Effect of Processing on Profenofos and Chlorpyrifos Residues in Cauliflower Curds

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ABSTRACT

Field and laboratory experiments were carried out to evaluate the effect of different decontamination processes on reduction of profenofos and chlorpyrifos residues in cauliflower curds like washing, cooking, washing plus cooking and dipping in chemical solutions after application of Profex 50EC (profenofos 50%) and Lethal 20EC (chlorpyrifos 20%) individually on the crop. Profex 50EC was applied twice at the rate of 0.8ml/L and Lethal 20EC @ 2.50ml/L at 15 days interval on cauliflower crop. Cauliflower curds were collected at 0 (2 hours) and 3 days interval for profenofos and for chlorpyrifos curds were sampled at 0 (2 hours), 3 and 7 days after the last spray and subjected to decontamination processes. Washing of zero day contaminated curd samples provided 26.06-67.09% relief from profenofos residues and 35.44-67.18% relief from chlorpyrifos residues. Cooking degraded profenofos residues up to 37.17-67.57% and chlorpyrifos residues by 36.00-56.80%. Washing plus cooking removed profenofos and chlorpyrifos residues up to 70% as compared to other processes and proved to be the best technique in removing the residues. Washing of curds with 2% NaOH solution reduced the profenofos residues up to 67.09-70.30%, whereas washing with 0.05% solution of HCl reduced the profenofos residues up to 63.48-65.52%. Similarly chlorpyrifos residues were reduced to 40.00-67.18% after treatment with 2% NaOH solution and up to 44.00-61.17% after treatment with 0.05% HCl solution.

Keywords
Cauliflower, Processing, Profenofos, Chlorpyrifos, Residues

Introduction

Vegetables are the inseparable component of Indian cuisine and are consumed throughout the country in different forms and preparations. They are the major source of vitamins and nutrients; hence they fulfill the requirements of our balanced diet (Chandra et al., 2015). Cauliflower (Brassica oleracea var. botrytis L.) is an important cash crop of Himachal Pradesh which is infested by a large number of insect-pests and diseases (Sharma and Bhalla, 1964; Sharma, 1975; Bhalla and Pawar, 1977). The key pests of cauliflower are diamond back moth, leaf eating caterpillar and aphids (Regupathy et al., 1985; Patel et al., 1999) thus affecting both the quantity and quality of curds. In a desperate bid to save the crop farmers sometime apply the pesticide repeatedly and at higher doses hence the repeated and intensive use of insecticides have led to the development of resistance in insect...
pests (Gaganpreet et al., 2017). In Himachal Pradesh pesticides such as profenofos and chlorpyrifos have been used extensively by the farmers to control these major insect-pests of cauliflower crop. Since, the effect of insecticides is considered more toxic hence extra care should be taken to reduce the health hazards to the consumers. The application of these pesticides near to harvest can leave residues on the curds which may be harmful to the consumers (Banshtu et al., 2015).

Cauliflower is consumed as cooked or raw; hence chances of carrying pesticide residues to the consumers are more (Raj et al., 1991). Hence Pesticide residues in cauliflower are of major concern to consumers due to their negative health effects.

They have been found in both raw and processed fresh produce. There have been various reports suggesting use of different simple household processes in dislodging pesticide residues from food commodities thus making them safe for human consumption (Sharma et al., 1994; Aktar et al., 2009; Chavarri et al., 2005; Dejonckheere et al., 1996; Elkins, 1989; Krol et al., 2000; Schattenberg et al., 1996).

Operations such as Washing, peeling, blanching and cooking play a crucial role in the reduction of residues (Elkins, 1989; Kaushik et al., 2009). Each operation has a cumulative effect on the reduction of the pesticides (Geisman et al., 1975).

So in the present scenario it is very important that some pragmatic solution should be developed to tackle this problem of food safety. Food safety is an area of growing concern worldwide on account of its direct bearing on human health. The presence of harmful pesticide residues in food such as cauliflower has caused a great concern among the consumers. Therefore, the present investigations were contemplated with the objective to study the effect of different decontamination processes in curds for the reduction of profenofos and chlorpyrifos residues after its application on cauliflower crop in the field. Hence the techniques used in the present study focused on commercial and home processing of tomato and they included washing alone, washing with chemicals, cooking and washing followed by cooking.

**Materials and Methods**

**Chemicals and reagents**

Profex 50EC containing 50% profenofos was obtained from M/S Nagarjuna AgriChem Ltd. and Lethal 20EC containing 20% chlorpyrifos was obtained from M/S Insecticides (India) Ltd. and reagents like acetone, dichloromethane, hexane, toluene, sodium chloride, sodium sulfate anhydrous (AR grade), Celite 545 were all procured from M/S Merck Specialities, Mumbai.

Activated charcoal decolorizing powder was obtained from M/S Darmstadt, Germany. All common solvents were redistilled in an all-glass apparatus before use.

**Field trials**

Cauliflower curds (*Brassica oleracea* var. *botrytis* L.) were raised during 2010 at Entomological Farm, Dr YS Parmar University of Horticulture and Forestry, Nauni, Solan, Himachal Pradesh following recommended agronomic practices (Anonymous, 2010). The experiment was conducted in randomized block design (RBD) with three replications for each treatment.

The first application of Profex 50EC (profenofos 50%) @ 0.8 ml/L and Lethal 20EC (chlorpyrifos 20%) @ 2.50ml/L were made at curd formation stage followed by
second application at an interval of 15 days. In control plots, only water was sprayed. Pesticide was sprayed as foliar application in three replications with the help of a knapsack sprayer, fitted with a hollow cone nozzle.

**Sampling procedure**

Curd samples (1kg) from each replication were collected randomly at 0 (2 hours after spray) and 3 days intervals after last foliar application. The samples from each replication were collected randomly, packed in bags and brought to the laboratory for processing.

**Decontamination processes**

Samples collected from the field were subjected to different decontamination processes viz. washing, cooking and washing followed by cooking (Patyal *et al.*, 2004).

**Washing**

Cauliflower curds were washed under running tap water and hand rubbed for 2 minutes.

Cauliflower curds samples were dipped in lukewarm water (50°C) for 5 minutes and then, placed on filter papers for drying.

Cauliflower curds samples were dipped in 2% NaCl (w/v) solution for 5 minutes followed by tap water washing.

Cauliflower curds Samples were dipped in 2% lukewarm salt solution (w/v) for 5 minutes followed by water washing.

Cauliflower curds samples were dipped in 0.05% HCl (v/v) for 5 minutes, followed by water wash.

Cauliflower curds samples were dipped in 2% (w/v) sodium hydroxide solution for 5 minutes, followed by washing with water.

**Cooking**

Open pan cooking: Unwashed samples from each replication were chopped and put in an open pan of 1 litre capacity containing 500 ml water and boiled till softness (10-15 minutes).

Steam cooking: Samples were chopped and steamed for 5 minutes in a pressure cooker.

Microwave cooking: Curd samples were kept in microwave for 5 minutes for cooking at 1400 W power output.

**Washing followed by cooking**

Washing + cooking: Curd samples were first washed by hand rubbing under a stream of running tap water for 2 minutes, followed by boiling in an open pan of 1 litre capacity containing 500 ml water till soft (10-15 minutes).

Washing + steam cooking: Samples were washed under running tap water and steamed for 5 minutes in a pressure cooker.

Washing + microwave cooking: Samples were first washed under the tap water and then, placed in microwave for 5 minutes for cooking at 1400 W power output.

After completing decontamination process, samples were extracted and cleaned up according to the method of Sharma (2007).

**Extraction and cleanup**

The samples were processed and analyzed at the Pesticide Residue Analysis Laboratory, Department of Entomology, Dr YS Parmar University of Horticulture and Forestry, Nauni, Solan, Himachal Pradesh.

Processed cauliflower curds samples were homogenised in a domestic mixture.
A representative 100 g homogenised sample was taken up with 200 ml acetone in a 500 ml conical flask and kept for overnight. The extract was filtered through Buchner funnel by fitting a Whatman No. 1 filter paper. An aliquot of 60 ml (30 g equivalent) of sample was transferred to 1 litre separatory flask and extracted with 200 ml mixture of hexane and dichloromethane (1:1, v/v). The lower aqueous phase was transferred to another 1 litre separatory funnel containing ten millilitre saturated sodium chloride solution and partitioned twice with 100 ml dichloromethane. Lower aqueous phase was discarded and upper organic phase was pooled with first organic fraction. Pooled organic phase was passed through anhydrous sodium sulfate and evaporated to dryness at 45\(^0\)C by using vacuum rotary evaporator. Finally, the residues were taken up in 3 ml (1+2) acetone for cleanup. Profenofos and chlorpyrifos samples were cleaned up on charcoal column. Two millilitres of sample fraction of each was loaded in a charcoal column which was prepared by placing one inch layer of Celite 545, 6 g adsorbent mixture (1:4 w/w Charcoal: Celite 545) and then, overlaid with 2 g sodium sulfate. The column was eluted with 200 ml of 2:1 acetone: dichloromethane mixture. Eluent was evaporated to dryness, residues were dissolved in 2 ml n-hexane and 1\(\mu\)l was injected into a gas chromatograph.

**Residue estimation**

Residues of profenofos and chlorpyrifos were estimated by using Gas-Chromatograph (Agilent 6890N) having ECD detector and DB-5 Ultra Performance Capillary column (Cross-linked Methyl Silicon, length 30 m, 0.25 mm internal diameter with 0.25 \(\mu\)m film thickness). Oven temperature was programmed as: 100\(^0\)C for 1 minute, 30\(^0\)C/minute up to 150\(^0\)C, 3\(^0\)C/ minute up to 205\(^0\)C and finally 260\(^0\)C at rate of 10\(^0\)C/ minute. Injection port and electron capture detector (ECD) temperature were kept at 250\(^0\)C and 300\(^0\)C, respectively.

Profenofos and chlorpyrifos residues (mg/kg) were determined for each replication and then mean residues were calculated. Per cent relief from residues in each treatment was calculated from the mean residues, by the following equation:

\[
\% \text{ relief} = 100 - \left( \frac{\text{Residue in processed sample (mg/kg)}}{\text{Residue in unprocessed sample (mg/kg)}} \right) \times 100
\]

**Validation of analytical method**

Unprocessed samples from untreated plot were spiked with profenofos insecticide at 0.05, 0.10, 0.20, 0.50 and 1.00 mg/kg and for chlorpyrifos it was 0.01, 0.05, 0.10, 0.50 and 1.00 mg/kg fortified levels. Data presented in Table 1 depicts reliability of analytical method, as the recovery of insecticides was above 88 per cent. Recovery of profenofos was between 88.00-94.00% with relative standard deviation (RSD) of 0.044-0.679% and for chlorpyrifos recovery was between 90.00-94.00% with RSD 0.112-1.030% (Table 1).

**Results and Discussion**

**Effect of Washing**

Washing is the most common form of processing which is a preliminary step in both household and commercial preparation. Loosely held residues of several pesticides are removed with reasonable efficiency by varied types of washing processes (Street, 1969). Washing of 0 day sampled cauliflower curds under running tap water provided 26.06% relief from profenofos residues whereas 36.17% relief was observed in 3 day old samples (Figure 1). After washing of chlorpyrifos treated cauliflower curds
observations were recorded in 0, 3 and 7 days sampled curds and per cent relief were 35.44, 31.46 and 16.00, respectively (Figure 2). Aktar et al., (2010) reported that washing of cabbage head under running tap water removed 27.72-32.48% quinalphos residues which are in accordance with my findings.

Similarly, Singh et al., (2004) also found that washing of okra fruits with tap water could remove the residues of cypermethrin to the extent of 36.25-42.76%. The initial diazinon residue level (0.822 ppm) on cucumbers was decreased by 22.3% by washing for 15 seconds rubbing under running water (Cengiz et al., 2006).

Lukewarm water washing of 0 day sampled cauliflower curds provided 28.34% relief from profenofos residues whereas 39.24% relief was observed in 3 days old samples (Fig. 1).

Similarly, in chlorpyrifos treated cauliflower curds observations were recorded on 0, 3 and 7 days and 38.58, 36.85 and 16.00% relief was observed respectively (Fig. 2) which are in accordance with Kanta et al., (1998) who reported 7-38 per cent reduction of alpha-cypermethrin residues by lukewarm water washing of cauliflower curds.

Kumari (2008) also reported 32-100 per cent reduction of OP’s insecticide residues by lukewarm water of cauliflower.

Chemical washing

Washing of treated cauliflower curds with sodium hydroxide and hydrochloric acid provided a good relief from profenofos and chlorpyrifos residues in comparison to washing with sodium chloride and lukewarm sodium chloride solution. It may be due to hydrolytic property of profenofos and chlorpyrifos in strong acids and alkalis (Tomlin, 1995). Sodium hydroxide provided 70.30% and 67.18% relief from profenofos and chlorpyrifos, respectively. Dip treatment of cauliflower curds with hydrochloric acid gave 65.52% relief from profenofos and 61.17% from chlorpyrifos residues.

The present findings are in agreement with Patyal et al., (2004) who found that washing of treated apple fruits with 2% (w/v) NaOH and 0.05% (v/v) HCl gave 77.06 and 75.96%, relief respectively from endosulfan residues.

Dipping of cauliflower curds samples in 2% sodium chloride solution (w/v) reduced profenofos and chlorpyrifos residues to 41.29% and 41.46% whereas lukewarm sodium chloride solution reduced residues to 55.29% and 48.88% respectively which is in agreement with the findings of Mukherjee et al., (2006) also observed that dipping of cauliflower curds in 1% brine solution followed by washing reduced the residues by 39.6% while in case of hot 1% brine solution, the reduction was 55.0%.

Cooking

Application of heat to the food commodities is commonly done through ordinary cooking, pressure cooking, microwave cooking, frying, sterilization and canning.

The effect of different cooking processing on removal of profenofos and chlorpyrifos residues in cauliflower was studied (Figure 1 and 2). In all of the processes, pressure cooking was found to be most effective than the other processes.

Pressure cooking reduced the residues up to 67.57%. These results are in accordance with the findings Muthukumar et al., (2010) who also reported that pressure cooking was the most effective in reducing both α- and β-endosulfan by 64.59% and 61.60% as compared to boiling and microwave cooking.
Table 1 Recovery of profenofos and chlorpyrifos from cauliflower curds

| Insecticides | CAULIFLOWER CURDS |
|--------------|------------------|
|               | Fortification level, (mg/kg) | Mean recovery (%) | Relative standard deviation (% RSD) |
| Profenofos    |                               |                  |                                   |
|               | 0.05                        | 88.00            | 0.679                              |
|               | 0.10                        | 89.00            | 0.298                              |
|               | 0.20                        | 90.00            | 0.195                              |
|               | 0.50                        | 93.00            | 0.242                              |
|               | 1.00                        | 94.00            | 0.044                              |
| Chlorpyrifos  |                               |                  |                                   |
|               | 0.01                        | 90.00            | 1.030                              |
|               | 0.05                        | 92.00            | 0.987                              |
|               | 0.10                        | 93.00            | 0.858                              |
|               | 0.50                        | 91.00            | 0.178                              |
|               | 1.00                        | 94.10            | 0.112                              |

Fig. 1 Per cent relief from profenofos residues from different decontamination processes (W= Tap water washing, LW= Luke warm, OPC=Open pan cooking, PC=Pressure cooking, MC=Microwave cooking)
Cooking of cauliflower curds in open pan or under pressure or in the microwave resulted in 36-68% relief from profenofos and chlorpyrifos residues. The findings are in agreement with Dikshit (2001) who observed that process of steaming dislodged the cypermethrin residues by 63-74% on stored pulses treated at 3 and 5 mg/kg levels. The disappearance of pesticide residues from boiling extract could be due to decomposition by the effect of heat, the stronger adsorption of pesticide onto plant tissues and/or the poor solubility of pesticides in water (Abou and Abou 2001; Ali, 1983). Walia et al., (2010) reported that microwave cooking reduced cypermethrin residues to the extent of 40.89 per cent in brinjal sprayed at 0.001 per cent concentration. Hence, processes involving heat can increase volatilization, hydrolysis or other chemical degradation and thus, reduce residue levels (Holland et al., 1994).

Washing followed by cooking

Washing is generally the first step in various types of treatments which are given to food commodities in combinations like washing followed by cooking, washing and drying, washing and peeling and washing, peeling and juicing to allow for effective decontamination from pesticides (Kaushik et al., 2009).

Washing of cauliflower curds followed by cooking lead to more than 72% removal of profenofos and chlorpyrifos residues (Figure 1 and 2). Similarly, Mukherjee et al., 2006 also reported that washing of cauliflower heads under running tap water removed 27.9% chlorpyrifos residues, cooking reduced residues to 41.4% and washing + cooking further reduced residues to 66.7%. Aktar et al., (2010) also reported that washing plus
cooking of cabbage heads reduce more quinalphos residues (66.45-68.19%) in comparison to washing alone (41.30-45.20%).

A critical analysis of whole decontamination data revealed that the washing plus pressure cooking removed much higher residues from contaminated fruits as compared to the simple washings. Although, sodium hydroxide and hydrochloric acid treatments were superior over all other decontamination processes but such treatments can be used in the industries where large quantity of vegetables are processed for decontamination. Washing of vegetables with water followed by pressure cooking removed maximum residues up to 72% as compared to the other processes and proved good household practice.

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