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Effect of Some Treatments on Decreasing the Level of Pesticides Residues in Some Fresh Eaten Vegetables

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ABSTRACT

Developing a procedure to remove pesticide residues from commonly eaten fresh vegetables is essential to avoid their adverse effects and risks. This study was to assess the effects of warm water at 40ºC and warm water plus citric acids 10%, or sodium bicarbonate 5%, or vinegar 5% or lemon 10% or crushed date kernels 20 % for 5 and 10 minutes to remove a multi-residues of pesticides in tomato, eggplant, cucumber and pepper. By using the QuEChERS method and GC-MS, these aforementioned residues were extracted and analyzed respectively. The processing factor (PF) values indicated a substantial reduction in the selected pesticide residues to lower than the maximum residue limits (MRLs). Chlorpyrifos and Lambda cyhalothrine residues were minimized by treatment with warm water plus crushed date kernels reaching 98.84% & 98.72%), (tomato), 98.65% & 98 .38% (eggplant), 99.03% & 98.09% (cucumber), and 99.05% & 97.93% (pepper) respectively. Malathion residues were removed by treatment with warm water plus vinegar by 98.20% (tomato), 98.64% (eggplant), 99.09% (cucumber), and 97.87% (pepper) respectively. Chlorfenapyr residues were removed by treatment with warm water plus vinegar by 97.45% (tomato), 97.46 %(eggplant), 98.67% (cucumber), and by warm water plus sodium bicarbonate to reach 98.74 %,(pepper) respectively. Regarding the result of PF and reduction %, freshly eaten vegetables could be consumed safely when using processed tools of warm water with acidic and alkaline solutions that can effectively minimize Chlorfenapyr, and Malathion residues and when using warm water plus crushed date kernels for Chlorpyrifos and Lambda cyhalothrine residues.
Keywords: Pesticide residues; removing; processing factor; reduction; vegetables

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INTRODUCTION

The use of pesticides to control pests in agricultural activities has been associated with several concerns, including the risks to human health, and the environment alteration **(Clarke et al., 1997)**. In different fruits and vegetables, for better yield and quality, pesticides are repeatedly applied during the entire period of growth and even at the fruiting stage (**Guler et al., 2010**). Residues of pesticides in food are influenced by the storage, handling and processing that occurs between the harvesting of raw agricultural commodities and the consumption of prepared foodstuffs (**Holland et al., 1994**). Levels of pesticides should be controlled at an optimum point due to their relative toxicity (**Mansour *et. al.*, 2009**). Pesticide residues are one of the most important issues affecting food safety (**Li et al., 2021**) and threatening ecological security (**Zhang et al., 2022**). It is necessary to strengthen pesticide abuse control and market surveillance and inspection, to reduce the harmful effects of pesticide residue in fruit and vegetables on human health **(Jiang et al., 2003**). To protect consumers' health, many countries have established legal directives to control levels of pesticides in food, through maximum residue levels, MRLs (**FAO/WHO, 2004**).

Fresh vegetables and fruits are considered an important part of a healthy diet because of the presence of significant amounts of nutrients and minerals in them and commonly used everywhere to meet the requirements of a balanced diet and good health (**Iqbal et al., 2009, Bempah et al., 2011**). However, they can also turn out to be the source of toxic substances such as pesticides (**Iqbal et al., 2009**). Tomato and Eggplants are affected by many pests due to favorable weather conditions during the growing season. Therefore, excessive amounts of different types of pesticides are applied to protect them. Pesticides are sprayed directly on the plants, which can persist for a long time in vegetables (**McCauley et al., 2006**). Root and leafy vegetables from eight Egyptian local markets in six different regions of the country showed the lowest contamination rates (1.9 and 4.7%, respectively), slightly exceeding the MRLs in leafy vegetables **(Dogheim et al., 2002).** Malathion was the most frequently found pesticide residue, being detected in 203 of 391 (52%) samples of leafy vegetables and some aromatic medicinal plants, followed by profenofos, which was detected in 131 of 391 (33%) samples **(Dogheim et al., 2004).**

The effectiveness of postharvest processes is controlled by various factors and leads to a substantial reduction of residual pesticides, metabolites of broken pesticides are of great concern (**Albaseer 2019**). Pesticide residue levels in post-harvest raw agricultural commodities (RAC) are affected by the storage, handling and processing steps (**Chauhan et al., 2014**). Processing leads to large reductions in residue levels in the prepared food, particularly through washing, peeling and cooking operations **(Kaushik et al., 2009**). Commercial and household food preparation (washing, peeling, blanching and cooking) is effective in removing most of the residues that are loosely attached to vegetables (**Farha et al., 2018**). Washing with water and the cooking process (blanching and frying) helped to eliminate most of the pesticide residues from the potato tubers (**Soliman 2001**). Blanching followed by stir-frying was the most effective combined operation for reducing pyridaben, procymidone, chlorothalonil, difenoconazole residues in cowpea (**Huan et al**., **2015**). Processing such as peeling, soaking in chemical baths and blanching can reduce pesticide residues more effectively than washing and soaking (**Chung 2018**). Ozonation is a safe and promising process for the removal of the tested pesticides from aqueous solution and vegetable surfaces under domestic conditions (**Wu et al., 2007**). Reduction of pesticide residue levels was indicated by blanching, boiling, canning, frying, juicing, peeling and washing fruits and vegetables with an average response ratio ranging from 0.10 to 0.82. Baking, boiling, canning and juicing indicated both reduction and increases for the 95% and 99.5% confidence intervals (**Keikotlhaile et al., 2010**). Washing, peeling and heat processing (boiling and blanching) were the most effective ways of pesticide residue dissipation (**Naman et al., 2022**).

The monitoring of pesticide residues in food products become an essential requirement for consumers, producers and institutions concerned with standards and quality control management (**Barakat 2004**). Pesticide residues in some consumed local horticultural products in some Egyptian governorates were analyzed by GCMS/MS and LC-MS/MS analysis. Out of the total 175 samples analyzed, 35 samples (20%) were free from pesticide residues, 140 samples (80%) were contaminated, and 59 samples (42%) from the contaminated samples exceeded the maximum residue limits (MRLs) (**Ibrahim et al., 2022**). Therefore, detecting pesticide residues in freshly eaten vegetables is essential to ensure that these vegetables do not exceed the maximum residue limits MRLs) associated with each pesticide and concerns about quality control measurements for protecting the health of consumers and generating awareness of the producers. It is important to reduce the daily intake of pesticides in fresh vegetables compared with the acceptable daily intake to estimate the potential health risks and to determine the future policy on pesticides. On the other side, several Egyptian studies investigated the residual levels of pesticides in foods without attention to their elimination methods while there are few studies deal with the effect of household processing to reduce pesticide residues on freshly eaten vegetables. These processing treatments may help pesticides degrade or wash or adsorb to the present adsorbent materials. Hence, there is a need for considerable research to monitor the level of residues after these household treatments of fresh vegetables in a cost-effective manner methods. Therefore, providing useful information about the removal levels of pesticide residues and the effects of some household treatments to reduce the risk potential of the most used pesticides to protect consumers for consumers and generate public awareness about the necessity of pesticide residue removal. The objective of the present research study was to assess the changes in Chlorpyrifos, Chlorfenapyr, Malathion and lambda cyhalothrine pesticide residues due to using warm water at 40ºC and warm water plus citric acids 10%, or sodium bicarbonate 5%, or vinegar 5% or lemon 10% or crushed date kernels 20 % and to compare the efficiency of these treatments in minimizing the residues in tomato, eggplant, cucumber and pepper vegetables.

MATERIALS AND METHODS

1. Chemicals

Pesticides formulations of Challenger (Suspension Concentrate, (SC) 36 % of chlorfenapyr), Malathion (Emulsifiable Concentrate, (EC) 57 % of malathion), Bestban H (Emulsifiable Concentrate, (EC) 48 % of Chlorpyrifos), and Katron 5 (Suspension Concentrate, (SC) 5% of Lambda-cyhaloethrin were obtained from BASF, kafr el zayat pesticides and chemicals, Alexandria for agriculture chemicals, National Company for agrochemicals respectively. Analytical standards of chlorfenapyr, Malathion and Lambda-cyhaloethrin from Dr. Ehrenstorfer Laboratories, Augsburg, Germany. QuEChERS analysis chemical of Primary secondary Amin (PSA) and Acetonitrile, Formic acid HPLC grade was purchased from Sigma–Aldrich (Germany). Sodium-acetate Magnesium sulfate Anhydrous, Sodium chloride, Trisodium citrate dehydrate, Zinc chloride, potassium metabisulphite, magnesium oxide and Ammonia solution 33 % purchased from El-Gomhouria for Trading Chemicals and Medical Appliances, Egypt.

2. Experimental design

Tomato, Eggplant, Cucumber, and Green pepper fruits were selected to determine the effect of different treatments on pesticide residues that are the most used fresh vegetables in Egypt. These vegetables were untreated without pesticides obtained from Borg Al-arab farm, Alexandria, Egypt and stored at -18 ^{o}C until the experiment. The experiments were based on a study from **Abou-Arab (1999**), the vegetables were spiked by multiple residues of selected pesticides through immersed into a mixture of the commercial formulations of the tested pesticide solution for 30 min at the application rate of 3.0 g of active ingredients per 1000 mL to simulate the real field application (**Hanafi et al., 2016**). Then, the treated vegetables were taken out and left to dry at room temperature. The representative replicates of each treatment of fruits were subject to initial analysis of pesticide residues. Then the representative samples of tomato, eggplant, cucumber, and pepper were treated for 5 and 10 minutes; warm water (40±2^{0}C, warm water plus citric acid 10%, warm water plus sodium bicarbonate 5%, warm water plus vinegar 5% and warm water plus lemon solution 10% and warm water plus finely crushed date pam kernel 20% (w/v). The control samples were collected and analyzed without removal treatment, while all the samples were stored at 4◦C until extraction. Three representatives after exposure to household removal treatments were taken for residue analysis to determine the effect of each solution.

3. Extraction

Vegetable samples (10 g) were chopped, blended and homogenized well, then we followed The QuEChERS method for extraction and clean up; about 15 ml of a homogenous sample was placed in a 50-mL Teflon tube and mixed with100 mL of 1%acetic in acetonitrile. Tubes were tightly closed and vigorously shaken for 1 min using a vortex mixer and kept in the freezer at –18°C for 15 min with 900 mg MgSO4 added to them. The tubes were centrifuged at 2000 rpm for 5 min. One milliliter of the upper layer was transferred into a 2 mL vial to a clean containing 500 mg MgSO4 + 150 mg PSA (Primary secondary amine). About 1 ml of supernatant was dried under a gentle stream of nitrogen at room temperature. The dry residues were reconstituted in 1 mL acetonitrile for GC-MS analysis.

4. Instrumentation

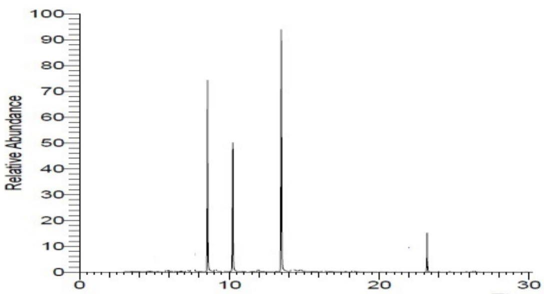
Gas chromatography-mass spectroscopy (TSTGC-UDSQ-II) Thermo Scientific Trace GC with Single Quadrupole MS DSQ II, USA was used for the determination of the target pesticide (Malathion, Chloropyriphos, Chlorfenapyr, and Lambda-cyhaloethrin). The instrument is equipped with an HP-5MS capillary column, Carrier gas: Helium at 1 ml/min., with an autosampler and split/splitless injector in the split mode at 260°C. The MS detector was run in the scan mode (from 50 to 500 *m/z*) and after that SIM mode was operated. The highest abundant ion functioned as the quantifier ion while the other three ions were used for confirmation as qualifier ions. The programmed temperature used was as follows; Initial temperature, 100˚ C held for 1 min, then at the rate of 20˚ C /min to 180˚ C, rate 10˚ C /min to 190˚ C, 3˚ C /min to 240˚ C and 10˚ C /min to 350˚ C and then maintaining this temperature 30 min. The temperature of the injection port was 250˚ C and a 1 ml volume was injected. The temperatures of the ionization source were kept at 230˚ C. The transfer line was respectively set at 250, 280 ^{0}C. Data compilation was performed by Mass Hunter Software under MRM mode. The peak area of the corresponding analytical residues was used to calculate the concentration of residues from the calibration curve (correlation = 0.996). The analytical method limit of detection was assessed. Method validation was carried out by three pesticides concentrations of 25, 50,100, 200, and 400 ppb, then extracted via the same method as described above in triplicate while, the limit of detection (LOD) and limit of quantification (LOQ) were found to be 0.01 and 0.1 mg/kg, respectively for analyzed samples (Fig 1). Processing factor (PF)= Residue level in processed food/ Residue level in raw agricultural food (mg/kg) whereas, A PF value lower than 1 indicates a reduction in the residue level and higher than 1 highlights a concentration effect (**Im and Ji 2016**).

The stock standard solution of the four target pesticides (0.35 mg ml^{-1}) was prepared in acetonitrile HPLC grade and stored at refrigerated conditions (4 °C) before use for the tested vegetables. The recovery of the used pesticides (Average recovery (%) ± SD**)** was as follows 95.0 ± 2.48 (Chlorfenapyr), 93.5 ± 1.56 Malathion, 96.0 ± 1.83 (Chloropyriphos), 90.00 ± 1.99 (Lambda-cyhaloethrin), respectively. Method validation was carried out in triplicate and extracted by the same method as described above. The recovery percentage was found to be commendable in the range of 85.00–97.5%. Relative standard deviation was calculated in % RSD and ranged between 1.64% and 2.44% (Table 1).

Table (1): GC/MS analysis of authentic pesticide retention time and monitoring ions

Pesticides	**Chemical group**	**Retention time (Rt, min.)**	**M.Wt**	**Monitored ions (*m/z*)**
Malathion	OCPs	8.55	253	173 ,121, 95, 76
Chlorpyrifos,	OCPs	11.24	349	314,258, 194,97
Chlorfenapyr	Pyrrole	13.47	408	247,227,200,177
Lambda-cyhaloethrin	Pyrethroids	23.20	449.8	208, 197,181

Standards pesticides



Calibration curve

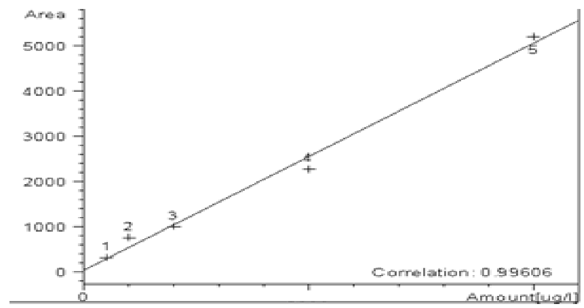


Fig (1): Targeted Pesticides standard by GC/MS and calibration curve.

5. Statistical analysis:

Pesticide data were analyzed in different vegetable samples via one-way ANOVA and LSD (Least Significant Difference) test at $p < 0.05$ levels. A two-way analysis of the variance of the pesticides was also conducted to compare the treatments.

RESULTS AND DISCUSSION

The selected vegetables of tomato, eggplant, cucumber and pepper were processed with warm water at 40 ºC and warm water at 40 ºC plus citric acids 10%, or sodium bicarbonate 5%, vinegar 5% or lemon 10%, crushed date kernels 20 % to remove Chlorpyrifos, Chlorfenapyr, Malathion and lambda cyhalothrine residues from selected vegetables.

Table 2 Removal of pesticide residues (mg/kg) in tomatoes by some processing treatments.

		Chlorpyrifos			Chlorfenapyr			Malathion			Lambda cyhalothrine		
Processing methods	**Time (min.)**	**Conc.**	**PF**	**R%**	**Conc.**	**PF**	**R%**	**Conc.**	**PF**	**R%**	**Conc.**	**PF**	**R%**
	Before processing	1.13		0.00	1.04		0.00	1.37		0.00	0.86		0.00
Warm water (40 ± 2^0C)	5	0.76	0.67	32.76^{e*}	0.49	0.47	52.99^{e}	0.47	0.34	65.83^{e}	0.42	0.48	51.66^{d}
	10	0.22	0.20	80.36^{c}	0.34	0.33	67.31^{d}	0.36	0.26	73.81^{d}	0.26	0.30	69.86^{cd}
Warm water + Citric acids 10%	5	0.50	0.44	56.12^{e}	0.33	0.32	68.48^{d}	0.37	0.27	72.74^{d}	0.38	0.44	56.09^{d}
	10	0.13	0.11	88.69^{b}	0.12	0.11	88.58^{b}	0.12	0.09	91.36^{b}	0.12	0.13	86.70^{b}
Warm water +Sodium bicarbonate 5%	5	0.38	0.34	66.44^{d}	0.26	0.25	74.89^{c}	0.25	0.18	81.79^{cd}	0.32	0.37	62.53^{c}
	10	0.11	0.10	89.26^{b}	0.02	0.02	98.45^{a}	0.12	0.09	91.07^{b}	0.12	0.14	80.68^{bc}
Warm water +Vinegar 5%	5	0.39	0.35	65.09^{d}	0.32	0.31	69.28^{d}	0.35	0.25	74.53^{d}	0.20	0.23	76.95^{c}
	10	0.03	0.03	97.34^{a}	0.13	0.13	87.52^{b}	0.03	0.02	98.20^{a}	0.12	0.13	86.49^{b}
Warm water +Lemon 10%	5	0.53	0.47	53.29^{e}	0.38	0.36	63.67^{d}	0.32	0.23	76.78^{d}	0.24	0.28	72.19^{c}
	10	0.11	0.10	89.88^{b}	0.11	0.11	89.12^{b}	0.11	0.08	91.71^{b}	0.12	0.14	86.48b
Warm water + Crushed date kernels 20%	5	0.30	0.27	73.09^{d}	0.27	0.26	73.65^{c}	0.33	0.24	75.83^{d}	0.13	0.15	84.96b
	10	0.01	0.01	98.84^{a}	0.12	0.12	88.04^{b}	0.13	0.09	90.85^{bc}	0.01	0.01	98.72a
F (Treatment x Tim)				18.342			11.699			9.638			21.803

*= Different letter of Duncan test means there is a significant between treatment ($p \leq 0.05$).

The results in Table (2) revealed that warm water plus crushed date kernels minimized Chlorpyrifos residue to the maximum possible extent reaching 98.84%, followed by warm water plus vinegar that achieved removal rates of 97.34% from tomatoes. Chlorfenapyr contents were removed by 98.45 % when using warm water plus sodium bicarbonate solution followed by using warm water plus lemon by 89.12%. Similar to this, warm water plus vinegar was the most successful tool with residue removal by 98.20%, followed by warm water plus lemon and warm water plus citric acid which minimized Malathion residues by 91. 36 % and 91.71% respectively. Warm water plus crushed date kernels eliminated Lambda cyhalothrine residues by (98.72%) followed by warm water plus 10% Citric acids by 86.70% in tomato. The processing factor (PF) values (mg/kg) were (0.67 to 0.01) Chlorpyrifos, (0.47 to 0.02) Chlorfenapyr, (0.34 to 0.02) Malathion and (0.48 to 0.01) Lambda cyhalothrine respectively indicated a reduction in the residue level from fresh tomato due to the household procedures.

The measured levels of removing pesticide residues from eggplant are given in Table 3. The most effective changes in pesticide residues were warm water plus crushed date kernels by 98.65% of Chlorpyrifos pesticides followed by warm water plus vinegar approach gave removal content with nearly 91.37% of its residues. The concentration of the Chlorfenapyr residue was reduced by 97.46% by using warm water plus vinegar and followed by warm water plus crushed date kernels that removed the remaining residues by 88. 69%. Similarly, warm water plus vinegar was the best method for removing Malathion residues by 98.64%. Warm water plus crushed date kernels were the most efficient method for eliminating Lambda cyhalothrine residues by 98.38% from eggplants. The PF values (mg/kg) ranged from (0.44 to 0.01) Chlorpyrifos, (0.62 to 0.03) Chlorfenapyr, (0.68 to 0.01) Malathion and (0.32 to 0.02) Lambda cyhalothrine respectively in Eggplants due to household treatments.

Table 3 Removal of pesticides Residues (mg/kg) in eggplant by some processing treatments.

		Chlorpyrifos			**Chlorfenapyr**			**Malathion**			**Lambda cyhalothrine**		
Processing methods	**Time (min.)**	**Conc.**	**PF**	**R%**	**Conc.**	**PF**	**R%**	**Conc.**	**PF**	**R%**	**Conc.**	**PF**	**R%**
	Before processing	1.11			0.99			0.95			1.05		
Warm water (40±2^{0}C)	5	0.48	0.43	57.29^{f}	0.61	0.62	38.52^{e}	0.65	0.68	31.54^{e}	0.34	0.32	67.96^{e}
	10	0.25	0.23	77.24^{e}	0.33	0.34	66.33^{d}	0.36	0.38	62.24^{d}	0.21	0.20	80.43^{d}
Warm water + Citric acids 10%	5	0.30	0.27	73.16^{c}	0.20	0.20	79.90^{c}	0.17	0.18	82.12^{c}	0.20	0.19	80.91^{d}
	10	0.15	0.14	86.37^{c}	0.12	0.12	87.88^{b}	0.11	0.12	88.20^{b}	0.12	0.11	88.97^{b}
Warm water +Sodium bicarbonate 5%	5	0.49	0.44	55.83^{f}	0.25	0.25	74.84^{c}	0.13	0.14	86.42^{b}	0.07	0.07	93.25^{b}
	10	0.12	0.11	89.44^{c}	0.12	0.12	88.17^{a}	0.11	0.12	88.02^{b}	0.12	0.11	89.07^{b}
Warm water +Vinegar 5%	5	0.39	0.35	65.04^{e}	0.12	0.13	87.39^{b}	0.13	0.13	86.59^{b}	0.15	0.14	86.13^{bc}
	10	0.10	0.09	91.37^{b}	0.03	0.03	97.46^{a}	0.01	0.01	98.64^{a}	0.12	0.11	88.79^{b}
Warm water +Lemon 10%	5	0.40	0.36	64.27^{d}	0.30	0.30	66.76^{d}	0.24	0.25	74.52^{d}	0.14	0.14	86.32^{bc}
	10	0.20	0.18	82.40^{c}	0.12	0.12	88.05^{b}	0.11	0.12	88.10^{b}	0.12	0.11	88.64^{b}
Warm water + Crushed date kernels 20%	5	0.33	0.29	70.85^{d}	0.33	0.33	66.80^{d}	0.33	0.35	65.485^{d}	0.12	0.11	88.66^{b}
	10	0.02	0.01	98.65^{a}	0.11	0.11	88.69^{b}	0.11	0.12	88.18^{b}	0.02	0.02	98.38^{a}
F (Treatment x Tim)				17.86			21.29			19.74			4.00

Minimizing pesticide residues from cucumber presented in Table 4, warm water with crushed date kernels that the most successful treatment in lowering Chlorpyrifos residues by 98.03%, followed by warm water with citric to achieve removal rates of 89.80% from cucumber. Warm water plus vinegar gave the optimum removal content of Chlorfenapyr nearly 98.67%, followed by warm water with a solution of citric acid and water plus sodium bicarbonate eliminated 93.19% and 93.19% respectively. Similar to this, warm water plus vinegar gave the optimum removal of Malathion content nearly by 99.09%, followed by warm water with citric acid, warm water with sodium bicarbonate and warm water plus lemon by 93.60, 93.49 and 93.20% respectively from cucumber. The most effective method for removing Lambada cyhalothrine residue was warm water with crushed date kernels, which achieved removal rates of 99.09% from cucumber fruits. These removing treatments resulted in a consistent concentration, which can easily be corrected to give MRLs when monitoring pesticide residues in some commodities. The PF values (mg/kg) ranged from (0.62 to 0.02) Chlorpyrifos, (0.47 to 0.01) Chlorfenapyr, (0.47 to 0.01) Malathion and (0.32 to 0.01) Lambda cyhalothrine respectively in cucumber.

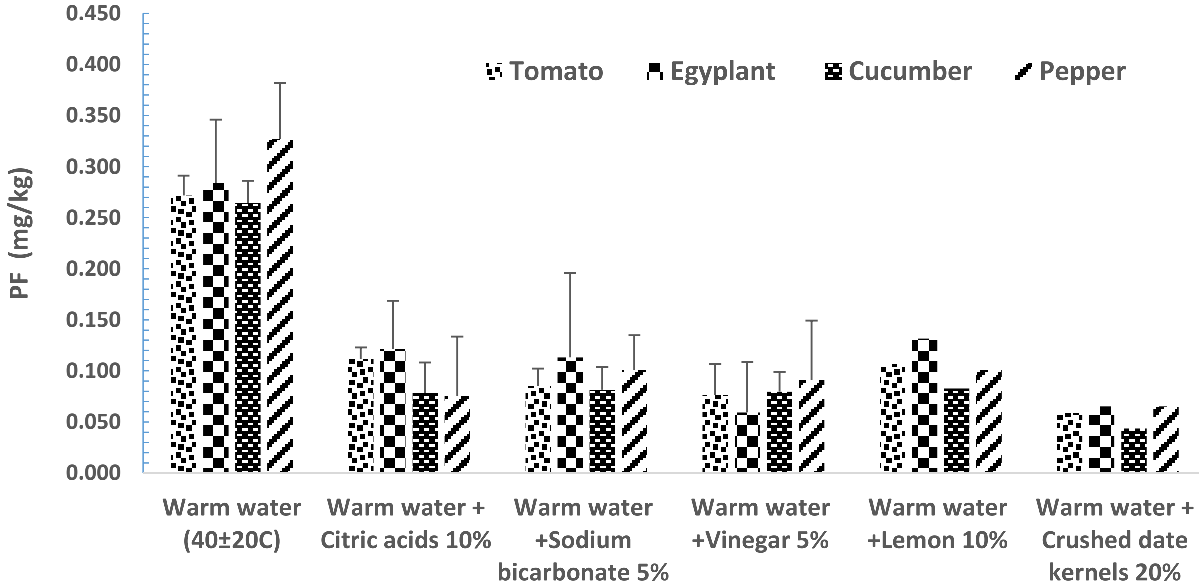
Table 4 Removal of pesticides Residues (mg/kg) in cucumber by some processing treatments.

		Chlorpyrifos			Chlorfenapyr			Malathion			Lambada cyhalothrine		
Processing methods	**Time (min.)**	**Conc.**	**PF**	**R%**	**Conc.**	**PF**	**R%**	**Conc.**	**PF**	**R%**	**Conc.**	**PF**	**R%**
	Before processing	1.02		0.00	1.66		0.00	1.77		0.00	1.43		0.00
Warm water (40 ± 2^0C)	5	0.63	0.62	38.13^{e}	0.78	0.47	52.89^{f}	0.83	0.47	52.99^{f}	0.46	0.32	68.04^{e}
	10	0.32	0.31	68.52^{d}	0.48	0.29	71.14^{e}	0.49	0.27	72.56^{e}	0.26	0.18	82.02^{c}
Warm water + Citric acids 10%	5	0.56	0.55	45.26^{e}	0.46	0.28	72.34^{e}	0.42	0.24	76.47^{d}	0.36	0.25	75.03^{d}
	10	0.10	0.10	89.80^{b}	0.11	0.07	93.19^{b}	0.11	0.06	93.60^{b}	0.12	0.08	91.95^{b}
Warm water +Sodium bicarbonate 5%	5	0.59	0.58	42.25^{e}	0.34	0.20	79.51^{d}	0.36	0.20	79.92^{d}	0.32	0.22	77.97^{d}
	10	0.12	0.11	88.72^{b}	0.11	0.07	93.19^{b}	0.12	0.07	93.49^{b}	0.12	0.08	91.95^{a}
Warm water +Vinegar 5%	5	0.43	0.42	58.13^{e}	0.12	0.07	92.55^{bc}	0.24	0.14	86.25^{c}	0.27	0.19	81.18^{d}
	10	0.18	0.18	82.25^{c}	0.02	0.01	98.67^{a}	0.02	0.01	99.09^{a}	0.17	0.12	88.03^{b}
Warm water +Lemon 10%	5	0.59	0.58	42.45^{e}	0.36	0.22	78.37^{d}	0.31	0.17	82.74^{c}	0.18	0.13	87.27^{c}
	10	0.12	0.12	88.43^{b}	0.12	0.07	92.95^{bc}	0.12	0.07	93.26^{b}	0.11	0.08	92.16^{a}
Warm water + Crushed date kernels 20%	5	0.34	0.33	66.86^{d}	0.31	0.19	81.38^{c}	0.29	0.16	83.76^{c}	0.16	0.11	88.95^{c}
	10	0.02	0.02	98.03^{a}	0.13	0.08	92.46^{b}	0.13	0.07	92.87^{b}	0.01	0.01	99.09^{a}
F (Treatment x Tim)				14.24			6.22			3.83			8.11

Quantify residues in pepper represented that the most successful lowering changes in Chlorpyrifo residues due to warm water plus crushed date kernels were 99.05%, followed by warm water with citric acid treatments that reduced residue by 91.03% respectively (Table 5). After exposure to the removal treatments, Chlorfenapyr residues are eliminated by 98.74 when using warm water plus sodium bicarbonate. Warm water with vinegar was the most effective method for removing Malathion residues (97.87 %) from the pepper. Warm water crushed date kernels and warm water plus citric acids had the highest removal rate for lambda cyhalothrine residues by 97.93% and 97.16% respectively from the pepper. The PF values (mg/kg) ranged from (0.53 to 0.01) Chlorpyrifos, (0.53 to 0.01) Chlorfenapyr, (0.45 to 0.02) Malathion and (0.48 to 0.02) Lambda cyhalothrine, respectively from pepper.

Table 5 Removal of pesticide residues (mg/kg) in pepper by some processing treatments.

		Chlorpyrifos			**Chlorfenapyr**			**Malathion**			**Lambada cyhalothrine**		
Processing method	**Time (min.)**	**Conc.**	**PF**	**R%**	**Conc.**	**PF**	**R%**	**Conc.**	**PF**	**R%**	**Conc.**	**PF**	**R%**
	Before processing	1.16		0.00	1.36		0.00	1.27		0.00	0.87		0.00
Warm water (40±20C)	5	0.61	0.53	47.06^{e}	0.72	0.53	46.89^{d}	0.81	0.64	35.91^{e}	0.42	0.48	52.10^{d}
	10	0.37	0.32	67.82^{d}	0.38	0.28	71.97^{c}	0.46	0.36	63.80^{d}	0.30	0.34	65.67^{d}
Warm water + Citric acids 10%	5	0.48	0.42	58.36^{e}	0.35	0.25	74.66^{c}	0.34	0.27	72.96^{c}	0.26	0.29	70.68^{c}
	10	0.10	0.09	91.03^{b}	0.12	0.09	91.25^{b}	0.12	0.09	$90. 58^{b}$	0.03	0.03	97.16^{a}
Warm water +Sodium bicarbonate 5%	5	0.42	0.36	63.70^{e}	0.53	0.39	61.19^{c}	0.57	0.45	55.22^{d}	0.24	0.27	72.94^{c}
	10	0.11	0.10	90.34^{b}	0.02	0.01	$98. 74^{a}$	0.12	0.09	90.87^{b}	0.18	0.20	79.72^{c}
Warm water +Vinegar 5%	5	0.44	0.38	62.15^{e}	0.36	0.27	73.34^{c}	0.35	0.27	72.85^{c}	0.17	0.19	80.71^{c}
	10	0.14	0.12	88.36^{bc}	0.13	0.09	90.73^{b}	0.03	0.02	97.87^{a}	0.12	0.13	86.52^{b}
Warm water +Lemon 10%	5	0.61	0.52	47.67^{e}	0.36	0.27	73.47^{c}	0.37	0.29	71.18^{c}	0.15	0.17	83.26^{c}
	10	0.12	0.10	90.08^{b}	0.11	0.08	91.62^{b}	0.12	0.09	90.02^{b}	0.11	0.13	87.10^{b}
Warm water + Crushed date kernels 20%	5	0.35	0.30	69.91^{d}	0.36	0.26	73.66^{c}	0.32	0.26	74.48^{c}	0.13	0.15	85.29^{c}
	10	0.01	0.01	99.05^{a}	0.16	0.12	88.19^{bc}	0.14	0.11	88.74^{bc}	0.02	0.02	97.93^{a}
F (Treatment x Tim)				21.41			7.76			10.09			8.09



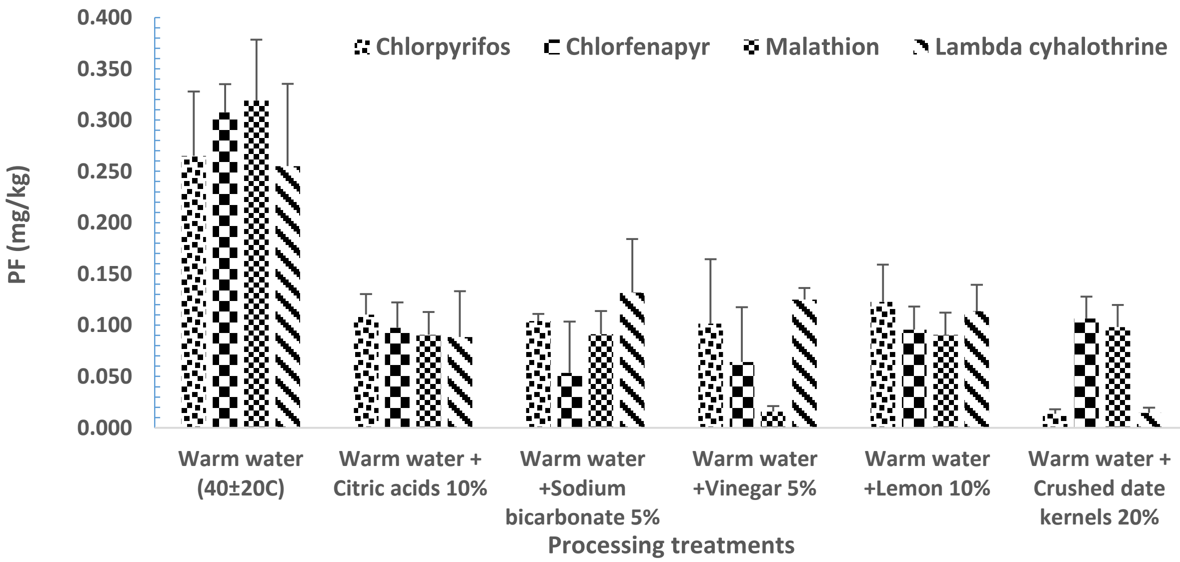


Fig 2: Processing factors (PF) of the household removal residue treatments after 10 minutes for selected vegetables and pesticides.

Pesticides are widely used for plant protection all over the world that become an unavoidable part of agriculture. However, pesticides leave residues and can cause serious health and environmental problems due to increasing and inappropriate use. At the same time, there is a lack of national plans to control these adverse effects and their impacts on human health and the environment. Therefore, removing pesticide residues seems to be very important to guarantee food quality and avoid public health risks. Tomato, eggplants, cucumber and pepper are the most often freshly consumed vegetables in Egypt, thus it is important to reduce pesticide residues that are employed during their cultivation to control pests using process procedures from these vegetables. Processing of foods can be one mechanism that substantially reduces the residues of pesticides (**Terfe et al., 2023**).Washing with water or other aqueous solutions, peeling, chopping, pickling, heat treatments, and processes such as drying, canning, fruit juice and concentrate production, malt, beer and wine production, oil production, and storage have certain effects on the presence of pesticide residues as well (**Yigit and Velioglu 2019**). The **World Health Organization (1997**) reported that washing often reduces pesticide residues, remarkably for non-systemic pesticides. However, this method has lower efficiency and is not suitable for all pesticides. Therefore, developing preferably locally available, safe and less expensive tools for removing pesticide residues is required as a preventive policy from any adverse effects of pesticide residue at the national level. The level of pesticide residues found in the analyzed samples are outlined in the above tables (2,3,4,5,) that include malathion and chlorfenapyr (as systemic pesticides) and chlorpyrifos and lambada cyhalothrine (as contact pesticides) which are commonly used for insect and mite control in tomato, eggplant, cucumber and pepper of Egypt. By employing various techniques on freshly harvested vegetable crops, there is a huge need to manage the use of pesticides and reduce their hazards and residues below the risk limit. Two times by six treatments of washing include warm water, warm water plus citric acids 10%, warm water plus sodium bicarbonate 5%, warm water plus vinegar 5% %, warm water plus lemon 10% and warm water plus crushed date kernels 20% were tested during the study to remove four pesticides residues from tomato, eggplant, cucumber and pepper.These chemicals and sorbent materials were compared to know the best one for removing the pesticide residues. Based on GCMS analysis, eggplant takes a low quantity of pesticide residues, however, cucumber takes a high quantity of pesticide residues after soaking for 30 min at the rate of 3.0 g of active ingredients per 1000 mL of water. Based on the results of removal percentage, the residues in tomato fruits were removed to the optimum by using warm water plus 20% crushed date kernels by (98.84%) Chlorpyrifos, (98.72%) Lambda cyhalothrine, respectively and by using warm water plus sodium bicarbonate solution reached (98.45 %)Chlorfenapyr and warm water plus vinegar (98.20%) Malathion respectively. Warm water plus 20% crushed date kernels removed 98.65% of Chlorpyrifos, and 98.38% Lambda cyhalothrine residue, respectively from eggplant. As for cucumbers, warm water plus vinegar was the best method to achieve the highest removal rates of Chlorfenapyr and Malathion residues by 97.46 and 98.64% respectively in eggplant. About 98.03 and 99.09% of the residues of Chlorpyrifos and Lambada cyhalothrine were eliminated from the cucumber by warm water plus 20% crushed date kernels. Conversely, warm water and vinegar eliminated 98.67% of Chlorfenapyr and 99.09% of Malathion residues from cucumbers. Adding warm water plus 20% crushed date kernels reduced Chlorpyrifos and Lambda cyhalothrine residues by 99.05% and 97.97% in pepper, warm water plus vinegar reduced Malathion residues by 97.87%, warm water with sodium bicarbonate reduced Chlorfenapyr residues by 98.74% in pepper. The efficiency of removal residue is proportional to the exposure times of washing. The processing of vegetables strongly decreases pesticide residues (**Kaushik et al., 2009**). Thus, the residue may be subjected not only to physical removal by washing or peeling but also to acid or base hydrolysis and thermal degradation to eliminate (**Chin 1991**). Soaking in warm water without any chemicals appeared the lowest efficiency in pesticide residue removal. So, It is anticipated that with warm water we should use sorbent materials such as crushed date kernels that have high efficiency in removing contact pesticides of Chlorpyrifos and Lambda cyhalothrine residues. While using reducing pH such as citric or lemon or vinegar is well efficient in moving systemic pesticides of Chlorfenapyr and Malathion that are present residue in the vegetable tissues. Hot washing and blanching are more effective than cold washing and the effectiveness may be further improved by detergent (**Geisman et al., 1975**). Hot caustic washes used in some commercial peeling operations can efficiently remove and degrade residues of hydrolyzable pesticides (**Farrow et al., 1969**). Deltamethrin has been reported to have a half-life of 9 minutes in boiling water and residues were reduced by 66 percent by the cooking of various vegetables **(Andrade et al., 2006**). Washing with water and/or detergent solution was necessary to decrease the intake of pesticide residues. (Abo-Arab 1999).Washing with water or other solutions, and peeling before consumption are shown to reduce pesticide residues in tomatoes (**Andrade et al. 2015**). Acetic acid (0.15 and 5%) and hypochlorite (1%) solutions had the greatest effect on minimizing pesticide residue contamination of tomatoes **(Rodrigues et al., 2017**). An acidic solution like citric acid, vinegar and lemon solution at a concentration of 5 and 10 percent was used to reduce the tested pesticide residues for 5 and 10 minutes. The acidic solutions of 5 and 10 percent eliminated pesticide residues while citric and ascorbic acid solutions of 5 and 10 percent eliminated pesticide residues by up to 80 percent (**Wheeler 2002**). An alkaline solution of sodium bicarbonate (NaHCO3) was used as a decontaminating agent by dipping vegetables in this solution for 5 and 10 minutes. It also has a good efficacy of removing more than 80 percent of pesticide residues. The processing factor (PF) values in Tables 2,3,4,5 & Figure 2, indicated a reduction in the selected pesticide residues due to the household process of fresh vegetables (0.67 to 0.01mg /kg). While the MRLs were (0.01 mg/kg EU/2020/1085) for Chlorpyrifos, (0.01mg/kg, EU/2012/899) for Chlorfenapyr, (0.02 mg/kg, EU/2015/399) for Malathion and (0.3 mg / kg EU/ 396/2005) for Lambda cyhalothrine respectively in fruiting vegetables. A processing factor (PF) has been used to define the maximum residue limits of pesticides in a variety of processed fruit products **(Im and Ji 2016)**. Processing factors are taken into account when verifying the compliance of residues in processed products with the MRL of agricultural commodities and refining dietary exposure intake to residues in processed products **(Scholz et al., 2017**). Moreover, the reduction of pesticides through processing is essential in decreasing the risk associated with the ingestion of pesticide residues, especially in vegetables (**Chandra et al., 2015).** So, to protect consumers' health from any levels of pesticide residues in foodstuffs and provide suitable recommendations for removing any residues and ensure the proper levels of pesticides in terms of granted authorization in different vegetables. Whereas, removing pesticide residues is becoming a major concern of food safety. Food safety can therefore partially be enhanced by employing suitable food processing techniques and appropriate storage periods, even in developing countries (**Chauhan et al., 2014**). Washing, peeling, cooking, drying, milling and industrial techniques like, baking, dairy products, fermentation, malting, etc can be used to provide a safer food culture for humans (**Padaliya et al., 2020**).

CONCLUSION

Finally, using warm water with acidic and alkaline solutions can effectively minimize the tested systemic pesticide residues of Chlorfenapyr, and Malathion and can be effectively applied in warm water plus crushed date kernels to minimize residues of contact pesticides of Chlorpyrifos and Lambda cyhalothrine by household's process from tomato, eggplants, cucumber and pepper vegetables to avoid their risks.

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