 mg/kg

Recoveries of Malathion, Phosalone, Quinalphos at various fortification levels in Tomato samples

Replication	**Malathion**		**Phosalone**		**Quinalphos**	
	0.5 mg/kg		**0.5 mg/kg**		**0.5 mg/kg**	
	Calculated Level (ppm)	**% Recovery**	**Calculated Level (ppm)**	**% Recovery**	**Calculated Level (ppm)**	**% Recovery**
Average/	**0.51**	**103**	**0.57**	**114**	**0.46**	**93**

The recovery of Malathion was 103 % from the Tomato samples fortified at 0.50 mg/kg and it was 114.0% for Phosalone and 93 % from Quinalphos

Recoveries of Triazophos, Lamda cyhalothrin at various fortification levels in Tomato samples

AV. Of three Replications	**Triazophos**		**Lamda cyhalothrin**	
	0.5 mg/kg		**0.5 mg/kg**	
	Calculated Level (ppm)	**% Recovery**	**Calculated Level (ppm)**	**% Recovery**
Average	**0.49**	**99**	**0.48**	**97**

The recovery of Triazophos was 99% from the Tomato samples fortified at 0.50 mg/kg. and the recovery of Lambda cyhalothrin was 97%

3. RESULTS AND DISCUSSION

The residues of dimethoate, profenophos, chlorpyrifos, malathion, phosalone, quinalphos, triazophos, λ-cyhalothrin in tomato samples have got substantial reduction by different house hold processing methods. The reduction percentage and residue levels have been presented in Table 3.

Table.2. Pesticide Residues (mg/kg) in Tomato Samples collected at 2 hrs after spray CONTROL

Pesticide	Residues (mg/kg)				SDEV	% RSD	MRL (mg/kg)	
	R1	R2	R3	AVERAGE			FSSAI	CODEX
Dimethoate	1.72	1.57	0.74	1.34	0.53	39.55	2.00	NA
Chlorpyriphos	0.92	0.89	0.81	0.88	0.06	6.29	0.20	NA
Quinolphos	1.33	1.27	1.09	1.23	0.13	10.28	NA	NA
Profenophos	1.60	1.56	1.35	1.50	0.13	8.93	NA	NA
Phosalone	2.28	2.22	1.51	2.00	0.43	21.32	1.00	NA
Lamda cyhalothrin	0.15	0.15	0.13	0.14	0.01	10.15	NA	0.300
Malathion	4.45	4.40	3.23	4.03	0.69	17.18	3.00	NA

Table3. *% removal of pesticide residues over control*

Pesticide	Table-3 % removal of pesticide residues over control								
	Tap Water	Lemon water	2% tamarind solution	2% salt solution	0.1% sodium bicarbonate solution	4% Acetic Acid solution	BIO WASH	Cooking	Formula-I
Dimethoate	30.700	39.000	26.800	45.300	25.400	24.400	36.500	64.000	24.100
Chlorpyriphos	35.300	41.500	24.100	43.000	21.500	14.800	42.700	45.900	25.900
Quinolphos	45.600	49.500	34.400	52.100	34.000	28.100	48.800	39.400	35.700
Profenophos	42.000	47.100	30.500	49.800	29.800	23.100	47.900	52.900	31.300
Phosalone	44.100	49.900	29.500	54.000	33.600	22.400	51.300	42.000	31.800
□ □ cyhalothrin	40.900	45.700	26.300	47.900	30.400	12.700	52.500	48.700	27.100
Malathion	70.300	69.900	65.300	76.500	61.300	54.200	72.500	81.400	59.100

3.1. Results:

In the process of washing under running tap water malathion residues were reduced up to 70.30%, whereas phosalone 44.10%, Quinolphos 45.60%, λ–cyhalothrin 40.90% , Profenophos 42%., Chlorpyriphos 35.30%, and dimethoate were reduced to 30.70% By washing the tomato samples under running tap water the residue levels of dimethoate were not degraded much..With the method of direct cooking malathion residues were reduced up to 81.40%, dimethoate 64%, Profenophos 52%.λ–cyhalothrin48.70%,and least reduction was seen in quinolphos 39.40%.

The direct cooking method has shown better effect when compared with Tap water washing. By washing with 2% s alt water malathion residues reduced by 76.50%, Dimethoate 45.30%, phosalone 54%,quinalphos 52.10%,and the lowest reduction was seen in chlorpyriphos residues with a reduction of 43%

Among all the treatments dipping in 2% tamarind solution, washing with 0.1% sodium bicarbonate solution ,4% acetic acid solution, washing with formula –I were less effective in reducing the pesticide residues compared to washing with tap water, lemon water, washing methods utilized. Among all the methods utilized Direct cooking and washing with 2% salt solution were most effective.

3.2. Discussion

Pesticides are used indiscriminately and excessively throughout the globe, and these residues remain in the food materials, water, fruits, vegetables (Baptista et al.,2008, Lazic et al., 2009) and in total

diet. Excessive use of pesticides, their toxic residues has been reported in various environmental commodities (Patel et al., 1999, Lazic et al.,2009). These pesticide residues enter in to the human body by consumption of the pesticide contaminated food which leads to the chronic disorders. Thus the removal of these residues from food commodities utilizing different processing methods is very essential) The different house hold preparations such as washing with tap water,washing with lemon water,dipping in 2% tamarind solution,cooking, dipping in 2% salt solution.washing with 4% acetic acid solution, biowash and washing with formula-Iplay a role in the reduction of pesticide residues (Wasim Aktar et al.),2010).

Thus, based on the results obtained in this study it can be concluded that by processing the tomato with the traditional processing methods if it helps in the removal of pesticide residues below MRL levels, then it is safe for human consumption.The results of earlier workers (Elkins ER. 1980, Dhiman et al., 2006, Kumari B.2008, WasimAktar et al., 2010, Saghir A. et al., 2012.) have shown similar results reducing the pesticide residues from tomato and other vegetables.

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