ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

EFFECT OF WASHING ON RESIDUES OF CHLORPYRIFOS AND MONOCROTOPHOS IN VEGETABLES

Subhash Chandra[1], Mukesh Kumar[2], Anil N. Mahindrakar[1], L.P. Shinde[1]

1. Department of Chemistry, N.E.S. Science College, Nanded - 431 605, Maharashtra, India.
2. Department of Chemistry, Vardhman College, Bijnaur-246701,Uttar Pradesh, India.

Manuscript Info

Manuscript History:

Received: 26 October 2014
Final Accepted: 29 November 2014
Published Online: December 2014

Key words: -
Monocrotophos, Chlorpyriphos, GC-ECD. Capsicum, Cauliflower

Corresponding Author

SUBHASH CHANDRA

Abstract

In this study the effect of washing on residue of chlorpyriphos and monocrotophos in capsicum and cauliflower was determined. The washing processes were carried out with normal and hot water with different span of time. The vegetables samples were washed with normal and hot water (~50^0C). The samples were extracted with 1% acetic acid in acetonitrile mixture and cleaned up with primary secondary amine (PSA) and magnesium sulphate and analysed by gas chromatography electron capture detection. The chlorpyriphos residue reduced in capsicum and cauliflower from 25 to 42% after normal water washing, and 36-74% reduced with hot water washing. Whereas monocrotophos residue was reduced in capsicum and cauliflower 23 to 39% after normal water washing and 35-72% reduced after hot water washing. The vegetable samples collected from the local market contained detectable residues representing approximate 80% rate of contamination. There were some of the vegetables samples contained chlorpyriphos and monocrotophos residues above maximum residue limits (MRLs). However, washing of vegetable reduced some extent of the pesticide residues. The average recoveries of pesticide residues in cauliflower and capsicum samples are 80.0 to 100.0 %.

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Introduction

Vegetables are the important food and highly beneficial for health. It contains valuable food ingredients, which can be successfully utilized to build up and repair the body. In India, vegetables are major constituents of diet as majority of people are vegetarian. Since the vegetables are important food item for Indian and limited availability for all population. However, several factors limit their productivity, mainly insect pests, and diseases. As several insect pests attack the vegetables, they are produced under very high input pressure. Among the vegetables, capsicum and cauliflower is very common and give better return over investment to the farmers.

Cauliflower (Brassica oleracea), an important vegetable crop grown in India, it is heavily attacked by various insects, resulting in severe loss of quality and production (Patel et al., 1999). Capsicum (C. annuum, C. baccatum, C. chinense, C. frutescens, and C. pubescens.) belongs to family solanaceae is also an important vegetable crop grown extensively in India. To control of numerous insect pests, different insecticides have been used (Singh et al., 2004; Sinha and Sharma, 2007). Chemical pesticides have been widely employed for effective controlling of a pest complex of various vegetable crops, but their indiscriminate use may create health hazards due to toxic residues that may persist in amounts above prescribed Maximum Residue Limits (MRL). The problem becomes more acute if the xenobiotics are used close to harvest as well as during transit and in vegetable yards. Contamination of vegetables with pesticide residues has been reported by several researchers (Madan et al., 1996; Kumari et al., 2002, 2003 and 2004; Deka et al., 2005; Geetanjali K. et al., 2009; Subhash Chandra et al., 2010; Subhash Chandra et al.,2012; Shinde L.P. et al.,2012; Dasika R. et al., 2012). In some studies it were also, observed the effects household methods for removal of pesticide residues from different vegetables by (Krol, W.J. et al., 2000, Soliman, K.M. 2001; Klinhom et al.,2008; Kumari B.,2008; Keikotlhaile et al. 2010; Ling, Y. et al., 2011; Reena and Beena 2011; Satpathy G. et al. 2012).

The aim of this study was to evaluate the chlorpyriphos and monocrotophos residue in capsicum and cauliflower to assess the effect washing on pesticides residues with normal and hot water washing of vegetables. The collected data can be used as a reference point for future monitoring and taking preventive measures to minimize human health risks.

This method has several advantages over most traditional methods of analysis. High recoveries (greater than 80%) were achieved for a wide polarity and volatility range of pesticides, solvent usage and waste is very small, and no chlorinated solvents are used. Applying this scheme, analysis time is shorter compared to other methods. Thus, high sample throughput can, therefore, be achieved, which is useful in pesticide monitoring programs with a large number of samples to analyse. In the present study, a method employing GC equipped with ECD detector for the separation, identification and quantification of two pesticides on cauliflower and capsicum.

Experimental

Chemical and reagents

The organic solvent acetic acid, acetonitrile HPLC grade, magnesium sulphate and sodium acetate AR grade purchased from E Merck and primary secondary amine purchased from Agilent Technologies. The technical grade pesticide standards were used for standardizations. The standards were stored in a freezer at -5^{o}C. Anhydrous magnesium sulphate used during residue extraction was maintained at 300^{o}C overnight and kept in air tight container.

Sample preparation and clean up

A total sixteen samples of cauliflower and capsicum was collected periodically from local market. 2 kg of each sample was taken for the experimental purpose. In order to assess the effects of washing with normal and hot water, the samples of vegetables were washed under normal tap water and hot water for 5, 10, and 15 minute, after washing the samples were kept on filter paper.

The samples were macerated and homogenized in a Bajaj Super Mix (equipped with stainless steel knives), a 15 g portion of the homogenized sample was weighed into a 50 ml polytetrafluoroethylene (PTFE) tube added 15 ml of acetonitrile containing 1% acetic acid (v/v not accounting for purity). Then, 6 g $MgSO_4$ and 2.5 g sodium acetate trihydrate (equivalent to 1.5 g of anhydrous form) were added, and the sample was shaken forcefully for 4 min and kept in ice bath. The sample was then centrifuged at 4000 rpm for 5 min and 6 ml of the supernatant were transferred to a 15 ml PTFE tube to which 900 mg $MgSO_4$ and 300 mg PSA were added. The extract was shaken using a vortex mixer for 20 s and centrifuged at 4000 rpm again for 5 min., approximately 2ml of the supernatant were taken in a vials. This extracts were evaporated to dryness under a stream of nitrogen and reconstituted in n-hexane in an auto sampler tube for GC-ECD analysis.

Standard preparation

For preparation of stock solution, standards were dissolved in ethyl acetate and four levels of intermediate standard solution of each pesticide were prepared maintaining the same matrix concentration for the preparation of calibration curve and stored at -4^{o}C in the dark .Working solutions were prepared daily by appropriate dilution with ethyl acetate.

Limit of detection and limit of quantification

The limit of detection (LoD) was calculated from the peak intensity at 0.01mg kg^{-1} and blank in recovery tests. LoD was defined as S/N>4 so that it is in the linear range of the standard calibration. The LoD of monocrotophos and chlorpyriphos was 0.005, and 0.003, mg kg^{-1} respectively. LoQ was obtained for monocrotophos and chlorpyriphos, was 0.0015, and 0.003mg kg^{-1} respectively (table 1). Linear calibration curves were found between peak areas and analyte concentration in the whole range of studies. The linear regression (y = a + bx) parameters for method calibration were taken (table 2). The correlation coefficients of analytical curves were near 0.99, with linearity for each compound, which allows the quantitation of these compounds by the method external standardization.

Recovery

Recovery studies were performed to examine the efficacy of extraction and clean up. Untreated cauliflowers and capsicum samples were spiked with known concentration of the pure pesticides standard solution and extraction and clean-up were performed as described earlier. The concentration of each pesticide in the final extracts was calculated (table 3). The average recoveries of pesticide residues in cauliflower and capsicum samples were in the range of 80.0-100.0%.

Estimation

The cleaned extracts were analysed on Hewlett Packard 5890A GC equipped with capillary columns using ^{63}Ni electron capture detector (ECD). Operating conditions were as : Detector : ECD (^{63}Ni), column: SPB-5 of 5% diphenyl/ 95% dimethyl fused silica capillary column (30 m×0.32 mm ID, 0.25 μm film thickness) with split system. Temperatures (^{0}C):150 (5 min)→8 ^{0}min^{-1} → 190^{0} (2 min) → 15 ^{0}min^{-1} 280° (10 min); injection port: 280; detector: 300; carrier gas: (N_2), flow rate 60 ml min^{-1}, 2 ml through column and split ratio 1:10. Carrier gas, N_2, flow rate 60 ml min^{-1}, 2 ml through column.

Results and discussion

The chlorpyriphos and monocrotophos are generally applied by the vegetables growers in these vegetables were analysed for their residue content. The samples of capsicum and cauliflower vegetables were collected from local market in fifteen days time of interval these samples were divided into four lots of each commodity. There was first lot having eight samples of each vegetable analysed for their chlorpyriphos and monocrotophos residue content. Washing of each vegetable was done with different duration of time viz. 5, 10 and 15 min these samples were analysed and recorded their residue content after each washing. Washing of the capsicum and cauliflower were carried out with normal water 5, 10, and 15 minute and the residues of chlorpyriphos were reduced from 25.0% to 42%. (Table: 3).

The second lot of the eight samples was taken for washing with normal water for the determination of monocrotophos content in capsicum and cauliflower. Washing of the capsicum were carried out with normal water 5, 10, and 15 minute and the residues of monocrotophos were reduced from 23 to 39% (Table: 4)

The third lot of the eight samples was taken for washing with hot water for the determination of chlorpyriphos content in capsicum and cauliflower. Washing of the vegetable were carried out with hot water 5, 10, and 15 minute and the residues of chlorpyriphos were reduced from 35 to 74% (Table:5)

The fourth lot of the eight samples was taken for washing with hot water for the determination of content in capsicum and cauliflower. Washing of the vegetable were carried out with hot water 5, 10, and 15 minute and the residues of monocrotophos were reduced from 35 to 72% (Table:6)

The average percent recoveries of the chlorpyriphos and monocrotophos residue were in the range of 80.0-100%. The study revealed that contamination level was maximum in cauliflower and minimum in capsicum. Most of the samples were found contaminated with pesticide contained residues above maximum residue limits (MRL) fixed by Prevention of Food Adulteration Act PFA (1954) and FAO/WHO (1996). The results obtained from the present study are concurrent with an earlier study that show residues of these pesticides are present in different vegetables (Madan et al., 1996; Kumari et al., 2002 and 2003; Deka et al., 2005).

Table 1: Molecular formula, retention time, LODs and LOQs of monocrotophos and chlorpyriphos.

Compound	**Molecular formula**	**RT (min)**	**LoDs (mg kg^{-1})**	**LoQs (mg kg^{-1})**
Monocrotophos	$C_7H_{14}NO_5P$	17.89	0.005	0.015
Chlorpyriphos	$C_9H_{11}Cl_3NO_3PS$	25.12	0.003	0.009

Table 2: Calibration range of monocrotophos and chlorpyriphos

Compound	**Calibration range (mg kg^{-1})**	**Correlation coefficient**	**Coefficient of variation (n=5) %**
Monocrotophos	0.02-1.00	0.994	5.8
Chlorpyriphos	0.02-1.00	0.995	6.0

Table: 3 Effect of washing on Chlorpyrifos residue in capsicum and cauliflower with normal water.

Pesticide detected	Vegetable	Initial residue (mg/kg)	Periods of washing in min					
			5min washing	% Reduction of pesticide	10min washing	% Reduction of pesticide	15 min washing	% Reduction of pesticide
Chlorpyrifos	Capsicum	0.160	0.119	25.6	0.109	31.8	0.068	42.5
Chlorpyrifos	Capsicum	0.094	0.070	26.1	0.064	31.9	0.039	41.4
Chlorpyrifos	Capsicum	0.024	0.017	29.2	0.016	33.3	0.010	41.6
Chlorpyrifos	Capsicum	0.048	0.036	25.0	0.030	37.5	0.027	43.7
Chlorpyrifos	Cauliflower	0.027	0.020	25.9	0.017	37.0	0.011	40.7
Chlorpyrifos	Cauliflower	0.009	ND	ND	ND	ND	ND	ND
Chlorpyrifos	Cauliflower	0.116	0.087	25.0	0.077	33.6	0.068	41.3
Chlorpyrifos	Cauliflower	ND	ND	ND	ND	ND	ND	ND

Table: 4 Effect of washing on monocrotophos residue in capsicum and cauliflower with normal water

Pesticide detected	Vegetable	Initial residue (mg/kg)	Periods of washing in min					
			5 min washing	% Reduction of pesticide	10 min washing	% Reduction of pesticide	15 min washing	% Reduction of pesticide
Monocrotophos	Capsicum	0.094	0.073	22.3	0.063	32.9	0.058	38.3
Monocrotophos	Capsicum	0.128	0.099	22.6	0.088	31.2	0.080	37.5
Monocrotophos	Capsicum	0.178	0.134	24.7	0.122	31.4	0.109	38.7
Monocrotophos	Capsicum	ND	ND	ND	ND	ND	ND	ND
Monocrotophos	Cauliflower	0.096	0.072	25.5	0.066	31.2	0.059	38.5
Monocrotophos	Cauliflower	0.260	0.196	24.6	0.177	31.9	0.162	37.7
Monocrotophos	Cauliflower	ND	ND	ND	ND	ND	ND	ND
Monocrotophos	Cauliflower	0.042	0.032	23.8	0.029	30.9	0.027	35.7

Table: 5 Effect of washing on chlorpyriphos residue in capsicum and cauliflower with hot water

Pesticide detected	Vegetable	Initial residue (mg/kg)	Periods of washing in min					
			5 min washing	% Reduction of pesticide	10 min washing	% Reduction of pesticide	15 min washing	% Reduction of pesticide
Chlorpyrifos	Capsicum	0.046	0.337	36.9	0.029	52.2	0.012	73.9
Chlorpyrifos	Capsicum	0.108	0.067	37.9	0.050	53.7	0.030	72.2
Chlorpyrifos	Capsicum	0.028	0.018	35.7	0.012	57.1	0.008	71.4
Chlorpyrifos	Capsicum	ND	ND	ND	ND	ND	ND	ND
Chlorpyrifos	Cauliflower	0.088	0.056	36.3	0.042	52.2	0.023	73.8
Chlorpyrifos	Cauliflower	0.112	0.070	37.5	0.053	59.0	0.029	74.1
Chlorpyrifos	Cauliflower	0.008	ND	ND	ND	ND	ND	ND
Chlorpyrifos	Cauliflower	0.110	0.072	34.5	0.052	52.7	0.031	71.8

Table: 6 Effect of washing on monocrotophos residue in capsicum and cauliflower with hot water

Pesticide detected	Vegetable	Initial residue (mg/kg) in unwashed samples	Periods of washing in min					
			5 min washing	% Reduction of pesticide	10 min washing	% Reduction of pesticide	15 min washing	% Reduction of pesticide
Monocrotophos	Capsicum	0.150	0.098	34.7	0.068	54.7	0.043	71.3
Monocrotophos	Capsicum	0.068	0.043	36.8	0.032	52.9	0.020	70.6
Monocrotophos	Capsicum	0.008	ND	ND	ND	ND	ND	ND
Monocrotophos	Capsicum	0.098	0.061	37.0	0.047	51.0	0.028	71.4
Monocrotophos	Cauliflower	0.210	0.137	34.7	0.093	55.7	0.058	72.3
Monocrotophos	Cauliflower	0.074	0.045	39.2	0.035	52.7	0.021	71.6
Monocrotophos	Cauliflower	ND	ND	ND	ND	ND	ND	ND
Monocrotophos	Cauliflower	0.004	ND	ND	ND	ND	ND	ND

ND = Non detected

MRL (mg kg^{-1}) from PFA: Chlorpyriphos: 0.05(for cauliflower)/ 0.2(for other vegetables) and Monocrotophos: 0.2

Conclusion

It can be concluded that most of the samples of the vegetables having pesticide residue their respective maximum residue limits. Processing (normal and hot water washing) substantially lowers the residues of pesticides in vegetables. The percentage reductions in the present study are supported by both early and most recent publications. Washing vegetables with the hot water reported here enhances in the dislodging of pesticide residues from produce more than that of normal water washing. The hot water washing was found to be most effective in reducing the pesticide residues which was due to the high degree in the pesticide solubility in this medium. This method was useful for detection of pesticide residue present in the vegetables. It is most effective and widely acceptable in terms of accuracy and reliability. The objective of this study was to create awareness among the vegetables consumers who were consuming contaminated vegetables. The developed processing method was reducing the residue to an acceptable and less harmful level. This method was very simple for removal of pesticide residue from the produce and consumer can apply this technique in their houses.

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