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Short Communication

Study on the effectiveness of five cleaning solutions in removing chlorpyrifos residues in cauliflower (*Brassica oleracea*)

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Nowadays, contents of pesticide residues in vegetables had become one of the hot topics closely related to human health. In order to investigate the effectiveness of several cleaning solutions in removing pesticide residues in vegetables, a polluted cauliflower was washed using five types of cleaning solutions which were soda-salt solution, vinegar solution, tamarind juice solution, filtered flour solution, and tap water. Chlorpyrifos was extracted from residues cleaning process and cauliflower itself. Gas chromatography-electron capture detector was used to identify content in residues cleaning process (RCP). Tamarind juice solution had the greatest removal effect, in relation to other of cleaning solutions, with 93.04% removal rate followed by filtered flour solution (17.03%) and vinegar solution (11.42%). However, soda-salt solution and tap water did not have any removal effect in removing chlorpyrifos in cauliflower. Tamarind juice solution was significantly higher than other types of cleaning solutions and tamarind juice solutions itself is a natural fruit juice and non-chemical substance with very easy preparation; therefore, the tamarind juice solution can be used as a general-purpose cleaning solution to remove chlorpyrifos residues in cauliflower.

Key words: Pesticide residues, chlorpyrifos, cleaning solutions, removal effect.

INTRODUCTION

Consuming vegetables and cereals in daily meals is very important. The nutrients that are provided mostly covered all of the reactions in the human body system (Keikotlhaile and Spanoghe, 2011). However, vegetables can be toxic to humans due to pesticide usage (EL-Saeid and Selim, 2013).

Twenty three years ago at Aging City of Anhui Province in China, eleven people have died because of breakfast. After the case investigation, expert found that all the victim had consumed wheat spoiled by organophosphorus pesticides (Hui et al., 2003). Vegetables contamination caused by pesticide residues causes a serious problem to human health. Pesticide residues in vegetables are noxious metabolites produced by usage of pesticide for

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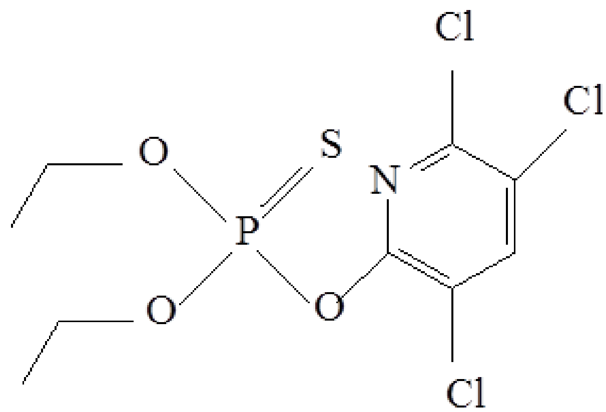

Figure 1. Structure of chlorpyrifos (Ion and Ion, 2012).

long duration in vegetables planting.

The existence of pesticide residues in vegetables can lead to contamination in its nutrient and may give a concern to the consumers regarding the maximum residue limits (MRLs) of vegetables (EL-Saeid and Selim, 2013; Dasika et al., 2012). Based on Food Regulation 1985, Ministry of Health Malaysia has set particular level of MRLs for all pesticides in specific food class to all farmers. Aly et al. (2010) mentioned that chlorpyrifos (O, O-diethyl-O-(3, 5, 6-trichloro-2-pyridyl)-phosphorothioate) is certified as a wide spectrum pesticide and commonly used to manage various types of pest in agriculture field and livestock (US EPA, 1986) and the structures of chlorpyrifos is as shown in Figure 1. Based on previous studies, there are several methods used to remove chlorpyrifos in vegetables and fruits. The methods include wash treatment using some acid (Osman et al., 2014), hydrostatic pressure process (Iizuka et al., 2013), ozonation (Kusvuran et al., 2012), and horizontal sub-surface flow constructed wetlands (SSFCW) (Agudelo et al., 2010). However, these methods were difficult to be conducted. In order to attain an effective technique in removing chlorpyrifos residues in cauliflower, five types of cleaning solutions were made to examine their effectiveness based on percentage of removal from the concentration of chlorpyrifos on samples before and after cleaning process.

MATERIALS AND METHODS

Preparation of cleaning solution

Five types of cleaning solutions were prepared as follows:

Soda-salt solution: For the soda-salt solution (5%), 5 g of edible soda and 5 g of salt was added into 1 L of water. Then, the solution was stirred until completely dissolved.

Tamarind juice solution: 50 g of tamarind without its seed was weighted. Then, 1 L of water was added to tamarind and it was soaked for 15 min.

Flour solution: For the flour solution, 50 g of flour was weighted. Then, the flour was poured into 1 L of hot water; the solution was stirred until completely dissolved and filtered from the suspension.

Vinegar solution: For the vinegar solution, 100 ml of vinegar was measured. Then, 900 ml of water was added into vinegar, the solution was stirred lightly to dissolve the solutions. If there was residue present in the solutions, the solution was filtered and supernatant was collected.

Preparation of simulated chlorpyrifos pollution in cauliflower

Preparation of chlopyrifos mixture: 2.0 L of water was added into the 0.95 ml of chlorpyrifos. After water was added, the mixture was stirred until dissolved.

Preparation of chlorpyrifos pollution in cauliflower: A cauliflower of 1000 g was bought from the supermarket and washed with tap water and dried with absorbent paper. Then, the cauliflower was soaked in chlorpyrifos mixture for 10 min and stored at room temperature in a dark room for 24 h.

Method of cleaning samples and extraction of pesticide residues

The contaminated cauliflower was divided into five parts, of which three parts each were soaked with tap water, soda-salt solutions, tamarind juice solutions, filtered flour solutions, and vinegar solutions for 10 min separately. Then, the cauliflower was rinsed off with running tap water for 1 min. The residues cleaning process was extracted using Solid Phase Extraction (SPE).

Gas chromatography-electron capture detector (GC- ECD)

Extracted samples were injected onto GC-ECD model 7890A-Agilent (Agilent Technologies, 5301 Stevens Creek Blvd, Santa Clara, CA 95051, US) for quantitative analysis. The GC-ECD instrument is made up of two parts. The GC portion separates the chemical mixture into pulses of pure chemicals and electron capture detector was equipped with GC. The GC separates chemicals based on their volatility which they evaporate into a gas. The chemicals in the mixture separate based on their volatility. Electron capture detector converted the sample and represents it via chromatogram. Table 1 shows the instrument set up for detection of chlorpyrifos in solutions after cleaning process.

RESULTS AND DISCUSSION

The concentration of the chlorpyrifos in which the cauliflower was soaked was 7.3407 $\times 10^{-4}$ mol/L.

Analysis of residues cleaning process

Cleaning solutions were made and the pH of each solution was checked before undergoing the cleaning process. The residues from cleaning process were analysed to determine the presence of chlorpyrifos. Table 2 tabulates the concentration of chlorpyrifos in the residues cleaning

Table 1. Instrument set up for detection of chlorpyrifos in solutions after cleaning process

Injector temperature	280°C
Detector temperature	300°C
Carrier gas flow rate	20.0 ml min^{-1} (nitrogen)
Column temperature	Initial temperature 165°C for 3 min, increase to 260°C at 3°C min^{-1} with final time of 2 min

Table 2. Concentration of chlorpyrifos in the residues cleaning process.

Types of cleaning solution	pH	Type of acidity	Concentrations of chlorpyrifos (mol/L)
Tamarind juices solution	1.88	Acid	6.8299×10^{-4}
Filtered flour solutions	5.52	Acid	1.2504×10^{-4}
Vinegar solutions	2.02	Acid	8.3828×10^{-5}
Soda-salt solutions	10.82	Base	0.0000
Tap water	6.39	Neutral	0.0000

process which had been analysed using GC-ECD. The concentrations of five RCP were calculated.

From Table 2, mostly acid cleaning solutions have shown the presence of chlorpyrifos in their residues. However, there is no presence of chlorpyrifos in the basic cleaning solutions by GC-ECD.

Comparison of the effect of five cleaning solutions in removing chlorpyrifos in cauliflower with control

The effectiveness of cleaning solution was determined based on their removal rates of chlorpyrifos in cauliflower shown in Table 3 which was determined after the cauliflower had been cleaned using five types of cleaning solutions.

As shown in Table 3, after the cauliflower had been cleaned using five types of cleaning solutions, the removal rates of chlorpyrifos by using tamarind juices solutions is very good compared to others cleaning solutions. While filtered flour and vinegar solutions removal rates are the same which is less than 20%. However, by using soda-salt solution and tap water, there are no removal of chlorpyrifos detected.

The effect of each cleaning solutions in removing pesticide residues

Tamarind juice solution

Based on Table 3, tamarind juices solution has great removal rates. By using tamarind juice, the chlorpyrifos in cauliflower can be removed at high percentages of removal rate is about 93.04%. The usage of tamarind juices solution as a cleaning solution in removing pesticide residues is undiscovered yet. However, the pH of tamarind juices solution is in acidic medium. In tamarind, there are two types of volatile constituent which contribute to the acidity of the tamarind juices which is furan derivatives and carboxylic acids which is about 44.4 and 38.2%. Based on previous study, chlorpyrifos degradation is very slow in acidic medium. The more the acidic of the solution react with chlorpyrifos, the slower the degradation of chlorpyrifos (Singh et al., 2003). Tamarind juices solutions can be used as universal cleaning solution to remove chlorpyrifos in cauliflower.

Filtered flour solutions

Using filtered flour solutions in cleaning process, the result have shown that the removal rates have big difference compared to tamarind juice solutions. The removal rate is about 17.03%. However, filtered flour solutions have better removal effect compared to vinegar solutions. In term of stability, filtered flour solutions are stable for three days only. After that, filtered flour solution start to release bad odour. Nicotinic acid was presented in large quantity of about 4.60 mg in 100 g of flour due to the manufacturer labelled. Based on consumer medicine information, nicotinic acid was used to reduce cholesterol. Chlorpyrifos have their own metabolites which can produce their own cholesterol after they had been consumed with food or contact with vegetables (Watts, 2013). In addition, filtered flour solutions can be used as cleaning solutions to partially reduce pesticide residues in term of preparation which is very simple.

Vinegar solutions

Vinegar solutions have shown the ability in removing chlorpyrifos residues in cauliflower. The removal rate is

Table 3. Removal effects of chlorpyrifos residues after cauliflower has been washed using five type of cleaning solution.

Cleaning solution	Removal rates of chlorpyrifos (%)
Tamarind juices solution	93.04
Filtered flour solutions	17.03
Vinegar solutions	11.42
Soda- salt solutions	0.00
Tap water	0.00

about 11.42% which is slightly lower than flour solutions. Vinegar solutions consist of acetic acid and water. Based on Howard (2012), 10% of vinegar with 90% of water can be used as a pesticide residues remover. In addition, vinegar solutions can be used as cleaning solution to certain kinds of pesticides. Thus, the use of vinegar solution in removing chlorpyrifos residues is proved; although, the removal rates are less than 20%.

Soda-salt solution and tap water

Compared to other cleaning solutions, soda-salt solution and tap water have no removal effect on chlorpyrifos residues. Based on previous study, it is shown that soda-salt has a good removal effect on other type of pesticides. Yu-shan et al. (2013) proved that soda-salts have very good removal effect on mixed pesticide residues consisting of three types of pesticides which are dimethoate, dicofol, and cyhalothrin. The removal rates of soda-salt solutions in removing these three types of pesticide residues are very good results which are 32.5% of dimethoate, 26.9% of dicofol, and 44.4% of cyhalothrin (Yu-shan et al., 2013). However, in this project, the removing of chlorpyrifos residues cannot be detected due to the degradation of chlorpyrifos in basic medium. Besides that, soda-salt solutions have very high basic pH which is 10.82. From the previous study, the degradation of chlorpyrifos is very fast in basic medium and it was stated that in pH 8.4, the degradation of chlorpyrifos with half-life is about 16 days (Singh et al., 2003). The higher the alkalinity of solutions, the degradation of chlorpyrifos became faster. So it is difficult to detect the presence of chlorpyrifos in the sample.

In soda-salt solutions, there is a factor that had effect on the percentages of removal. After the residues cleaning process was extracted using Solid-Phase Extraction, the sample was stored for long before its analysis. So, the chlorpyrifos in the sample was degraded due to long period of time kept in basic condition.

For tap water, the removal rate is same as soda-salt solution. However, soda-salt solutions can be used as pesticides remover for other kind of pesticides. In tap water, there is no component that can contribute in removing pesticide residues. So, using tap water in removing chlorpyrifos residues in cauliflower is not good.

Conflict of interests

The authors have not declared any conflict of interests.

REFERENCES

Agudelo RM, Peñuela G, Aguirre NJ, Morató J, Jaramillo ML (2010). Simultaneous removal of chlorpyrifos and dissolved organic carbon using horizontal sub-surface flow pilot wetlands. Ecol. Eng. 36(10):1401-1408.

Aly N, EL-Gendy K, Mahmoud F, El-Sebae AK (2010). Protective effect of vitamin C against chlorpyrifos oxidative stress in male mice. Pestic. Biochem. Physiol. 97(1):7-12.

Dasika R, Tangirala S, Naishadham P (2012). Pesticide residue analysis of fruits and vegetables. J. Environ. Chem. Ecotoxicol. 4(2):19-28.

EL-Saeid MH, Selim MT (2013). Multiresidue Analysis of 86 Pesticides Using Gas Chromatography Mass Spectrometry: II-Non-leafy Vegetables. J. Chem. 2012:1-10.

Food Regulation (1985). Sixteenth Schedule, Regulation 41, Food Safety Information System of Malaysia (FoSIM), Ministry of Health Malaysia. Available at: http://fsis2.moh.gov.my/UploadFosim/FAR/040810103612F595SIXTEENTH%20SCHEDULE.pdf

Howard G (2012). Simple trick removes pesticides from your vegetables and fruits. Natural health. Available at: http://articles.mercola.com/sites/articles/archive/2012/08/20/vinegar-as-non-toxic-cleaner.aspx

Hui X, Yi Q, Bu-zhuo P, Xiliu J, Xiao-mei H (2003). Environmental pesticide pollution and its countermeasures in China. AMBIO: J. Hum. Environ. 32(1):78-80.

Iizuka T, Maeda S, Shimizu A (2013). Removal of pesticide residue in cherry tomato by hydrostatic pressure. J. Food Eng. 116(4):796-800.

Ion I, Ion AC (2012). Determination of chlorpyriphos in broccoli using a voltammetric acetylcholinesterase sensor based on carbon nanostructure–chitosan composite material. Mater. Sci. Eng. C 32(4):1001-1004.

Keikotlhaile BM, Spanoghe P (2011). Pesticide residues in fruits and vegetables. InTech. pp. 243-252.

Kusvuran E, Yildirim D, Mavruk F, Ceyhan M (2012). Removal of chloropyrifos ethyl, tetradifon and chlorothalonil pesticide residues from citrus by using ozone. J. Hazard. Mater. 241(242):287-300.

Osman KA, Al-Humaid AI, Al-Redhaiman KN, El-Mergawi RA (2014). Safety methods for chlorpyrifos removal from date fruits and its relation with sugars, phenolics and antioxidant capacity of fruits. J. Food Sci. Tech. 51(9):1762-1772.

Singh BK, Walker A, Morgan JAW, Wright DJ (2003). Effects of Soil pH on the Biodegradation of Chlorpyrifos and Isolation of a Chlorpyrifos-Degrading Bacterium 69(9):5198-5206.

United State Environmental Protection Agency (USEPA) (1986). Ambient Water Quality Criteria for Chlorpyrifos, Report, US, Washington, DC.

Watts M (2013). Chlorpyrifos, Pesticide Action Network Asia and the Pacific (April). 68 p.

Yu-shan SZ, Li XP, Liu HM, Zhang YK, Zhao FF, Yu Q (2013). Study on universal cleaning solution in removing blended pesticide residues in Chinese cabbage. J. Environ. Chem. Toxicol. 5(8):202-207.