Methods for Removal of Pesticide Residues in Tomato

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Abstract  Tomato is highly cultivated vegetables consumed both as fresh salad and cooked in Andhra Pradesh, attacked by variety of insect pests, of which fruit borer is economically significant. Farmers use variety of pesticides, of which organophosphates and synthetic pyrethroids are predominant. However, farmers are not looking at the safety intervals while harvesting the tomato thus resulting in pesticide residues in tomato at both farm gate and market points. Hence, it is essential to look for cheap and best method which can be adopted easily at home, thus keeping the requirement in mind, a study was planned to evaluate certain methods for removal of pesticide residues from tomato. Ripe tomato fruits (fresh, undamaged, stalks removed) were divided into lots, and each lot was dipped in 0.2% insecticide solutions (dimethoate, Methylparathion, profenophos, endosulfan) separately for 5 minutes and air dried on clean surface. The randomly selected fruits were analysed for initial deposit of pesticides, and each lot of pesticide treated sample was subjected to different decontamination methods viz., washing under running tap water, 2% salt solution, direct cooking, dipping in 2% salt solution and cooking and analysed for final remaining residues after treatment using validated QuEChERS method utilising GC-ECD, FPD and GC-MS. Cumulative effect of all four household process caused substantial reduction in residues up to 95%. However, cooking with pressure cooker for 5 minutes reduced pesticides from 30-93%.

Keywords  Decontamination, Pesticide Residues, Tomato, Household Preparations

1. Introduction

Vegetables are Sources of essential biochemical’s and nutrients such as carbohydrates, carotene, proteins, vitamins, calcium, iron ascorbic acid and palpable concentration of trace minerals (Jimoh and Oladiji, 2005). These vegetables will continue to remain the basic source of energy for the developing countries. Vegetables are having pesticide residues (Baptista et al., 2008, Lazic et al., 2009) upon repeated application during entire period of growth in non prescribed manner to control different pests and to get better yield and quality. These residue are causing chronic disorders to the human health by consuming without processing. Removal of these residues is important before consumption of vegetables. In this study efforts were made to remove the pesticide residues by following different household preparations viz., Running tap water washing, 2% salt water washing, direct cooking, salt water washing plus cooking (Wasim Aktar et al., 2010) in tomato samples.

2. Materials and Methods

| Table 1. Operated GC Parameters |
|--------------------------------|
| **Gas Chromatograph** | SHIMADZU-2010. |
| **Detector** | ECD. |
| **Column** | Factor four Capillary Column, VF 1MS, 30 meters, 0.25 mm ID. |
| **Injector Tem** | 260°C. |
| **Split Ratio** | 100. |
| **Carrier Gas** | Nitrogen (Praxair). |
| **Carrier gas flow** | ml/min. |
| **Column Oven Temperatures** | 90°C5.00 min Hold@5°C/min150°C, 5min Hold, 3°C/min 240°C, 40 min Hold. TOTAL 90 min. |
| **ECD** | 300°C. |
| **Makeup flow** | 25 ml/min. |

Tomato samples were collected from the control plots of the field during the period January 2012. The collected samples were treated with the Dimethoate, Methylparathion, Quinalphos, Endosulfan, and Profenofos by preparing 0.2% solution by diluting 2 ml of formulations in 1 liter of water. The formulations were purchased from local vendors of Hyderabad The selection of the pesticides was based on the highest usages by farmers on vegetables in Andhrapradesh. These samples were divided in to four equal parts to follow different household preparation decontamination methods, viz.,(Running tap water washing, 2% salt water washing, direct cooking, salt water washing plus cooking (Wasim Aktar et al., 2010) in tomato samples.
plus cooking) with the intention of removal of residues from the surface of tomato samples. After processing of the samples the residues were extracted and cleanup was done with QuEChERS method (Multi residue Analysis method) and finally estimated with gas chromatography (GC) equipped with an electron capture detector. The operating parameters have been mentioned in (Table 1).

3. Method Validation
In order to validate the analytical method the fortification and recovery studies were done by spiking of 0.1, 0.5 and 1ppm concentrations of analytical grade Endosulfan (97% purity Dr. Ehrenstorfer), Dimethoate (98.5% purity, Dr. Ehrenstorfer), Quinolphos (99% purity, Dr. Ehrenstorfer), Methylparathion (98.5% purity, Dr. Ehrenstorfer), Profenophos (92% purity, Dr. Ehrenstorfer), standards to the control tomato samples. The spiked samples were processed according to the QuEChERS method along with the control sample, without spiking any standard, and each spiked concentration was replicated twice. The average percent recovery values for Dimethoate were 98.00 and 98.00 at 1ppm level, at 0.5ppm level the recovery values were 92.12 and 91.00 and at 0.1 ppm the level of recoveries are 89.00 and 88.00 percent. The recovery percentage for Methylparathion at three fortification levels are 99.00 and 98.50 at 1ppm level at 0.5ppm level the recovery values are 90.02 and 91.00 and at 0.1 ppm the level of recoveries are 80.00 and 78.10 percent. For Quinolphos the recoveries are 95.00 and 98.20 at 1ppm level 88.00 and 85.00 at 0.5ppm level, 84.00 at 0.1 ppm level. For Endosulfan the recoveries are 125.00 and 123.00 at 1ppm level, 98.00 and 95.00 at 0.5ppm level 85.30 and 87.00 at 0.1ppm level. For Profenophos the recoveries are 97.00 and 97.00 at 1ppm level, 82.00 and 81.10 for 0.5ppm level, at 0.1 ppm level the recoveries are 78.03 and 77.00 percent respectively (Table 2).

4. Reagents
Activated anhydrous magnesium Sulphate GR grade (MERK) Activated anhydrous Sodium Sulphate GR grade (MERK), Primary Secondary Amine (PSA) Sorbent (Agilent Technologies) Acetonitrile (MERK), n-Hexane (MERK), Sodium chloride (MERK).

5. Extraction
Chopped 1kg of tomato sample with robot coupe blixer. Weigh out of 15±0.1g sample in to 50 ml centrifuge tube, add 30±0.1ml Acetonitrile to the 50ml centrifuge tube cap well & shake, homogenize the sample at 14000-15000 rpm for 2-3 min using Heidolph silent crusher, add 3± 0.1g sodium chloride and mix it by shaking gently then centrifuge for 3 min at 2500-3000 rpm to separate the organic layer, taken approximately 16ml of organic layer to the test tube and add 9±0.1g anhydrous sodium sulphate to remove the moisture content.

### Table 2
Method Validation Result by Recovery Analysis.

| Substrates       | Standards (Analytical grade) | Amount fortified (mg kg⁻¹) | Amount recovered (mg kg⁻¹) | Average Recovery (%) |
|------------------|-----------------------------|---------------------------|----------------------------|----------------------|
| Dimethoate       | 0.1                         | 0.088                     | 88.50                      |
|                  | 0.5                         | 0.457                     | 91.56                      |
|                  | 1                           | 0.98                      | 98.00                      |
| Methylparathion  | 0.1                         | 0.079                     | 79.00                      |
|                  | 0.5                         | 0.452                     | 90.51                      |
|                  | 1                           | 0.98                      | 98.75                      |
| Quinolphos       | 0.1                         | 0.084                     | 84.00                      |
|                  | 0.5                         | 0.432                     | 86.50                      |
|                  | 1                           | 0.96                      | 96.60                      |
| Endosulfan       | 0.1                         | 0.086                     | 86.15                      |
|                  | 0.5                         | 0.482                     | 96.50                      |
|                  | 1                           | 1.24                      | 124.00                     |
| Profenophos      | 0.1                         | 0.077                     | 77.51                      |
|                  | 0.5                         | 0.407                     | 81.55                      |
|                  | 1                           | 0.097                     | 97.00                      |
6. Dispersive Solid Phase Cleanup (d-SPE-Cleanup)

Weighed out 0.4gr±0.01g PSA sorbent and 1.2±0.01g anhydrous magnesium sulphate in to 15ml centrifuge tube for 8ml organic layer (extract), transfer 8ml extract in to 15ml centrifuge tube with PSA and anhydrous magnesium sulphate cap the tube well and vortex for 30sec then centrifuge the tube for 5min at 2500-3000rpm, transfer 2ml extract to the test tube and evaporate the solvent (Acetonitrile) using turbovap concentrator for GC analysis, reconstitute with 1ml n-hexane for GC analysis.

7. Results

The residues of Dimethoate, Methylparathion Quinalphos, Endosulfan and Profenofos in tomato sample have got substantial reduction by different house hold processing methods. The reduction percentage and residue levels have been presented in Table 3.

| Treatment Method         | Treated Pesticides | Reduced Residue Levels (mg kg⁻¹) | Reduction (%) |
|--------------------------|--------------------|---------------------------------|---------------|
| Running Tap Water Washing| Dimethoate         | 1.44                            | 48.00         |
|                         | Methylparathion    | 1.45                            | 50.00         |
|                         | Quinolphos         | 1.47                            | 52.00         |
|                         | Endosulfan         | 1.49                            | 53.00         |
|                         | Profenophos        | 1.31                            | 47.07         |
| Direct Cooking           | Dimethoate         | 1.69                            | 56.41         |
|                         | Methylparathion    | 1.68                            | 58.00         |
|                         | Quinolphos         | 1.65                            | 58.20         |
|                         | Endosulfan         | 1.76                            | 61.00         |
|                         | Profenophos        | 1.64                            | 59.00         |
| 2% Salt Water Washing    | Dimethoate         | 2.35                            | 78.00         |
|                         | Methylparathion    | 2.38                            | 82.00         |
|                         | Quinolphos         | 2.58                            | 91.30         |
|                         | Endosulfan         | 2.57                            | 89.00         |
|                         | Profenophos        | 2.45                            | 88.20         |
| 2% Salt Water Washing plus Cooking | Dimethoate | 2.98                            | 99.00         |
|                         | Methylparathion    | 2.90                            | 100.00        |
|                         | Quinolphos         | 2.77                            | 98.02         |
|                         | Endosulfan         | 2.86                            | 99.01         |
|                         | Profenophos        | 2.77                            | 99.70         |

In the process of under running tap water washing Dimethoate residues were reduced up to 48%, whereas Methylparathion 50%, Quinolphos 52%, Endosulfan 53% and Profenophos were reduced to 47%. By washing the tomato samples under running tap water the residue levels were not degraded below the MRL levels.

With the method of direct cooking Dimethoate residues were reduced up to 56.41%, the residues of Methylparathion were 58%, Quinolphos 58.20%, Endosulfan 61.00% and Profenophos reduced to 59%. The direct cooking method has shown slightly better effect when compared with Tap water washing.

By washing with 2% salt water Dimethoate is reduced to 78%. 82% of reduction in Methylparathion, Quinolphos reduced to 91%. Endosulfan has got reduction up to 89% and 88.20% of reduction shown in Profenophos. A notable effect has got with 2% salt water washing when compared with above three processing methods. By processing with 2% salt water plus cooking the entire residues from the tomato sample were drained out up to ±1 to 100%. All the residues were below MRL levels.
8. 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, cooking, washing plus cooking, salt water washing play a role in the reduction of pesticide residues (Wasim Aktar et al., 2010). While plain tap water washing have not shown any promising effect in the removal of residues below MRL levels, washing with 2% salt water yielded very good effect in the removal of the residues below MRL levels.

Direct cooking Process has shown less effect in the removal of residues when compared with 2% salt water washing because of all the processed pesticides are having the property of highly water solubility, but in the case of Endosulfan and Profenophos the cooking process has shown slight effect in the removal of residues because of their fat soluble property. With the process of 2% salt water plus cooking the residues were reduced by 98-100%, the fat soluble and water soluble pesticides have been removed with this process.

Thus, based on the results obtained in this study it can be concluded that by processing the tomatoes 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, Wasim Aktar et al., 2010, Saghir A. et al., 2012.) have shown similar results reducing the pesticide residues from tomatoes and other vegetables.

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