A study on the pesticide residues in cauliflower and the efficacy of household processing methods in their reduction

Vidisha Tomer[1,3*], Jaswinder Kaur Sangha[1], Sonika Sharma[1], Balwinder Singh[2], Reenu Takkar[2]

1- *Dept of Food and Nutrition, College of Home Science, Punjab Agricultural University, Ludhiana*
2- *Dept of Entomology, College of Agriculture, Punjab Agricultural University, Ludhiana*
3- *Dept of Food Technology and Nutrition, School of Agriculture, Lovely Faculty of Technology and Sciences, Lovely professional University, Phagwara*

**email of the corresponding author: vidishatomer@gmail.com*

Abstract

Present study was undertaken to observe the effect of different household processing methods on pesticides residues in cauliflower. Samples were extracted using QuEChERS method. Effect of household processing on pesticide reduction was analyzed through simulated trials. Cauliflower samples spiked with chlorpyrifos, quinalphos and cypermethrin were subjected to different household processing treatments like washing with tap water, potassium permanganate, sodium hydroxide, acetic acid, sodium chloride solutions, peeling, blanching, open pan cooking, pressure cooking and frying and extracted. Results indicated low but measurable amounts of residues in 47.5 percent of the collected samples. The theoretical maximum residue intake obtained for all the income groups in rural and urban respondents was significantly lower than maximum permissible intake. Pressure cooking and frying was most effective treatment and caused 70 percent reduction of pesticide, while, tap water washing was least effective. Present study tried to explore different processing methods that can easily be adopted at household level. Such methods can make significant contribution in reducing dietary exposure to pesticide residues.

Keywords: *cauliflower, household processing, pesticide reduction, pesticide residues*

Introduction

Cauliflower, a member of family Brassicaceae is one of the commonly consumed vegetables in both rural and urban sectors of India. It has high nutritive value, contains high amount of fibre, omega 3 fatty acids and provides more than 77 percent of the daily value of vitamin C along with other micronutrients (Van Duyn and Pivonka, 2000; Manchali et al., 2012).

Cauliflower plants are susceptible to attack from many species of insects and pests like diamond black moth, Plulellaxylostella (L.), Spodopteralitura (Fab.), Crocidolomiabinotalis Zeller and Hellulaundalis etc. (Surinder and Yadav, 1998). To minimize crop losses from these biological factors, farmers apply pesticides on several stages throughout the production cycle (Jeyanthi and Kombairaju, 2005). The persistent nature of some of these pesticides paves way as residues into the human body through food chain, where these impose long term impacts (Srivastava et al., 2011). Consumption of such vegetables even with moderate contamination level can accumulate in the receptor's body and mat lead to significant health fatalities (Bhanti and Taneja, 2007). Pesticides affect almost every part of human body and lead not only to placid effects like rashes and dyspnoea but also to severe health complications like infertility, still births, kidney failure, cancer etc. (Tomer et al., 2014). Considering the multiple health hazards associated with pesticides, it is the need of time to monitor the dietary load of pesticide residues.

Cauliflower, commonly consumed by people of all income groups in winters makes it a crucial dietary source of these contaminants. Therefore, analysis of pesticide residues and estimation of risk imposed after consuming contaminated vegetables has become an essential requirement (Margni et al., 2002). Also, antidote to the above discussed adversities lies in developing new strategies at household level for minimizing exposure of pesticides to individual. Hence, it is pertinent to develop and assess simple, cost effective approaches to augment food safety from harmful pesticides for general populace. Processing of food at household level would offer an appropriate tool to provide solution for unsafe food (Tomer et al., 2014)

Present study was conducted in Punjab with an objective to determine the exposure of household women of different income strata to pesticide residues. Efficacy of different food processing treatments that can be practised at household level was also evaluated and finally the most acceptable treatment was determined by subjecting the samples for consumer preference.

Material and Methods

Procurement of samples

A list of vegetable growing areas of District Ludhiana (Punjab) was collected from department of Vegetable Sciences, Punjab Agricultural University, Ludhiana. Three blocks namely, Sudhar, Ludhiana I and Pakhowal were selected on the basis of location to make the sampling uniform. Among selected blocks further, villages namely Saholi, Chappar, Abbuwal, Bains, Jodha and Dollan Kalan were selected for sample collection based on the productivity of cauliflower.

For studying the extent of contamination in these areas, forty marketable size cauliflower curds (1 Kg) were collected. To observe the impact of different household processing treatments on reduction in pesticides cauliflower samples (40 Kg) were procured from local market.

Processing treatments

Common household processing treatments viz., Washing in tap water, dipping in 2% NaOH, 5% $NaHCO_3$, 2% $KMnO_4$, 10% NaCl, 4% acetic acid, blanching, frying, steam cooking, microwave cooking and pressure cooking were applied to the spiked samples. The spiked samples were dipped in different concentrations of chemical solutions for thirty minutes and then washed to remove excess chemical depositions on the surface. Different cooking operations were conducted until the vegetable was done. Effect of processing treatments was observed by post-treatment analysis of the samples by the method described below.

Preparation of samples for analysis

Effect of processing on different pesticide residues in cauliflower was observed through simulated trials. For this, cauliflower samples were spiked with chlorpyrifos and quinalphos with a dose of 10 $mgkg^{-1}$. Cypermethrin was applied to the extent of 30 $mgkg^{-1}$. Level of spiking was kept high to clearly observe the impact of different processing treatments.

Laboratory analysis of cauliflower samples

Chemicals and reagents

Solvents and reagents i.e. acetone, hexane, magnesium sulphate, primary secondary amine (PSA), sodium chloride (ASC reagent grade, ≥99.9 %), and anhydrous sodium sulphate (AR grade) were obtained from Merck (Darmstadt, Germany). Activated charcoal decolorizing powder was procured from Qualigens' Fine Chemicals (Mumbai). The analytical solvents were redistilled before use to ensure their purity. Before the actual analysis, the suitability of all the reagents was ensured by running reagent blanks.

Preparation of standard solution

A standard stock solution of a mixture of organophosphates (OP), organochlorines (OC) and synthetic pyrethriods (SP) was prepared in acetone. The concentration of stock solution was kept to be 1 $mgmL^{-1}$. As per the requirement, stock solution was diluted to various concentrations to prepare standards as per the requirement.

Extraction and cleanup

Analysis of pesticides residues was carried out in Pesticide residue analysis laboratory, Department of Entomology, Punjab Agricultural University, Ludhiana. Cauliflower samples were extracted by QuEChERS method with slight modifications (Anastassiades et al., 2003; Tomer et al. 2015)

Evaluation for consumer preference:

For determining the acceptability and thus applicability of the processing treatments on practical grounds, the processed samples were displayed to a total no of 50 food preparers for their preferences. Preferences were judged using nine-point hedonic rating scale. The respondents were asked to rate the samples on the basis of their preferences ranging from 'like extremely' with score 9 to 'dislike extremely' with score 1. The parameters included were appearance, flavour, colour, texture, taste and overall acceptability. Taking the mean scores for all the parameters, overall acceptability was judged.

Statistical Analysis

Statistical analyses were performed using the SPSS 16.0 software package. Extent of reduction was calculated in the form of percentages. For determining statistical significance, one-factor factorial ANOVA was used. For determination of inter-treatment significance *post-hoc* analysis using Tukey's HSD test was done.

Results and discussion

Analysis of farm-gate cauliflower samples

Quality assurance of the analytical method

Before analysing test samples, evaluation of the extraction efficiency, cleanup and determinative steps, the analytical method was standardized by processing samples spiked with a mixture of OP, OC and SP insecticides. The area of peak so obtained was compared with the area of standard and recoveries were calculated in terms of percentage. Consistent recoveries (greater than 80%) were obtained at different concentrations (0.01, 0.05, 0.1 $mgKg^{-1}$) with an RSD below 15% (Table 1).

Pesticide residues in cauliflower samples

OP and SP insecticides like cypermethrin, chlorpyriphos, methyl parathion, profenophos, deltamethrin and quinalphos were detected in cauliflower samples (Table 2). From a total of forty samples, 47.5% were contaminated with single or multiple residues. However, none of the samples contained residues of any of these pesticides above their respective MRL's (Table 2). Chlorpyrifos was the most frequently detected pesticide found in 30% of the samples. Cypermethrin was detected in highest concentration (0.65 mg/Kg) in 20% cauliflower samples. Quinalphos was detected in 22.5 percent of the samples with a mean concentration of 0.07 mg/Kg. Least detection rate was observed for methyl parathion which was found in only 5% of the cauliflower samples. It was noted that none of the pesticides detected belonged to organochlorine class of pesticides. The trend obtained in present study was different from that in similar study which detected OC insecticides in cauliflower (Mandal and Singh, 2010). The results obtained were in line with the fact that there had been a decline in organochlorine residue in food after the ban on highly persistent organochlorine pesticides. However, these have been replaced with OP and SP which are comparatively less persistent but possess higher toxicity.

Of the detected pesticides, only quinalphos is recommended in 'Package of practices for cultivation of vegetables' published by Punjab Agricultural University for vegetable growers (PAU, 2013).The occurrences of residues of non-recommended insecticides reflect the misuse of insecticides on cauliflower.

Efficacy of household processing on pesticide residues in cauliflower

Dissipation of pesticides by processing treatments

To determine the effectiveness of processing treatments, simulated trials were conducted. Different processing methods reduced the pesticides in cauliflower by a considerable level. Results of simulated trials are expressed in Table 3. Significant reductions were observed in quinalphos and cypermethrin (20.12 and 17.58%) on washing with tap water. Washing reduced chlorpyrifos residues to 8.36 mg/kg depicting a reduction of 9.6%. Water solubility can be considered as an important contributory factor in residue reduction; however, water solubility and reduction of residues are concluded as independent factors for deltamethrin residues in cauliflower and other vegetables (Randhawa et al., 2008). Nevertheless, non-systemic nature of synthetic pyrethroids can be recognized for this decrease.

Impact of chemical solutions (2% NaOH, 5% $NaHCO_3$, 2% $KMnO_4$, 10% NaCl, 4% acetic acid) followed by gentle washing was highly significant in comparison to simple tap water washing operation. Chemical solutions usually have a positive impact on pesticide reduction due to electrolytic properties, pH change. Dipping in a solution of 2% NaOH reduced chlorpyrifos by 47.38% (mean residue content-4.87 mg/kg). Maximum reduction by treatment with 2% NaOH was found in quinalphos with a reduction percentage of 69.38 followed by cypermethrin (56.76%).

Ten percent NaCl reduced chorpyrifos residues by 52% which had no statistical significance to reductions by blanching and steam cooking (Table 3). Reductions by NaCl can be because of its electrolytic nature. Solutions with high tendency to dissociate into positively and negatively charged ions influence the capacity of pesticide decomposition (Rasolonjatovo et al., 2017). In a previous study 10% NaCl solution reduce OPs in the range of 80-90% (Soliman 2001). Comparatively lower reductions (52% for chlorpyrifos and 39.86% for quinalphos) were obtained in the present study on treatment with 10% NaCl (Figure 1 a).

Higher reductions were observed by treating cauliflower heads with 2% $KMnO_4$ as compared to other washing solutions used in study. Application of $KMnO_4$ showed reductions of more than 60 percent for both quinalphos and cypermenthrin. However, chlorpyrifos residues reduced from the concentration of 9.25 mg/kg to 6.19 mg/kg depicting a dissipation of 52.39%. $KMnO_4$ is a strong oxidizing agent. High redox potential of the solution might be responsible for the reduction of residues (Satpathy, 2011, Zhang et al., 2007). Following $KMnO_4$, highest reduction rates were observed in cauliflower samples treated with 5% Sodium bicarbonate which reduced chlorpyrifos, quinalphos and cypermethrin residues by 52.97, 53.89 and 55.56 respectively (Figure 1a).

As given in Table 3, 4% percent acetic acid reduced chlorpyrifos residues to 7.97 representing a decline of 33.09%. Quinalphos residues were reduced to 5.21 mg/kg after treating with a solution of 4% acetic acid for thirty minutes. Maximum reduction with acetic acid solution was observed for cypermethrin (61.12%). Highly unstable structure of cypermethrin and quinalphos molecules which dissociate rapidly in highly acidic and alkaline conditions can be a possible explanation for the decline. Reductions by acetic acid and sodium hydroxide were similar to a study conducted by Kin and Huat (2010) in which dipping of cucumbers in 10% acetic acid solution for thirty minutes reduced profenofos (another pesticides belonging to the organophosphate group) residues by 67.8 percent.

Findings of the present study indicate heat treatments to be more effective than dipping and washing. Rate of residue dissipation due to cooking depends upon factors like temperature, process time, the amount of water and type of system (open/ closed). The dislodging of pesticide residues by pressure cooking, frying and blanching can be explained through decomposition effect of heat (Sheikh et al., 2012). Among the heat treatments applied, pressure cooking was found to be most effective for quinalphos and cypermethrin which reduced their residues to 1.72 and 6.48 mg/kg respectively (Table 3) showing a reduction of 82.43% and 78.04% respectively (Figure 1b). The changes that normally occur during cooking are volatilization, hydrolysis and thermal breakdown (Stepan, 2005). The results obtained in the current study were in corroboration with Dhiman et al., (2006) who reported 100 percent removal of deltamethrin by canning of cauliflower. Similar findings have also been reported by other researchers that heat treatments were observed to be more effective in reducing the residues (Sheikh et al., 2012, Dhiman et al., 2006).In this study, frying was the most effective heat treatment observed for chlorpyrifos with a reduction percentage of 63.58% (Figure 1b). High reductions in blanching and frying can be explained by leaching of surface residues of cypermethrin to a greater extent in excess oil and water in comparison to that in other cooking process where moisture loss may have led to concentration of pesticide.

Evaluation for consumer preference

The effect of different washing and heat treatments on cauliflower can be observed in Figure 2 (a) and (b). The consumer preference was taken using 9-point scale. The scores obtained for different washing and heating methods are represented using spider plot in Figure 3 (a) and (b). It can be observed that washing treatments using potassium permanganate, sodium hydroxide and acetic acid were the least preferable treatments for all sensory parameters. Washing and dipping cauliflower curds in sodium hydroxide led to yellow discoloration while dipping in potassium permanganate led to purple discoloration of the curds. The colour change was permanent and had no effect even after repeated washings. Use of acetic made the cauliflower curds soft thereby getting low score on the texture parameter. Amongst heat treatments, frying was the most preferable method followed by microwaving and steaming. Pressure cooking of cauliflower curds was least preferred.

Conclusion

The results of the present study concluded that consumption of cauliflower in both rural and urban sectors for all the three income groups was below the recommended levels. Farm-gate analysis revealed that cauliflower samples were contaminated with residues of seven pesticides. Pesticides were below the MRLs butwereabove the detectability limit. None of the pesticides imposed any health hazard to the household women.Household processing treatments were proven quite effective in minimizing residue exposure. Washed samples were the most acceptable by the consumers but reduced all the three pesticides least in comparison to all other treatments. Blanching reduced the residues to a considerable extent and was also readily accepted by the consumers. It is the need of the hour to optimize household processing techniques for reduction of pesticide residues in vegetables to reduce exposure and develop strategies that can be applied at household level which are readily acceptable by the consumers.

References

Anastassiades, M., Maštovská, K., & Lehotay, S. J. (2003). Evaluation of analyte protectants to improve gas chromatographic analysis of pesticides. *Journal of Chromatography A*, *1015*(1-2), 163-184.

Bhanti, M., & Taneja, A. (2007). Contamination of vegetables of different seasons with organophosphorous pesticides and related health risk assessment in northern India. *Chemosphere*, *69*(1), 63-68.

Dhiman, N., Jyot, G., Bakhshi, A. K., & Singh, B. (2006). Decontamination of various insecticides in cauliflower and tomato by different processing methods. *Journal of Food Science and Technology-Mysore*, *43*(1), 92-95.

Jeyanthi, H., & Kombairaju, S. (2005). Pesticide use in vegetable crops: frequency, intensity and determinant factors. *Agricultural Economics Research Review*, *18*(347-2016-16688), 209-221.

Kin, C. M., & Huat, T. G. (2010). Headspace solid-phase microextraction for the evaluation of pesticide residue contents in cucumber and strawberry after washing treatment. *Food Chemistry*, *123*(3), 760-764.

Manchali, S., Murthy, K. N. C., & Patil, B. S. (2012). Crucial facts about health benefits of popular cruciferous vegetables. *Journal of Functional Foods*, *4*(1), 94-106.

Mandal, K., & Singh, B. (2010). Magnitude and frequency of pesticide residues in farmgate samples of cauliflower in Punjab, India. *Bulletin of environmental contamination and toxicology*, *85*(4), 423-426.

Margni, M., Rossier, D., Crettaz, P., & Jolliet, O. (2002). Life cycle impact assessment of pesticides on human health and ecosystems. *Agriculture, ecosystems & environment*, *93*(1-3), 379-392.

PAU (2013), "Package of practices for cultivation of vegetable crops", in Dhillon T.S. (Ed.), PAU printing press, Ludhiana, India.

Randhawa, M. A., Anjum, F. M., Randhawa, M. S., Ahmed, A., Farooq, U., Abrar, M., & Randhawa, M. A. (2008). Dissipation of deltamethrin on supervised vegetables and removal of its residue by household processing. *Journal of the Chemical Society of Pakistan*, *30*(2), 227-231.

Rasolonjatovo, M. A., Cemek, M., Cengiz, M. F., Ortaç, D., Konuk, H. B., Karaman, E., ... & Göneş, S. (2017). Reduction of methomyl and acetamiprid residues from tomatoes after various household washing solutions. *International journal of food properties*, *20*(11), 2748-2759.

Satpathy, G., Tyagi, Y. K., & Gupta, R. K. (2012). Removal of organophosphorus (OP) pesticide residues from vegetables using washing solutions and boiling. *Journal of Agricultural Science*, *4*(2), 69-78.

Sheikh, S. A., Nizamani, S. M., Jamali, A. A., Panhwar, A. A., Channa, M. J., & Mirani, B. N. (2012). Removal of pesticide residues from okra vegetable through traditional processing. *Journal of Basic & Applied Sciences*, *8*(1), 79-84.

Soliman, K. M. (2001). Changes in concentration of pesticide residues in potatoes during washing and home preparation. *Food and Chemical Toxicology*, *39*(8), 887-891.

Srivastava, A. K., Trivedi, P., Srivastava, M. K., Lohani, M., & Srivastava, L. P. (2011). Monitoring of pesticide residues in market basket samples of vegetable from Lucknow City, India: QuEChERS method. *Environmental Monitoring and Assessment*, *176*(1-4), 465-472.

Takkar, R., Sahoo, S. K., Singh, G., Mandal, K., Battu, R. S., & Singh, B. (2011). Persistence of indoxacarb on cauliflower (Brassica oleracea var. botrytis. L.) and its risk assessment. *American Journal of Analytical Chemistry*, *2*(08), 69.

Thompson, F. E., & Subar, A. F. (2013). Dietary assessment methodology. Nutrition in the Prevention and Treatment of Disease. *Nutrition in the Prevention and Treatment of Disease, 2nd ed.; Coulston, AM, Boushey, C., Eds*.

Tomer, V., Sangha, J. K., & Ramya, H. G. (2015). Pesticide: An appraisal on human health implications. *Proceedings of the National Academy of Sciences, India Section B: Biological Sciences*, *85*(2), 451-463.

Tomer, V., Sangha, J. K., Singh, B., & Takkar, R. (2014). Efficacy of processing treatments on cypermethrin residues in okra (Abelmoschus esculentus). *Nutrition & Food Science*, *44*(6), 545-553.

Van Duyn, M. A. S., & Pivonka, E. (2000). Overview of the health benefits of fruit and vegetable consumption for the dietetics professional: selected literature. *Journal of the American Dietetic Association*, *100*(12), 1511-1521.

Zhang, Z. Y., Liu, X. J., & Hong, X. Y. (2007). Effects of home preparation on pesticide residues in cabbage. *Food Control*, *18*(12), 1484-1487.

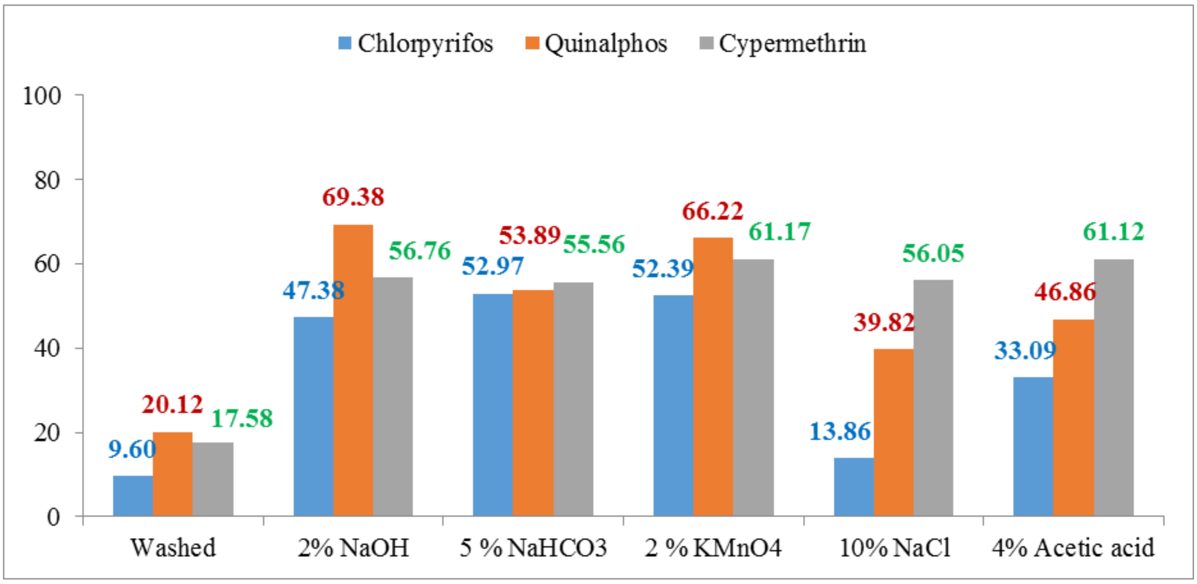

Fig. 1 (a): Percentage reduction obtained in chlorpyrifos, quinalphos and cypermethrin by different processing treatments

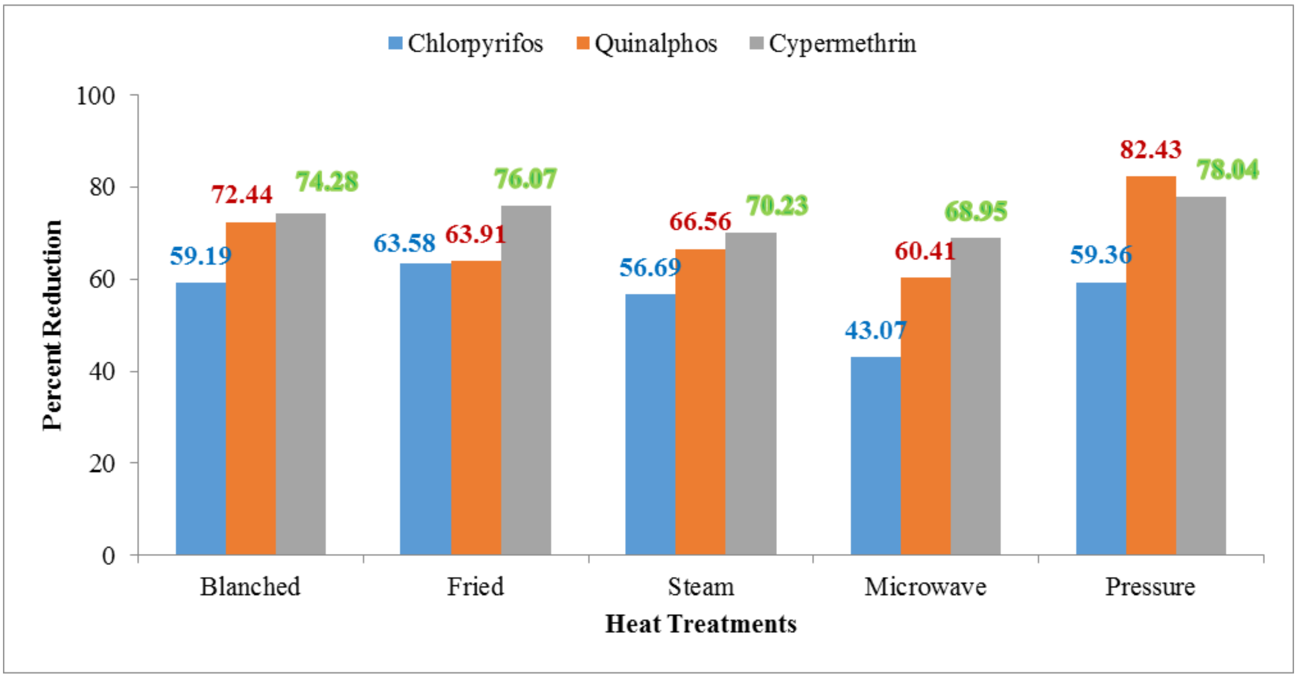

Fig. 1 (b): Percentage reduction obtained in chlorpyrifos, quinalphos and cypermethrin by different heat treatments

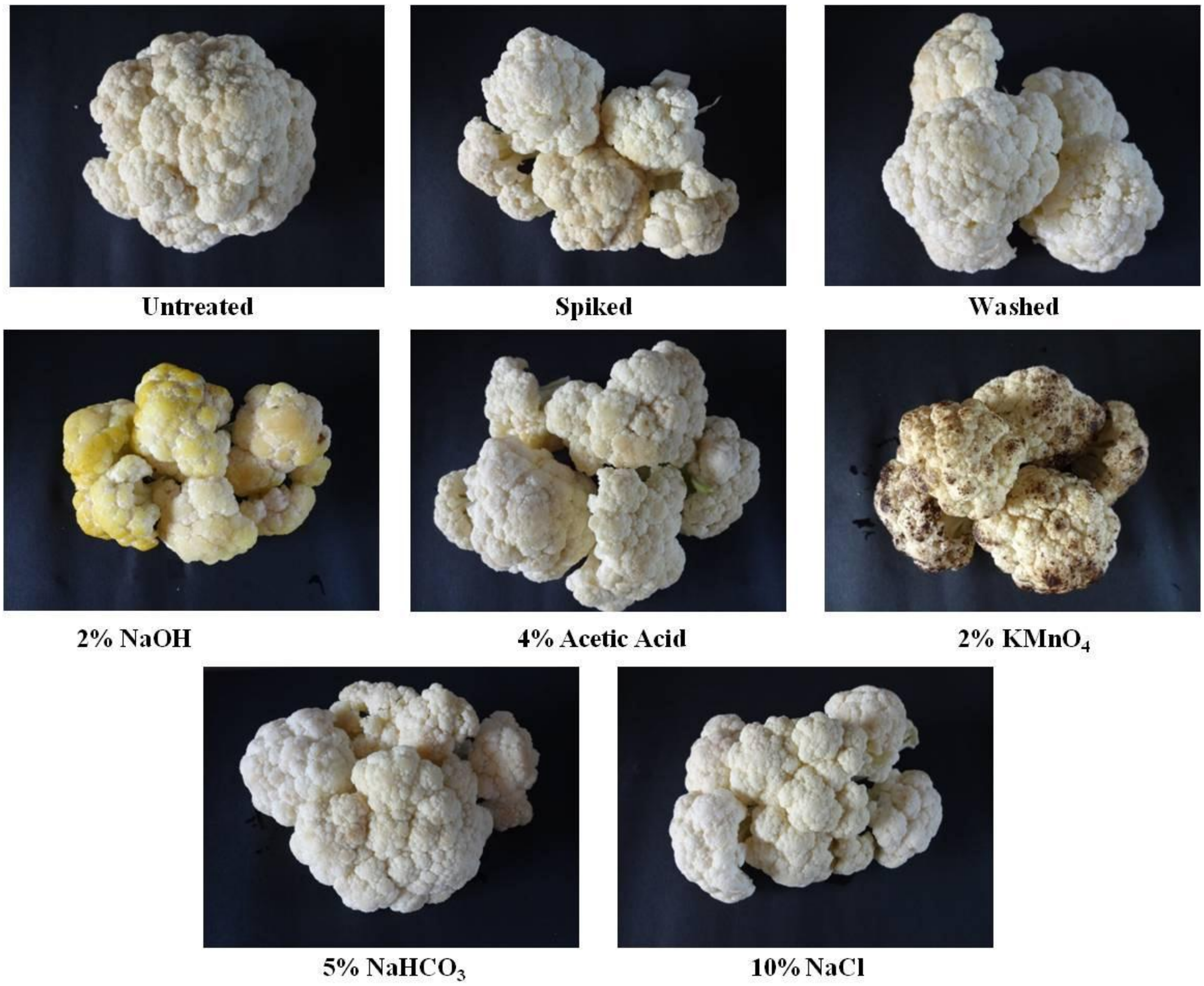

Fig. 2 (a): Cauliflower samples after different processing treatments

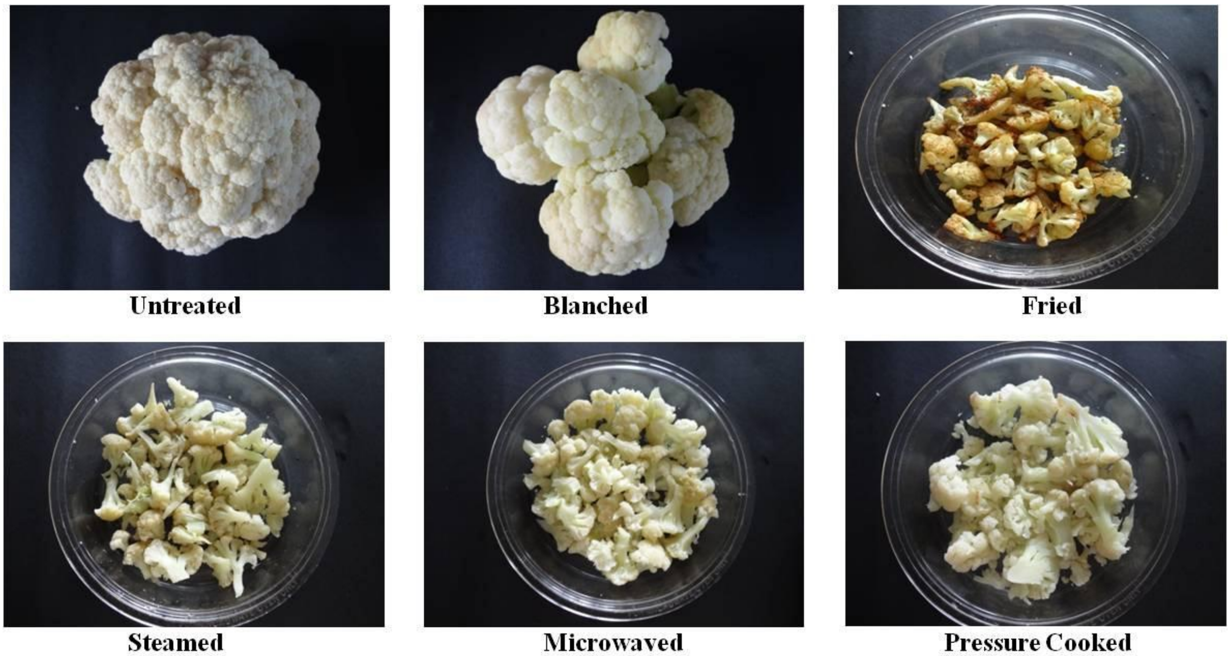

Fig. 2 (b): Cauliflower samples after different heat treatments

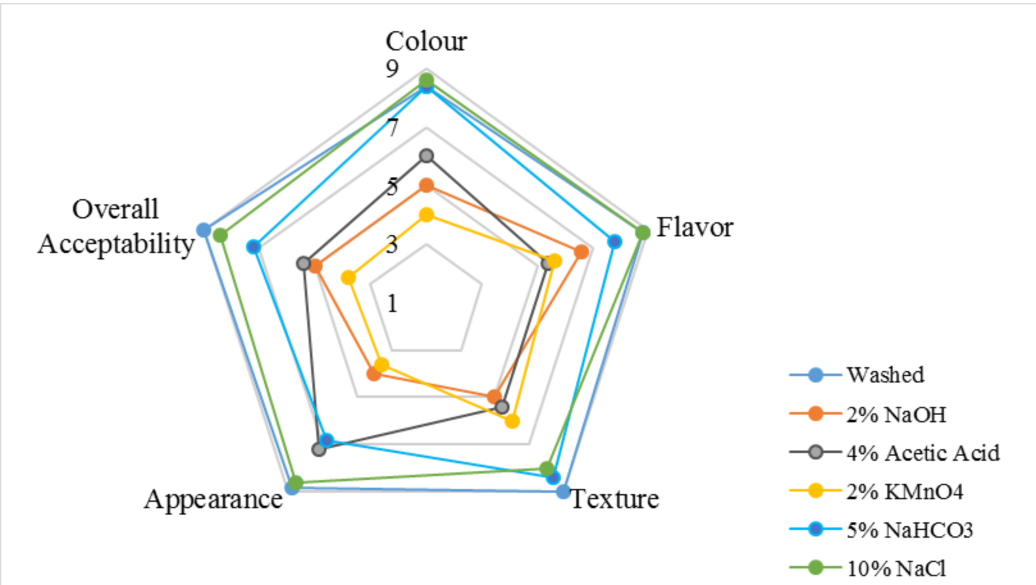

Fig. 3 (a): Spider plot representing sensory scores on different parameters for various washing treatments.

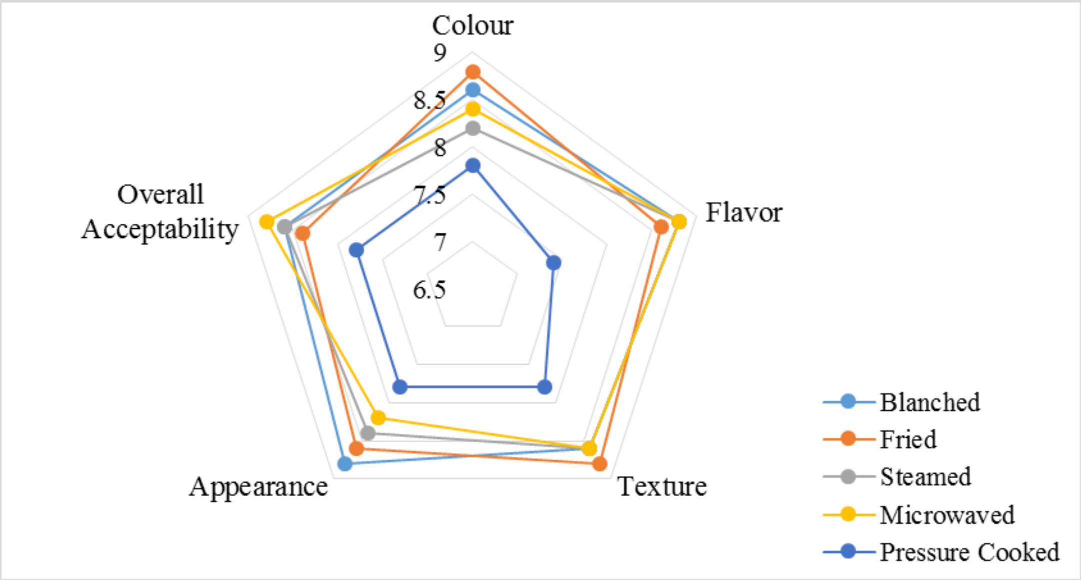

Fig. 3 (b): Spider plot representing sensory scores on different parameters for various heat treatments.

Table 1: Recoveries of different pesticide standards in gas chromatography

Pesticide	Concentration	Recovery (%)	RSD (%)
Chlorpyrifos	0.01	88.27	5.32
Cypermethrin	0.05	86.43	4.86
methyl parathion	0.1	85.67	6.19
Deltamethrin	0.05	87.43	5.49
Profenofos	0.1	88.38	8.83
Triazophos	0.1	85.07	1.88
cyhalothrin	0.05	83.23	0.48
β-cyfluthrin	0.1	89.38	7.27
Fenpropathrin	0.1	89.57	6.36
Quinalphos	0.05	91.70	2.73

Table 2: Residues of pesticides detected in farm-gate samples of cauliflower

Pesticide	No of contaminated samples (%)	Mean ($mgkg^{-1}$)* ± SD	MRL**

			(Maximum Residue Limit)
Total	19 (47.5)		
Chlorpyrifos	12 (30.0)	0.03 ± 0.02	0.05 mg/kg
Cypermethrin	8 (20.0)	0.65 ± 0.28	-
Methyl Parathion	2 (5.0)	0.09 ± 0.05	-
Deltamethrin	7 (17.5)	0.08 ± 0.14	-
Profenofos	9 (22.5)	0.37 ± 0.15	-
Triazophos	7 (17.5)	0.31 ± 0.23	-
Cyhalothrin	6 (15.0)	0.18 ± 0.22	-
β-cyfluthrin	3 (7.5)	0.10 ± 0.06	2 mg/kg
Fenpropathrin	4 (10.0)	0.49 ± 0.40	-
Quinalphos	9 (22.5)	0.07 ± 0.12	-

* Values are mean of three replications

** MRL values taken from WHO/FAO database, 2013

Table 3: Efficacy of different processing treatments on reduction of pesticide residues in cauliflower

Treatments	Chlorpyrifos (mg/kg)	Quinalphos (mg/kg)	Cypermethrin (mg/kg)
Spiking Level	10	10	30
Before Treatments	9.25^{e}	9.81^{h}	29.49^{f}
Wash in Tap Water	8.36^{de}	7.84^{g}	24.31^{e}
2% NaOH	4.87^{abc}	3.00^{bc}	12.75^{d}
5% NaHCO3	5.71^{bc}	4.52^{de}	13.11^{d}
2% KMnO4	6.19^{cd}	3.31^{bc}	11.45^{cd}
10% NaCl	4.4^{abc}	5.90^{f}	12.96^{d}
4% Acetic acid	7.97^{d}	5.21^{ef}	11.47^{cd}
Blanching	3.78^{ab}	2.70^{ab}	7.58^{ab}
Frying	3.37^{a}	3.54^{bcd}	7.06^{ab}
Steam Cooking	4.01^{abc}	3.28^{bc}	8.78^{ab}
Microwave Cooking	5.27^{bc}	3.88^{cd}	9.16^{bc}
Pressure Cooking	3.76^{ab}	1.72^{a}	6.48^{a}

a- h Means in the same column without common superscripts differ (P=0.05).

* Ranked on 9-point hedonic scale for consumer acceptability