ELIMINATION OF PESTICIDES FROM FRUITS USING CHEMICAL NEUTRALIZER

D.S.MORE[1], U.GUPTA[2], A.DABADE[3]
[123]School Of Biotechnology and Bioinformatics, D.Y. Patil Deemed to be University, Food Science and Technology, CBD Belapur, Navi Mumbai, India

ABSTRACT

Pesticides are substances that are used to control pests or weeds and diseases in crops Pesticides compounds represent an important class of pollutants for food, soil and surface water resources Organophosphate (OP) pesticides, as a group, are most widely used insecticides in India. An organophosphate(OP) or phosphate ester is the common name for estersof phosphoric acid. OP pesticides are generally used on fruits, vegetables, grains, and pasture seed, cotton, on livestock and domestic animals as well as for building pest control. The widely used pyrethroids are an synthetic insecticides is based on the pyrethrin, which are derived from chrysanthemums. They have been changed to extend their stability within the surrounding. The pesticides remain in the fruits and vegetables and cannot be fully removed by washing which is very harmful and affects the human health, so to remove or neutralize these harmful pesticides need to find some alternatives. The main objective of this chemical neutralizer is to eliminate the organophosphate and pyrethroid pesticides from fruits.The suitable method was used to eliminate or neutralize the organophosphate and pyrethroid pesticides from fruits. Chlorpyrifos, Dichlorvos ,Bifenthrin and Deltamethrin pesticides were used. These pesticides were applied on fruit as per normal practices.The D-limonene was diluted in n-hexane at concentration 0.33ml/ml. This can be used for reduction of current pesticides limit in final production.The pesticide treated sample was kept in D-limonene solution for 15 mins and further washed with distilled water. The results obtained were very positive and effective. The pesticide analysis was carried out by GCMS. The reduction of Chlorpyrifos 90%Bifenthrin 74%, Deltamethrin 85%, Dichlorvos 5% in was observed.

Keywords: Pesticides, D-Limonene, Chlorpyrifos, Deltamethrin, Bifenthrin, Dichlorvos, GCMS.

INTRODUCTION

Pesticides are a numerous and diverse group of chemical compound, which are used to eliminate pests in agriculture and households. Pesticides (or farm chemicals, agro chemicals) are those substances which are used to control, destroy, repel or attract pests in order to minimise their detrimental effects. Pests are those organisms like weeds, insects, bacteria, fungi, viruses and animals which adversely affect our way of life. Pests can reduce the quality and quantity of food produced by lowering production and destroying stored produce; they can harm our animals (like fleas, worms and diseases); they compete with humans for food and affect the health, welfare and way of life of people; they can destroy buildings (termites) and are a major cause of land degradation (noxious weeds, rabbits, feral pigs, etc). Pests are also a major nuisance around our homes (prickles in the lawn, flies ,etc). Pest activity greatly increases the costs of farming.(Fenik, Tankiewicz, & Biziuk, 2011)

Pesticides represent an important class of pollutants in food, soil and surface water resources. Pesticides are applied to control specific pests and diseases and are used according to good agricultural practice. This practice aims to ensure that minimal levels of residues (if any) are remaining on the harvested crop and that

the food is safe to consume. The maximum residue limit (MRL) is the highest level of a pesticide permissible in food.(Of, 1996)

According to United Nations agency estimates, one thousand thousand cases of poisoning occur per annum and consequently there are a unit 20,000 deaths globally.

Chlorpyrifos, [O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl)-phosphorothioate], is a broad-spectrum, chlorinated organophosphate insecticide that was first registered in 1965 to control foliage- and soil-borne insect pests on a variety of food and feed crops.Chlorpyrifos is an organophosphate insecticide. Pure Chlorpyrifos is created from white or colorless crystals. It has a ratherskunkyodor, like rotten eggs or garlic.Chlorpyrifos is employed to manage many various forms of pests, together with termites, mosquitoes, and roundworms. The only legal indoor use for Chlorpyrifos is in containers with treated baits.

Dichlorvos is an insecticide, which is manufactured by industry. Dichlorvos may also be called DDVP. Pure Dichlorvos is a dense colorless liquid. It has got property of evaporating in air and dissolving in water. Dichlorvosincorporates a sweet smell and without delay reacts with water. The Dichlorvos utilized in gadfly management is diluted with alternative liquids and used as a twig.

Bifenthrin is an insecticide in the pyrethroid family. Pyrethroids are manmade versions of pyrethrins, which come from chrysanthemum flowers.it is an insecticide used heavily in the control of red imported fire ants. Due to its high toxicity to aquatic organisms, it is listed as a restricted use pesticide, although it can be purchased for residential use in lower concentrations.

Deltamethrin is an insecticide belonging to the pyrethroid family. Pyrethroids are the man-made versions of pyrethrins, natural insecticides from chrysanthemum flowers Deltamethrin is a broad-spectrum insecticide that affects the nerve cell'sability to send a normal signal. Products used in agriculture, on golf courses, gardens, and lawns, indoors normally containsdeltamethrin.

The Environmental unit (EWG), a non-profit advocacy agency has released their list of the most contaminated fruits and vegetables and apples have been ranked as the most contaminated - fifth year in a row. The Dirty Dozen list includes the highest 12 fruits and veggies with the best quantity of chemical residues. The agency hopes to enlighten folksin order that they study the list, stay away from this produce and go for the organic options instead, at least for these 12 items. According to an announcement, the EWG's Shopper's Guide to Pesticides in Produce ranked pesticide contamination on 48 popular fruits and vegetables based on an analysis of more than 34,000 samples taken by the United States Department of Agriculture (USDA) and federal Food and Drug Administration. It was found that pesticides persisted on fruits and vegetables even once they were washed or peeled.This can’t be good, especially when pesticides have been linked to a range of health problems, including cancer, developmental problems and lower IQ in children. A single grape sample contained 15 pesticides (most of them OPs) due to which the grapes are banned in European countries(Cabras & Angioni, 2000)“Journal of Agricultural and Food Chemistry"

D-limonene (1-methyl-4-(1-methylethenyl) cyclohexane) is a monocyclic monoterpene with a lemon-like odour and could be a major constituent in many citrus oils (orange, lemon, mandarin, lime, and grapefruit). Because of its pleasant citrus fragrance, D-limonene is widely used as a flavour and fragrance additive in perfumes, soaps, foods, chewing gum, and beverages. D-limonene is listed in the Code of Federal Regulation as generally recognized as safe (GRAS) for a flavouring agent. The typical concentration of D-limonene in orange juice, ice cream, candy, and chewing gum is 100 ppm, 68 ppm, 49 ppm, and 2,300 ppm, severally.1 Dietary intake of D-limonene varies depending on the types of foods consumed(Sun, 2007)

The objective of the present work was to eliminate the pesticides from fruits and using chemical neutralization and comparing the reduction percentage of fruits washed with only water and D-limonene plus water.

MATERIALS AND METHODS

Preparation of D-limonene solution: Food grade D-limonene (97%) was purchased from Hi-Media, dissolved in n-hexane to make a solution of 0.33 ml/ml.

Preparation of Pesticide solution: Chloropyrifos (20%EC), Dichlorvos (76%EC), Deltamethrin (36%EC), Bifenthrin (2.5%EC), were purchased from NamdeoUmajiAgritech(India)Pvt.Ltd, Bycalla and was dissolved in distilled water to make 500mg/ml

Sample preparation: Sample 'A' was treated with pesticide and was not given a washing, Sample 'B' was treated with pesticide and washed with distilled water and Sample 'C' was treated with pesticide and was washed first with 0.33ml/ml D-limonene and then with distilled water

Sample treatment: Pesticides namely Chlorpyrifos, Dichlorvos, Bifenthrin, Deltamethrin were taken. the 150gm of each grapes sample were taken and dipped in these pesticides. The grapes were kept for drying before dipping in each of the pesticides. After the pesticide application, the grapes were dried, dried sample b was dipped in distilled water and sample c were dipped in D-limonene 0.33ml/ml concentration. Sample a (control sample) were not washed with distilled water and D-limonene**.** The grapes were kept for about a 15 mins in D-limonene and distilled water. After 15 mins, the grapes were removed and kept for drying. The grapes removed from D-limonene solution and washed with distilled water to remove the excess of D-limonene. The grapes were kept for drying before sample preparation for GCMS analysis.

Sample was prepared by QuEChERS method for GCMS pesticide analysis: Weigh 150 gm of grape sample. Chop it and transfer into homogenizer. Take 10 gm of above sample. crush the sample into 50ml centrifuge tubes. Add 10ml 1%acetic acid in acetonitrile. Add 6gm of magnesium sulphate and add 1.5gm of sodium acetate. Homogenize on vortex for 2 mins. Centrifuge the tubes at 5000 Rpm for 5 mins. Then clean up method for GCMS. Take 2ml of supernatant into 15 ml of centrifuge tube. Add 50 mg PSA,100 mg C18 and 150 mg $MgSo_4$.

Vortex for 2 mins.Centrifuge the tubes at 12000 Rpm for 5 mins. Take 1.5ml of supernatant layer in test tube. Keep the test tubes in nitrogen evaporator at 30-40°C. Reconstitute the sample using 1.5ml ethyl acetate. Ready for injection in GCMS.

RESULTS AND DISCUSSION

- Compare % reduction in sample A and sample C,74.35% reduction of Bifenthrin pesticide residue was observed.90.35% reduction of Chlorpyrifos pesticide residue was observed.85.09 % reduction of Deltamethrin pesticide residue was observed.5.11% reduction of Dichlorvos pesticide residue was observed.

- Compare % reduction in sample A and sample B,25.06% reduction of Bifenthrin pesticide residue was observed.13.85% reduction of Chlorpyrifos pesticide residue was observed.15.68 % reduction of Deltamethrin pesticide residue was observed.4.5% reduction of Dichlorvos pesticide residue was observed

- Pesticide treated grape sample A which were not washed with neutralizers and distilled water has Bifenthrin 0.39 mg/kg, Chlorpyrifos 12.34 mg/kg, Deltamethrin 0.51mg/kg, Dichlorvos 122.89 pesticide residues.

- Pesticide treated grape sample B which were washed with distilled water reduces as Bifenthrin 0.29 mg/kg, Chlorpyrifos 10.63 mg/kg, Deltamethrin 0.43mg/kg, Dichlorvos 117.33 mg/kg.

- Pesticide treated grape sample C which were washed with D-limonene and then distilled water reduces as Bifenthrin 0.1mg/kg, Chlorpyrifos 1.19 mg/kg, Deltamethrin 0.076mg/kg, Dichlorvos 116.6g/kg.

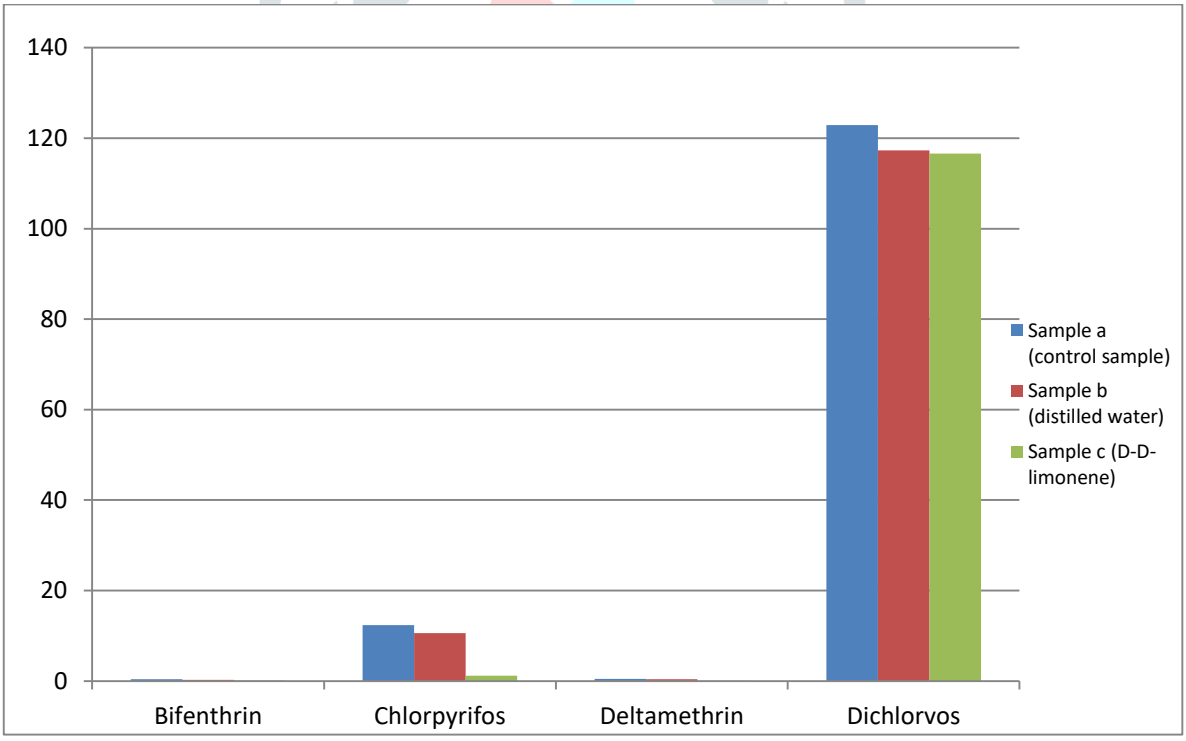
- The OPs and pyrethroid pesticides are denatured and neutralized with chemical neutralizer.

- D-limonene solution. In these experiments the Chlorpyrifos which has class II toxicity level gets neutralized up to 90%. The Deltamethrin which has class II toxicity level also gets neutralized up to 85%. The Bifenthrin which has class Ib toxicity level also gets neutralized up to 74%. The Dichlorvos which has class II toxicity level gets neutralized up to 5%. These all results are very effective and help in neutralization of all the Ops as well as pyrethroid pesticides. Chlorpyrifos 13%, Bifenthrin 25%, Dichlorvos 4.%. Deltamethrin 15.68% are washed by using distilled water.

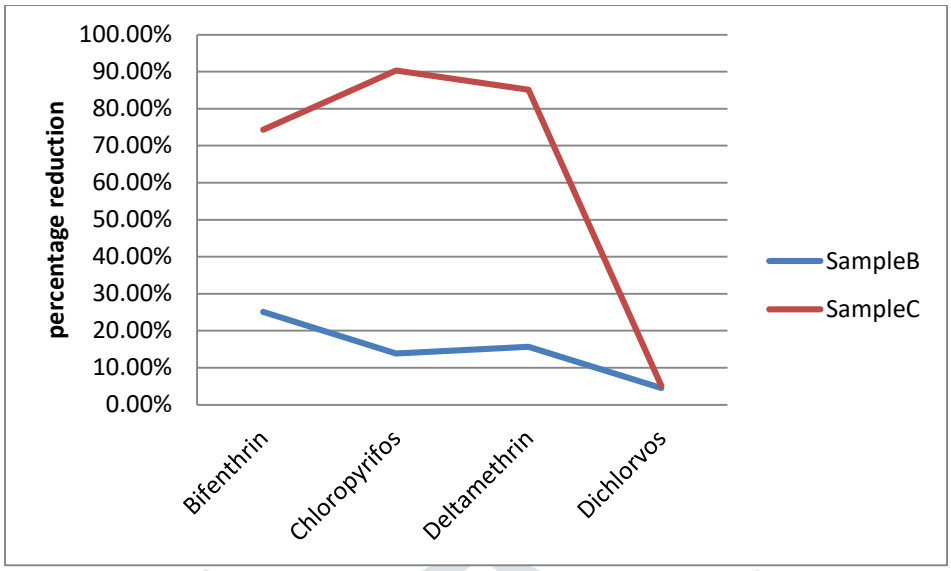
Table no.1- Reduction of pesticide residue

Pesticides	Sample a (control sample)	Sample b (distilled water)	Sample c (D-D-limonene)
Bifenthrin	0.39	0.29	0.10
Chlorpyrifos	12.34	10.63	1.19
Deltamethrin	0.51	0.43	0.076
Dichlorvos	122.89	117.33	116.6

Graph no.1-Reduction of pesticide residue



Graph no.2-Reduction in percentage



CONCLUSION

The limonene solution treatment for grapes showed significant reduction in the pesticides content. Reduction of amount of pesticides is more when washed with limonene solution when compared to wash with distilled water.

This method can be used on large scale for fruits and vegetables which serve as a raw material for various food products like in jam or non-carbonated beverages we can find pesticides residue but if these industries can use this method will washing their raw materials i.e. fruits that can reduce the pesticide content of the fruits which will lead to decrease in the pesticides content of their products. The method uses hexane as the solvent hence certain measures are to be taken for loss of solvent due to evaporation. This can be prevented by working in an air lock environment and incorporation of conveyer belt systems in which the resident time for fruit or vegetable is adjusted to 15mins.

Bibliography

- Analysis, F. O. R., Sustainable, F. O. R., & Of, D. (n.d.). RESEARCH REPORTS FOR ANALYSIS AND ACTION FOR SUSTAINABLE DEVELOPMENT OF HYDERABAD Pesticides, Residues and Regulation A case of vegetables in Hyderabad Market Centre for Sustainable Agriculture, Hyderabad.

- Cabras, P., & Angioni, A. (2000). Pesticide residues in grapes, wine, and their processing products. Journal of Agricultural and Food Chemistry, 48(4), 967–973. https://doi.org/10.1021/jf990727a

- Chaiyachate, P., & Chaiyachate, S. (2014). Detection of Pesticide Residues in Vegetables and Fruits Using Piezoelectric Crystal Biosensor. Advanced Materials Research, 979, 16–19. https://doi.org/10.4028/www.scientific.net/AMR.979.16

- Chen, C., Qian, Y., Chen, Q., Tao, C., Li, C., & Li, Y. (2011). Evaluation of pesticide residues in fruits and vegetables from Xiamen , China. Food Control, 22(7), 1114–1120. https://doi.org/10.1016/j.foodcont.2011.01.007

- Cunha, S. C., Fernandes, J. O., Alves, A., & Oliveira, M. B. P. P. (2009). Fast low-pressure gas chromatography – mass spectrometry method for the determination of multiple pesticides in grapes , musts and wines, 1216, 119–126. https://doi.org/10.1016/j.chroma.2008.11.015

- Fenik, J., Tankiewicz, M., & Biziuk, M. (2011). Properties and determination of pesticides in fruits and vegetables. Trends in Analytical Chemistry, 30(6), 814–826. https://doi.org/10.1016/j.trac.2011.02.008

- Filipsson, A. F., Bard, J., &Karlsson, S. (1998). Limonene-Concise

- International Chemical Assessment Document 5. World Health Organization Geneva.

- Grimalt, S., & Dehouck, P. (2016). Review of analytical methods for the determination of pesticide residues in grapes. Journal of Chromatography A, 1433, 1–23. https://doi.org/10.1016/j.chroma.2015.12.076

- Hebeish, A., Fouda, M. M. G., Hamdy, I. A., EL-Sawy, S. M., & Abdel-Mohdy, F. A. (2008). Preparation of durable insect repellent cotton fabric: Limonene as insecticide. Carbohydrate Polymers, 74(2), 268–273. https://doi.org/10.1016/j.carbpol.2008.02.013

- Kumari, B., Madan, V. K., & Kathpal, T. S. (2006). Monitoring of pesticide residues in fruits. Environmental Monitoring and Assessment, 123(1–3), 407–412. https://doi.org/10.1007/s10661-006-1493-7

- Lu, H. Y., Shen, Y., Sun, X., Zhu, H., & Liu, X. J. (2013). Washing effects of limonene on pesticide residues in green peppers. Journal of the Science of Food and Agriculture, 93(12), 2917–2921. https://doi.org/10.1002/jsfa.6080

- Miranda, J. (2003). Neurotoxicity after poisonings with organophosphate pesticides in Nicaragua. Occupational Medicine.

- Of, J. (1996). Determination of pesticide residues in fruit and vegetables, 754, 301–331.

- Smegal, D. C.(2000).Human Health Risk Assessment Chlorpyrifos, 1–131. https://doi.org/10.1017/CBO9781107415324.004