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Reduction of Imidacloprid, Fenitrothion and Malathion Residues from Cucumber and Tomatoes Using Washing Solutions.

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ABSTRACT

Four aqueous solutions of 5% commercial acetic acid, 5% commercial sodium hypochlorite, 0.01 % potassium permanganate and 1% Hula-san[®] in addition to tap water, were evaluated for their removal efficiency of imidacloprid, fenitrothion and marathion residue deposits on cucumber and tomato samples. Cucumber and tomato samples were treated imidacloprid, fenitrothion and marathion at the manufacture recommended rates of application and subjected to the decontamination solutions. The tested washing solutions treatments achieved various reduction rates which were depended on the morphological structure, pesticide types, water solubility of tested pesticides and the octanol-water partition coefficient (K_{ow}). The 0.01 % $KMnO_4$ washing solution was found to be high effective in reducing the pesticide residues due to the high degree of the pesticides degradation in this treatment. However, 1 % Hula-san[®] exhibited the high reduction capability ($P < 0.05$) with percent reduction 87.18, 78.95 and 88.50 % in cucumber and 78.36, 74.11 and 85.51 % in tomato for imidacloprid, fenitrothion and marathion, respectively. The present study recommended the use of 1% Hula-san[®] as chemical washing solution to reduce the pesticide residues from cucumber and tomato.

Keywords: imidacloprid, fenitrothion, marathion, cucumber, tomato, Hula-san, washing, reduction and LC-MS/MS.

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INTRODUCTION

Fresh vegetables are an important part of a healthy diet as they are a significant source of vitamins and minerals. However, vegetables can be vehicle toxic substances, such as pesticides. Vegetables are internationally traded commodities which can carry undeclared pesticides. (Stan, 2000).

Pesticides constitute a major group of potentially hazardous compounds to humans. They are an integral part of modern farming practices, in most countries as a tool for controlling harmful pests. The stability of certain pesticides which is a requirement for long term effect, and the fact that residues can remain in food, increases the hazard of human exposure and subsequent damage to health. To avoid exposure to pesticides, there is a need to monitor the pesticide residues in food to assure the consumers that the maximum residue permissible limits are not exceeded. Cucumber and tomato are eaten fresh, in salads or used in food decoration with no cooking treatments, thus decontamination interventions are available apart from washing and simple preparation such as peeling (Abou-Arab1999). However, these vegetables are commonly eaten without preparations in the many countries making the need for efficient decontamination strategies an important issue.

Organ phosphorus pesticides such as marathion, fenitrothion are widely used in agriculture (Madam *et al.*, 1996; Kumara *et al.*, 2002, 2003 and 2008). Many organophosphates are potent nerve agents, functioning by inhibiting the action of acetyl cholinesterase (AChE) in nerve cells. Their toxicity has been demonstrated in acute phase as well as its chronic effects have long been noted. (Krejcová *et al.*, 2005). Imidacloprid has is used for seed, soil and foliar treatment due to its good systemic properties. (Wamhoff and Schneider, 1999).

Traditional methods of washing vegetables with water or water containing- aid compounds to remove debris and dirt prior to consumption have been assumed to reduce pesticide residues. Various solutions (e.g. chlorine solution, assonated water and strong acid) were used successfully at commercial scale to decontaminate crops from pesticide residues (On *et al.*, 1996; Mohair, 2001; Puglisi *et al.*, 2004). In most houses hold washing as a process is prevalent, it can be done with readily available solutions formulated from chemicals in a house hold kitchen (Karol *et al.*, 2000). Salt, potassium permanganate, baking soda and distilled vinegar are the chemicals recommended for the purpose of removing residues (Extension Toxicology Network, 1996). Pickling cucumber and eggplant vegetables for 5min. in rice-barn past resulted removal efficiency (95%) of chlorthalonil and tetradifon (Adachi and Okano, 2006).

Given the importance of removal of these compounds from food and eliminate them before consumption, there is need for new decontamination strategies to be established. In the present study, the effect of some non-toxic chemical solutions, that can be used on industrial and house hold levels, on removal of of certain pesticide residues [marathion and fenitrothion (organophosph hours), imidacloprid (neonicotinoids)] which have different chemical groups, and possess different physical properties.

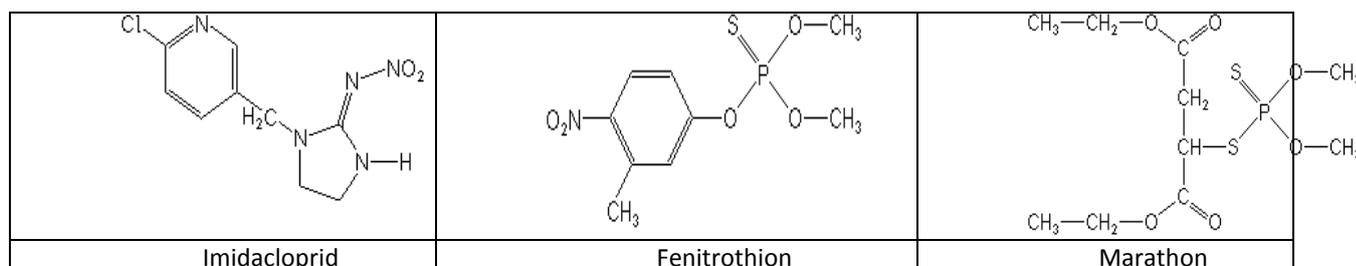
MATERIALS AND METHODS

Reagents and Chemicals:

All reagents and solvents were pesticide, HPLC or analytical grade. Acetonitrile and methanol were purchased from Fisher Scientific (Loughborough, UK). Acetic acid glacial, potassium permanganate and sodium acetate anhydrous from Panacea (Spain). Imidacloprid [(E)-1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine], fenitrothion [O, O-diethyl O-4-nitro-m-tolyl phosphorothioate] and marathion [diethyl (dimethoxyphosphinothioylthio) succinct], (figure 1, table 1) pure reference standard, formic acid and primary secondary amine (PSA) were purchased from Sigma-Aldrich (St Louis, MO, USA). Magnesium sulphate anhydrous from Across® (New Jersey, USA). Imidacloprid formulation (Admire 25 %WP, Bayer crop science, Canada), fenitrothion formulation (Fenitrothion 50 % EC, SCIDCO company, KSA) and marathion (Marathon 57 % EC, Modern pesticides company, India). Commercial acetic acid 6.25% (Pamella®, Al Farris Food Industries, and KSA) and sodium hypochlorite 5% (Clorox®) were obtained from local market (KSA). Hula-San® TR-50 from Roam Chemise Company (Belgium).

Table 1: physical properties of the tested pesticides.

Compound	Water Solubility (mg/l)	K _{ow} (log p)
Imidacloprid	610	0.57
Fenitrothion	38	3.32
Marathon	145	2.36

Fig 1: Chemical structure of the tested pesticides.

Instrumental analysis:

Analysis of pesticides was carried out using a waters® separation module 2975e system equipped with waters® quarto micro mass spectrometer (LC-MS/MS) electro spray ionization (ESI⁺) and multiple reaction monitoring (MRM) mode. Compounds were separated on X-Bridge column C₁₈, 2.1mm x 150mm at temperature of 40^o C. –under a flow rate of 0.2ml/min. The mobile phase consisted of solvent A (9:1 water: methanol containing 0.2% formic acid) and solvent B (100% methanol containing 0.2% formic acid) under gradient condition (Table 2). Mass conditions were capillary voltage: 3.5KV Ion modems positive, source temperature of 120^o C, desolation temperature at 350^o C, desolation gas at rate of 500L/h, and cone gas rate at 50L/h. these conditions, resulted in good separation and high sensitivity were obtained, Table (3) and Fig (2).

Table 2: LC mobile phase gradient

Time	flow rate ml/min	%A	%B
0.00	0.2	100%	0.00%
2.00	0.2	0.00%	100%
10.00	0.2	0.00%	100%
10.00	0.2	100%	0.00%
20.00	0.2	100%	0.00%

Table3: Two MRM transitions monitored, cone voltage, collision voltage, retention time R_{at}. limit of detection (LOD), limit of quantification (LOQ) for Imidacloprid, fenitrothion and marathon.

Compound	R _{at} (min.)	LOD (pap)	LOQ (pap)		Parent ion (m/z)	Product ion (m/z)	voltage	
			Cucumber	Tomato			Cone	Collision
Imidacloprid	7.17	0.005	0.02	0.02	256.1	209.2	22	21
					256.1	175.1*		39
Fenitrothion	8.15	0.008	0.015	0.025	278.3	125	40	29
					278.3	109		25
Marathon	8.39	0.01	0.01	0.01	331.4	127	24	17
					331.4	98.9		29

*the bold number indicated the quantification ions

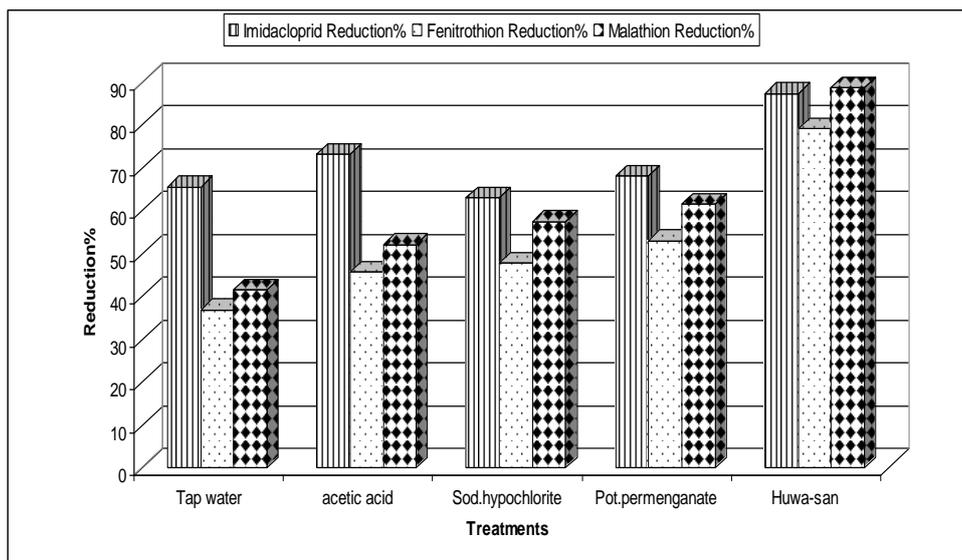


Fig 2: Pesticide residues percent reduction in cucumber after treatment

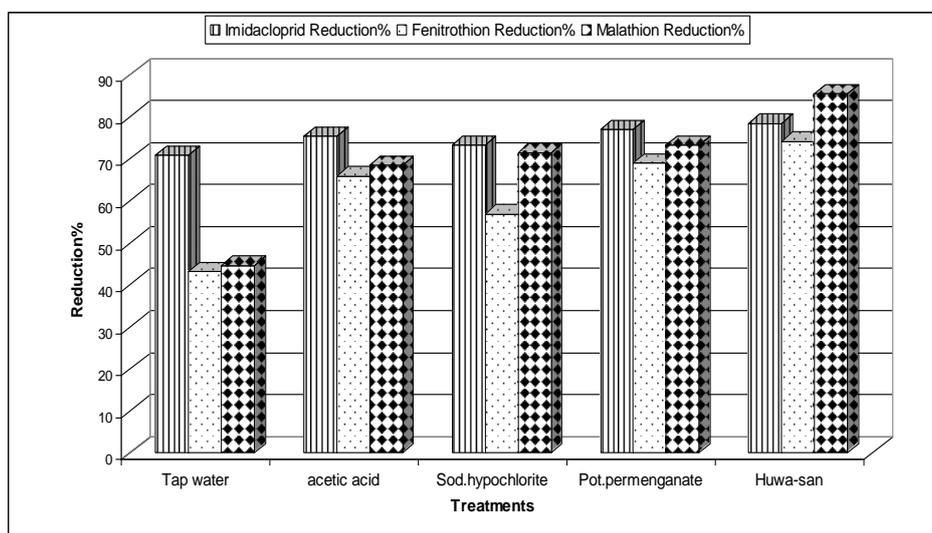


Fig 3: Pesticide residues percent reduction in tomato after treatment

Calibration curves:

Imidacloprid, fenitrothion and marathion standard solutions were prepared in methanol. Matrix matched calibration standard at the concentration of 0.02, 0.05 and 0.1 ppb were prepared. Each concentration was injected under the above mentioned chromatographic conditions. The peak area was plotted against each concentration and the calibration curve for each pesticide was established. Values for r^2 were 0.996, 0.998, and 0.999 for imidacloprid, fenitrothion and marathion, respectively. The limit of detection (LOD) of the test compounds was determined by considering a signal to noise ratio of 3 with reference to the background noise obtained for the blank sample, whereas, the limits of quantification (LOQ) were determined by considering a signal to noise ratio of 10.

Recovery study:

Untreated Cucumber and tomato were spiked with the tested pesticides at 0.05 ppm and extracted using Quenchers method stand for (Quick, Easy, Cheap, Effective, Rugged and safe) (Lehotay, 2007). Each

recovery was replicated three times. The recovery percents ranged (91, 96 and 98 % in cucumber and 93, 98 and 99 % in tomato for imidacloprid, fenitrothion and marathon, respectively.

Sample treatment and analysis:

Cucumber and tomato samples (30 kg for each) were obtained from local market and analysis for absence of the tested pesticides was carried. The samples were immersed in the pesticides formulations at the recommended rates of 25 g/100L, 50 and 75 ml/100L for imidacloprid, fenitrothion and marathon, respectively. Immersion time was 5 min and the samples were removed out and left to dry over-night in a dark chiller. Three replicates samples of 500 g each were taken to determine the initial residue level and remaining of the samples were used for the washing treatments.

The washing treatments involved the immersing of the treated cucumber and tomato samples with pesticides in aqueous solutions as the following; tap water, 5% acetic acid, 0.01 % potassium permanganate, 5 % sodium hypochlorite and 1% Hula-San for 10 min.

The Quenchers method (Lehotay, 2007) was used for sample extraction and clean-up. About 15 g of homogenized samples were weighed in 50 ml centrifuge tube and 15 ml of 1% acetic acid in Acetonitrile was added. The tubes were hand shaken for 1 min. before adding 6 gm of anhydrous magnesium sulfate and 1.5 g anhydrous sodium acetate and then the tubes were hand shaken again for 1 min. The samples were then vortex for another 1 min, and centrifuged at 5000 rpm (Centurion Scientific Company, K3 series, BRK 5308) for 5 min. A 4 ml of the aliquot of the Acetonitrile extract (upper layer) was transferred to 15 ml centrifuge tube containing 600 mg anhydrous magnesium sulfate and 200 mg PSA, shaken and vortex for 1 min, and centrifuged for 5 min at 5000 rpm (BRK 5431). A 2 ml of the cleaned sample was filtered through 0.2 micron nylon syringe filter and evaporated to dryness under steam nitrogen then re-dissolved in methanol for chromatographic analysis.

Statistics:

The data were analyzed using (SPSS version 10) program. A two way analysis of variance (ANOVA Test) was performed to examine the effects of wash solution and the pesticide type on the decontamination level in each material, and the differences among the means were established by using LSD at P < 0.05.

RESULTS AND DISCUSSIONS

The mean initial residues of the tested pesticides on cucumber and tomato are shown in table (4). The mean initial residue deposits of the tested pesticides on cucumber before washing treatments were 0.78, 3.42 and 6.12 mg.kg⁻¹ for imidacloprid, fenitrothion and marathon, respectively. The rate of reduction of imidacloprid, table (5), on cucumber surface after washing treatments was 65.38, 73.07, 62.82, 67.95 and 87.18 % after washing with tap water, 5% acetic acid, 5% sodium hypochlorite, 0.01% potassium permanganate and 1% hula-san[®], respectively. Fenitrothion residue was reduced by 36.84, 45.61, 47.66, 52.92 and 78.95 %, whereas, marathon residue was reduced by 41.50, 51.96, 57.35, 61.44 and 88.50 %, after tap water, 5% acetic acid, 5% sodium hypochlorite, 0.01% potassium permanganate and 1 % Hula-san[®] respectively.

Table 4: Initial deposits and MRL values for the tested pesticides in Cucumber and Tomato

Compound	Initial residue deposit (µg.k ⁻¹) ±SD*		MRL ** (µg.k ⁻¹)	
	Cucumber	Tomato	Cucumber	Tomato
Imidacloprid	0.78 ± 0.39	1.34 ± 0.42	1	0.5
Fenitrothion	3.42 ± 1.77	2.55 ± 0.61	0.01	0.01
Marathon	6.12 ± 2.51	4.28 ± 1.38	0.02	0.02

*. Values given are the means of three replicates.

** (Maximum residue limit according to European Commission Regulation (EU) updated 2012)

Table5: Pesticide residues remained and percent reduction in cucumber after treatment

	Imidacloprid		Fenitrothion		Marathon	
	$\mu\text{g.k}^{-1} \pm \text{SD}^*$	Reduction%	$\mu\text{g.k}^{-1} \pm \text{SD}$	Reduction%	$\mu\text{g.k}^{-1} \pm \text{SD}$	Reduction%
Initial	0.78 ± 0.39	-	3.42 ± 1.77	-	6.12 ± 2.51	-
Tap water	0.27 ± 0.06	65.38	2.16 ± 1.28	36.84	3.58 ± 1.44	41.50
Acetic acid	0.21 ± 0.18	73.07	1.86 ± 0.97	45.61	2.94 ± 1.13	51.96
Sod. hypochlorite	0.29 ± 0.11	62.82	1.79 ± 0.59	47.66	2.61 ± 1.20	57.35
Pot. permanganate	0.25 ± 0.04	67.95	1.64 ± 0.72	52.92	2.36 ± 0.85	61.44
Hula-san [®]	0.10 ± 0.03	87.18	0.72 ± 0.26	78.95	0.70 ± 0.39	88.50

*. Values given are the means of three replicates.

All treatments significantly ($P < 0.05$) reduced the initial deposit of imidacloprid on cucumber surface. There were no significant ($P < 0.05$) differences between acetic acid, potassium permanganate and Hula-san[®] washing treatments, but there were significant ($P < 0.05$) differences between tap water, sodium hypochlorite and Hula-san[®] treatments. Acetic acid showed high efficacy in removing imidacloprid whereas Hula-san[®] solution was the most effective in the reducing of imidacloprid residues from cucumber surface. Tap water wash and 5% acetic acid were not effective ($P < 0.05$) in reducing fenitrothion residue on cucumber compared with the initial deposited concentration, table (5). However, treatments with 5% sodium hypochlorite, 0.01% potassium permanganate and 1% Hula-san[®] significantly ($P < 0.05$) reduced the initial deposits of fenitrothion on cucumber.

The most effective reduction was obtained by 1% Hula-san[®] solution treatment. Marathon was significantly ($P < 0.05$) reduced by all treatments, table (5). 0.01% Potassium permanganate had high significant reduction on marathon (61.44%). The most effective solution in removing marathon was 1% Hula-san[®] Which was significantly higher than the other treatments?

The initial residue deposit of imidacloprid, fenitrothion and marathon on tomato were 1.34, 2.55 and 4.28 mg.kg^{-1} , respectively, (table 4). Imidacloprid residue was reduced by 70.90, 75.37, 73.13, 76.86 and 78.36 % after treatments with tap water, 5% acetic acid, 5% sodium hypochlorite, 0.01% potassium permanganate and 1% Hula-san[®] solutions, respectively. Fenitrothion residue on tomato surface was reduced by rates 43.13 % (tap water), 65.88 % (5% acetic acid), 56.85% (5 % Sodium hypochlorite), 69.02% (0.01 % potassium permanganate) and 74.11% (1 % Hula-san[®]) solutions. Marathon residue on tomato reduced by 44.62 % (tap water), 68.46 % (5% acetic acid), 71.50 % (5% sodium hypochlorite), 73.13% (0.01 % potassium permanganate) and 85.51% (1% Hula-san[®]) solutions. (Table 6).

Table6: Pesticide residues remained and percent reduction in tomato after treatment

	Imidacloprid		Fenitrothion		Marathon	
	$\mu\text{g.k}^{-1} \pm \text{SD}^*$	Reduction%	$\mu\text{g.k}^{-1} \pm \text{SD}$	Reduction %	$\mu\text{g.k}^{-1} \pm \text{SD}$	Reduction%
Initial	1.34 ± 0.42	-	2.55 ± 0.61	-	4.28 ± 1.38	-
Tap water	0.39 ± 0.17	70.90	1.45 ± 0.31	43.13	2.37 ± 0.75	44.62
Acetic acid	0.33 ± 0.14	75.37	0.87 ± 0.22	65.88	1.35 ± 0.49	68.46
Sod. hypochlorite	0.36 ± 0.03	73.13	1.10 ± 0.52	56.85	1.22 ± 0.18	71.50
Pot. permanganate	0.31 ± 0.08	76.86	0.79 ± 0.43	69.02	1.15 ± 0.25	73.13
Hula-san [®]	0.29 ± 0.11	78.36	0.66 ± 0.29	74.11	0.62 ± 0.23	85.51

* Values given are the means of three replicates.

There were significant effects for washing treatments on reducing imidacloprid residue deposit on tomato. However there were no significant differences among the various washing solutions. 0.01 % Potassium permanganate had high reduction effect by 76.86%, but 1% Hula-san[®] solution achieved the highest reduction of imidacloprid on tomato surface (78.36%). Tap water did not reduce the residue of fenitrothion on tomato surface compared with initial concentration ($P < 0.05$) whereas other treatments were significant in

reducing the contamination concentration of imidacloprid. The 1% Hula-san[®] solution also had the highest reduction effect for marathion residues deposit on tomato surface.

The data clearly indicated that; the initial residues of marathion and fenitrothion in cucumber samples were higher than in tomato samples. This could be attributed to the difference of surface area and the difference of the morphological structure of both. Also the type of formulation and their ability to deposit on the surface of tested crops. Penetration is the most dynamic process that may control the fate of a pesticide residue on Raw Agriculture Commodities during washing. However, all examined washing solutions showed, in general, similar reduction percents of imidacloprid residues in both crops. This might be due to the type of imidacloprid formulation. Imidacloprid is formulated as wet table powder which means that the residue is in the form of very fine particles on the surface after pesticides treatment, these fine particles will be easily removed by any washing solution. Cobras *et al* (1998) reported that diazinon, bitertanol, iprodione, phosalone, and procymidone were adsorbed during treatment on the dusts which located upon plum fruits surfaces and washing removed both the dust and the adsorbed residues. Water solubility of pesticides is not always the dependent factor of the risibility of a pesticide is not always correlated with its water solubility (Congas *et al.*, 2007; Outlaid *et al.*, 2005). The removal of pesticides with the washing of Raw Agriculture Commodity may be performed not only through the dissolution of pesticide residues in the washing water or the rinsing with chemical baths (detergents, alkaline, acid, hypochlorite, metabisulfite salt, assonated water etc) (Holland, 1994) but also through the removal of dust or soil particles previously absorbed residues from the outer layer of RAC (Guardia Rubio *et al.*, 2007).

The variation in each pesticide reduction depended upon the specification of washing solution. In cucumber and tomato samples, 0.01 potassium permanganate had high effectiveness in reducing the tested compounds Also acetic acid revealed high efficacy in reducing of imidacloprid residue on tomato surface. Potassium permanganate is strong oxidizing agent, thus the oxidative properties could have significant effect on degradation which shall contribute the reduction of studied pesticides after the washing treatments. Also the extent of acetic acid for the reduction of pesticides may be due to the high acidity and/or high redox potential of this solution.

Hula-san[®] solution treatment exhibits the highest reduction effect of the tested pesticides. Care must be taken when using Hula-san[®] as a washing solution because excess concentration than 1 % will remove the green colour layer on the surface as in cucumber, which lead to quality reduction. Washing with different chemicals can be replaced by washing with 1 % Hula-san[®] which does not have any side effect unlike some of the current decontamination solutions in addition to its effect as a disinfectant. For example, the highly effect of potassium permanganate can retain some Man residue on the vegetables which is not degradable upon cooking (Gourd Apathy *et al.*, 2012).

CONCLUSION

Pesticide residues studied in the cucumber and tomato samples were reduced to various degrees, depending on the behavior and physiochemical properties and the specificity of chemicals used for washing preparation. Washing vegetables with the chemical reported here enhances the removal of pesticide residues from product more than that of washing with water alone. Among the washing solution treatments, the 0.01 % potassium permanganate washing solution was found to be high effective in reducing the pesticide residues which was due to the high degree in the pesticide degradation. Washing with 1 % Hula-san[®] exhibited high efficient reduction capability more than 0.01 % potassium permanganate. Hence, this study suggests that the use of chemical washing solution, that can reduce the pesticide residues from cucumber and tomato.

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