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Study on universal cleaning solution in removing blended pesticide residues in Chinese cabbage

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Food safety problems caused by pesticide residues in vegetables have become one of the top issues of public interest. In order to find an effective method of removing pesticide residues in vegetables, Chinese cabbages were processed as simulated pesticide pollution using three types of pesticides, namely; organophosphorus pesticide, organochlorine pesticide and pyrethroid pesticides. The polluted Chinese cabbages were washed using five types of cleaning solutions namely; glycyrrhiza-mung bean solution, garlic juice solution, soda-salt solution, tap water and washed-rice water. Gas chromatograghy (GC) was adopted to detect the contents of pesticide residues in the cabbages after washing them using five types of cleaning solutions. The results showed that soda-salt solution had the best removal effects on three types of pesticide residues among the five types of cleaning solutions used. And the washed- rice water had worse effects on three types of pesticide residues than tap water. Glycyrrhiza-mung bean solution had better removal effects on pyrethroid pesticide residues than tap water; and garlic juice solution had better removal effects on organochlorine pesticide residues than tap water. Although the different cleaning solutions had different removal effect on different types of pesticides; the pesticide removal efficiency of soda-salt solution was significantly higher than that of tap water; and soda-salt solution itself is a non-chemical substance and it's easily prepared; therefore, the soda-salt solution can be used as a general-purpose cleaning solution to remove mixed pesticide residues in vegetables.

Key words: pesticide residue; washed-rice water; glycyrrhiza-mung bean solution; garlic juice solution; soda-salt solution; cleaning solution.

INTRODUCTION

Pesticide residues in vegetables are toxic metabolites formed by using pesticide for a long period in vegetables farming. Most pesticides detected in vegetables are pesticide mixtures, including common types of pesticides in vegetables such as organophosphate, organochlorine and pyrethroid. Table food safety problems caused by exceeding the standard of pesticide residues in vegetables has become urgent health problems waiting for solution in China. In April 2009, a survey was carried out in which it was found that residents in Beijing, Shanghai and Guangzhou almost drank a cup of health threat "pesticide cocktail" including 5 kinds of possible carcinogenic pesticides every day (Wu, 2010), due to the mixing of pesticide residue in vegetables and fruits.

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Fantke et al. (2012) quantified health impacts and related damage costs from exposure to 133 pesticides applied in 24 European countries. Children's dietary pesticide intakes can also be measured. Riederer and Lu (2012) compared organophosphorus and pyrethroid pesticide intakes from conventional fruit, fruit juices and vegetables measured for two cohorts of children aged 3-11 years. Therefore, it is a very urgent task to develop vegetable pesticide residue cleaning solution.

However, development of various analytical methodologies can help the early detection of pesticide residue in foods (Farajzadeh and Khoshmaram, 2013; da Silva et al., 2013), there has not been much study on removal methods of pesticide residue in foods. Despite earlier reports that detergent (Zhang et al., 2008; Li et al., 2005; Liu et al., 2010) and potassium permanganate has good effect on the removal of pesticide, these are chemical substances and can cause secondary pollution of vegetables.

There were also reports that natural purification agents made using shell as raw material and processing high-temperature calcination can have better removal effects on omethoate (Guo et al., 2009). But the natural purification agent reported only has a very good effect on omethoate, whether it has a very good removal effect on other kinds of pesticide is still unclear.

Although theoretically, using comprehensive methods such as drying, washing, peeling, cooking and washing etc, may have better removal effect of the residual pesticide in vegetables as previously reported by Zhang et al. (2008); however, ordinary families are very difficult to implement these methods due to the complicated steps. It is imminent therefore, to look for a kind of general cleaning solution with good removal effects on mixed pesticides in vegetables.

At present, it is impractical to plant vegetables in large area without the use of pesticides in China. Therefore, studies on general cleaning solution with good removal effect on the main types of pesticide residues will have great practical significance. A good idea is to search for effective cleaning solutions from ingredients or Chinese herbal medicine. Many studies reported garlic has detoxification effects (Su et al., 2003) and glycyrrhiza-mung bean solution also has a detoxifying effect (Zhou, 2009).

Inspired by these studies, Chinese cabbages polluted by three types of mixed pesticide such as organophosphorus, organochlorine and pyrethroid were cleaned by five types of ingredients cleaning solutions such as glycyrrhiza-mung bean solution, garlic juice solution, soda-salt solution, tap water and washed-rice water. Gas chromatography (GC) was used to detect the removal effect of these five cleaning solutions.

The purpose of this study is to develop a high quality cleaning solution with good removal effect on three types of pesticide residues in vegetables; and to explore feasibility and the removal effect of pesticide residues in vegetable using edible materials.

MATERIALS AND METHODS

Reagents

The main extraction reagents used includes acetonitrile, acetone, sodium chloride and hexane (steamed) etc. The ingredients used include sodium carbonate, licorice，mung bean, garlic, washed-rice water, Chinese cabbage. And the main pesticides used include cyhalothrin (Nuopuxin) with 2.5% effective components, dimethoate with 40% effective ingredients and dicofol with 20% effective ingredient.

Instruments and equipments

The main instruments and equipments used include gas chromatograph (Agilent GC-6890), pressure blowing concentrator (HGC-36A), digital oscillator (IKAKS501), solid phase extraction automation workstation (SPE12), Philips tissue triturator and refrigerated high-speed centrifugator (SIGMA) among others.

Preparation of cleaning solution

The method of Glycyrrhiza-mung bean solution is described here. The licorice 30 g and mung bean 60 g were weighed. And 60 g of mung bean was poured into a soy-milk grinder in which appropriate amount of water was added and the mung bean was pulverized. Then the ground mung bean was poured into the pot and 30 g licorice and 3L of water were added and boiled for 15 m. The solutions were filtered and the supernatant collected.

For the soda-salt solution (5%), 10 g of edible soda and 10 g of salt were added into 2L of water successively. And the solution was stirred fully until completely dissolved. For the washed-rice water solution, after 500 g rice was rinsed for 2 times, 2 L of the cleaning liquid was collected. As for garlic juice solution, after mashing the peeled garlic of 100 g, 2 L of water was added to the mashed garlic and soaked for 15 m. The residue was filtered and the supernatant was collected.

Method of pesticide pollution in Chinese cabbage

Firstly, 3 kinds of pesticide mixture were prepared. Then 4 L of water was poured into the pot, 3 kinds of pesticides, namely cyhalothrin, dimethoate and dicofol were sequentially added, including the prepared pesticide mixture. All pesticides were diluted 1600 times, the mixture was then ready for use.

Secondly, the Chinese cabbage of 1000 g bought from the supermarket was washed with tap water and dried surface water with absorbent paper. Then the cabbage was soaked into the mixture of 3 pesticides for 10 m and stored at room temperature in a dark room for 12 h.

Method of cleaning samples and extraction of pesticide residue

The pesticide contaminated Chinese cabbage was divided into 6 parts, of which 5 parts each was soaked with tap water, washed-rice water; glycyrrhiza-mung bean solution; garlic juice solution; soda-salt solution for 10 m respectively, then rinsed off with running tap water for 1 m.

The washed Chinese cabbages were dried the surface water with

absorbent paper and marked, respectively. The control group was not soaked with running tap water. Method for the extraction of pesticide residues was according to the GB /T 5009.145-2003 (GB /T5009, 2003), each treatment was replicated 4 times.

The effect of removing pesticide residues among the five kinds of cleaning solutions

One-way ANOVA was used to test differences between multiple means of five kinds of cleaning solutions in removing pesticide residues. Based on the F test significance, the least significance difference (LSD) method was used for multiple comparisons of multiple means. The effectiveness of various cleaning solution in removing pesticide residues was based on the comparison with the control group. The statistical significances of various cleaning solutions in removing pesticide residue were compared with tap water.

Pesticide residue detection conditions using GC

Detection conditions of pyrethroid pesticide and organochlorine pesticide:
Chromatographic column: HP-5 30.0 m × 320 × 0.25 µm;
Column air flow: 3.0 ml/m, N2 60 ml/m;
Chromatographic column temperature: 190°C (2m), 8°C/m; 270°C (4);
The injector temperature: 280°C;
The inject mode: split, split ratio 10:1;
The detector and temperature: ECD, 300°C;
Volume of sample: 1µl.

Detection conditions of organophosphorus pesticides:
The chromatographic column: DB-1701P 30.0 m × 320 µm × 0.25 µm;
Column air flow: 3.2 ml/m, N2 60 ml/m; H2: 75 ml/m; Air: 100 ml/m;
The chromatographic column temperature: 80°C 20°C/m 190°C (10 m); 30°C/m 220°C (2 m) 4°C/m 250°C (5 m);
The injector temperature: 220°C;
The inject mode: splitless;
The detector and temperature: FPD 250°C; volume of sample: 1 µl

Removal rates of pesticide residues

Removal rates = (1-pesticide residue of Chinese cabbage after cleaning solutions, cleaning/ corresponding control) ×100%.

RESULTS

The effect of comparison of five cleaning solutions in removing three kinds of pesticides with the controls

As shown in Table 1, after the cabbage had been cleaned by the 5 kinds of cleaning solutions, residues of dimethoate pesticide were in 21.21-43.76 mg/kg. Except for glycyrrhiza-mung bean solution and washed-rice water achieving significant differences (P<0.05), and the effect of the other cleaning solutions, soda-salt solution, tap water and garlic juice solution reached extremely significant differences (P<0.01) compared with that of the control.

These results showed that the 5 cleaning solutions have some cleaning effect of dimethoate. And for the cleaning effect of dicofol, only soda-salt solution and garlic juice solution reached extremely significant differences (P<0.01) compared with that of the control, while the cleaning effects of 3 kinds of cleaning solutions, glycyrrhiza-mung bean solution, tap water and washed-rice water had no differences with that of the control. These results indicated these three kinds of cleaning solution have no effect on the removal of dicofol.

For the cleaning effect of cypermethrin, the removal effect of 5 kinds of cleaning soltutions reached an extreme difference compared with that of the control. These results showed that the 5 kinds of cleaning solutions have a certain effect on the removal of cyhalothrin. Considering that ordinary families commonly use tap water to wash vegetables, it is more significant that taking tap water as the control to measure the cleaning effect of 4 kinds of cleaning solutions.

The effect of comparison of four cleaning solutions removing dimethoate pesticides compared with tap water

As shown in Table 2, the pesticide residues removal effects of 3 kinds of cleaning solutions such as washed-rice water, glycyrrhiza-mung bean solution and soda-salt solution reached an extremely significant difference (P<0.01).

The soda-salt solution had the best positive removal effect of dimethoate, while the washed-rice water and glycyrrhiza-mung bean solution had a significant negative effect, namely the washed- rice water and glycyrrhiza-mung bean solution can enrich more the amount of dimethoate residues than tap water.

The garlic juice solution is not different from tap water in removing residual effect. The good and bad effect of removal of dimethoate pesticide can be expressed as soda-salt solution > garlic juice solution = tap water > washed- rice water = glycyrrhiza-mung bean solution.

The effect of comparison of four cleaning solutions removing dicofol pesticides compared with tap water

As shown in Table 3, soda-salt solution and garlic juice solution have the significant removal effect of dicofol compared with the tap water. While the glycyrrhiza-mung bean solution and washed- rice water have the significantly negative removal effect of dicofol, indicating that two kinds of cleaning solutions can enrich more dicofol residue than tap water. The good and bad effect of removal of dicofol pesticide can be expressed as: soda-salt solution = garlic juice solution > tap water > washed-rice water = glycyrrhiza-mung bean solution.

Table 1. Pesticide residues after different cleaning solutions cleaning Chinese cabbage (mg/kg).

Cleaning solutions	Dimethoate（mg/kg）	Dicofol（mg/kg）	Cypermethrin（mg/kg）
Soda-salt solution	21.21±1.08**	7.03±0.20**	0.99±0.08**
Glycyrrhiza-mung bean solution	39.11±2.08*	10.90±0.48	1.44±0.07**
Tap water	31.41±1.21**	9.62±0.32	1.78±0.05**
Garlic juice solution	27.79±0.22**	7.43±0.50**	1.63±0.10**
Washing rice water	39.30±0.58*	10.88±0.51	2.11±0.04**
Control CK	43.76±1.94	10.60±0.28	2.39±0.02

Note: The pesticide residue of control is the one in Chinese cabbage which is not cleaned by any cleaning solution; " * " and " * * " represent the average values of treatment reaching significant level and extremely significant level compared with control, respectively.

Table 2. Removal effects of dimethoate pesticide residues after four kinds of cleaning solutions washing Chinese cabbage compared with tap water.

Cleaning solutions	Residues (mg/kg)	Significant differences	Removal rates (%)
Washing rice water	39.3	B	-25.10
Glycyrrhiza-mung bean solution	39.11	B	-24.50
Tap water CK	31.41	C	
Garlic juice solution	27.79	C	11.50
Soda-salt solution	21.21	D	32.50

Note: Capital letter represents the average values of treatment reaching extremely significant level compared with tap water. The symbol "-" indicates pesticide residues in Chinese cabbage treated by cleaning solution are higher than that in Chinese cabbage treated by tap water.

Table 3. Removal effects of dicofol residues on Chinese cabbage after five types of cleaning solutions washing Chinese cabbage (LSD method) (mg/kg)

Cleaning solutions	Residues	Significant differences	Removal rates
Glycyrrhiza-mung bean solution	10.9	A	-13.30%
Washing rice water	10.88	A	-13.10%
Tap water CK	9.62	B	0
Garlic juice solution	7.43	C	22.80%
Soda-salt solution	7.03	C	26.90%

Note: Capital letter represents the average values of treatment reaching extremely significant level compared with tap water. The symbol "-" indicates pesticide residues in Chinese cabbage treated by cleaning solution are higher than that in Chinese cabbage treated by tap water.

The effect of comparison of four cleaning solutions removing cypermethrin pesticides compared with tap water

As shown in Table 4, glycyrrhiza-mung bean solution and soda-salt solution had significant effect of removal of cypermethrin compared with tap water, while the washed-rice water had a very significantly negative removal effect. Garlic juice solution and tap water were no different in removal of cypermethrin residue.The good and bad effect of removal cyhalothrin pesticide can be expressed as: soda-salt solution> glycyrrhiza-mung bean solution > garlic juice solution= tap water > washed- rice water.

The effect of comparison of four cleaning solutions removing 3 kinds of pesticides residues

Compared with tap water, removal of pesticide residue results of four kinds of cleaning solutions were summarized in Table 5. In summary, pesticide removal effects of soda-salt solution are better than tap water in the removal of three kinds of pesticides, while pesticide removal effects of washed- rice water are not better than tap water. The pesticide removal effects of garlic juice solution are as good as tap water. As for dimethoate and dicofol, the pesticide removal effects of glycyrrhiza-mung bean solution were worse than tap water, while for cypermethrin, glycyrrhiza-mung bean solution had better

Table 4. Removal effects of cyfloxylate residues on Chinese cabbage after five types of cleaning solutions washing Chinese cabbage (LSD method) (mg/kg).

Cleaning solutions	Residues	Significant differences	Removal rates (%)
Wahing solutions	2.11	B	-18.50
Tap water CK	1.78	C	0
Garlic juice solution	1.63	CD	8.40
Glycyrrhiza-mung bean solution	1.44	D	19.10
Soda-salt solution	0.99	E	44.40

Note: Capital letter represents the average values of treatment reaching extremely significant level compared with tap water. The symbol "-" indicates pesticide residues in Chinese cabbage treated by cleaning solution are higher than that in Chinese cabbage treated by tap water.

Table 5. The removal effect summary of four kinds of cleaning solutions removing three kinds of pesticide residues in Chinese cabbage (tap water as control).

Cleaning solutions	Dimethoate	Cypermethrin	Dicofol
Tap water			
Garlic juice solution	=	=	+
Glycyrrhiza-mung bean solution	−	+	−
Soda-salt solution	+	+	+
Washing rice water	−	−	−

Note: the symbols "+ , =,− " indicate removal effects treated by cleaning solutions are better or the same as or inferior to that treated by tap water, respectively.

removal effect than tap water.

DISCUSSION

In summary, the main conclusions of this study are that:
(1) Soda-salt solution can be used as a universal cleaning solution to remove mixed pesticide residues in vegetables;
(2) Glycyrrhiza-mung bean solution and garlic juice solution can be used as cleaning solution for removing certain kind of pesticide residues;
(3) Washed- rice water is not as good as tap water in removing pesticide residues. Now the conclusions above are discussed respectively below:

Soda-salt solution can be used as a universal cleaning solution to remove mixed pesticide residues in vegetables

The most important finding of this study is screening general cleaning solution successfully to remove pesticide residues in vegetables. In China, the main types of pesticide residues are organophosphorus and organochlorine and pyrethroid etc (Sun, 2005). Some kind of vegetable usually contains several types of pesticide, and usually some kind of cleaning solution such as glycyrrhiza-mung bean solution (removal of cyhalothrin) or garlic juice solution (removal of dicofol) only has a good effect for certain types of pesticide. Liu et al. (2002) reported that 5% salt solution and 5% alkali solution has certain removal effect on organic phosphorus. And 5% salt solution has better removal effect on organic phosphorus than 5% alkali solution.

Based on this, soda-salt solution with 5% salt and soda was prepared in this experiment. The experimental results showed that soda-salt solution had better removal effects of three kinds of pesticide residues than tap water. In addition, washing vegetables with soda-salt solution will not cause second pollution due to the non chemical cleaning agent such as detergent or potassium permanganate; and for ordinary families, soda-salt solution preparation is very simple. Therefore, soda-salt solution can be used as a general cleaning solution to remove mixed pesticide residues in vegetables and is worthy to be popularized.

Removal of pesticide rates of soda-salt solution

From the experimental results, soda-salt solution removal pesticide rates on dimethoate, dicofol and cyhalothrin were 32.5%, 26.9% and 44.4%, respectively. The removal pesticide rates of soda-salt solution seem not high. This is mainly because more polluted cabbage samples and less cleaning solution in the experiment and the background concentration of Chinese cabbage

already was much higher than the national standard, so the removal pesticide rates of soda-salt solution is not high. However, this does not affect relative results of the cleaning solutions removing pesticide residues. Experiments of cleaning solutions screening were conducted under the condition of the same concentration of pesticide residue, and the experimental results were analyzed with one-way ANOVA, so the results are scientific and credible.

More so, if soda-salt solution was used to remove the edible vegetable pesticide residues, no doubt removal rate of pesticide residue would rise substantially due to background concentrations in the edible vegetable far below the experimental control background concentration.

Glycyrrhiza-mung bean solution and garlic juice solution can be used as cleaning solution for removing certain kind of pesticide residues

The main innovation of this study is the use of ingredients of Chinese herbal medicine as cleaning solutions of pesticide residue such as glycyrrhiza-mung bean solution and garlic juice solution, which was not reported in the previous studies. Previous reports that glycyrrhiza-mung bean solution (Jin, 2001) and garlic juice solution have detoxification effects (Su et al., 2003). Inspired by this report, glycyrrhiza-mung bean solution and garlic juice solution were used as cleaning solution of pesticide residue in this study.

The experimental results showed that removing cyhalothrin residues using glycyrrhiza-mung bean solution was significantly better than that of tap water, and removing chlorine chlorfenetholis using garlic juice solution was significantly superior to that of tap water. In short, using glycyrrhiza-mung bean solution or garlic juice solution as cleaning solution is better than tap water in removing certain kinds of pesticide residues. This indicates glycyrrhiza-mung bean solution and garlic juice solution can be used as cleaning solution for removing certain kinds of pesticide residues.

Washed- rice water is not as good as tap water in removing pesticide residues

Compared with the control shown in Table 1, although the washed- rice water partly has removal effect in removing residual pesticide of dimethoate and cyhalothrin; as previously reported, the washed- rice water can remove the pesticide residue on vegetable surface in varying degrees (Xue,1994), since the washed-rice water contains starch and has certain adsorption capacity of pesticides. Washed- rice water is alkaline and has certain dissolving ability for pesticide residues.

However, washed- rice water is not as good as tap water in removing three kinds of pesticide residues in this study. This might be because the starch content of washed- rice water was not high enough; or higher pesticide residues in rice resulted in higher residual pesticides in washed- rice water. Therefore, the experimental results pointed out unscientific practice for some families insisting to use washed- rice water removing pesticide residue in vegetables and has important practical significance.

REFERENCES

da Silva SJ, de Castro RC, de Albuquerque AG, Lima CG, Lima LK, Milhome MA, do Nascimento RF (2013). Evaluation of an analytical methodology using QuEChERS and GC-SQ/MS for the investigation of the level of pesticide residues in Brazilian melons. Chem. 141(3):2675-81.

Fantke P, Friedrich R, Jolliet O (2012). Health impact and damage cost assessment of pesticides in Europe. Environ. Int. 49:9-17.

Farajzadeh MA, Khoshmaram L (2013). Air-assisted liquid-liquid microextraction-gas chromatography-flame ionisation detection: A fast and simple method for the assessment of triazole pesticides residues in surface water, cucumber, tomato and grape juices samples. Food Chem. 141(3):1881-1887.

GB /T5009. 145- 2003. Methods of food hygienic analysis--Physical and chemical section-General principles (Second)[S](in Chinese). Beijing: China Standard Press, 2003.

Guo M, Qin BX, Dong LJ (2009). The exploitation and preparation of natural purificant to pesticides residues in vegetables. Environmental Science and Management. 34(11):79-81.

Jin Y.S (2001). Detoxificationin traditional Chinese Medicine. J. Beneficial Readings Drug Information & Medical Advices. 3:47.

Li L, Jiang SR, Liu FM (2005). Methods for Removing Pesticide Residues from Vegetables (in Chinese). Chin. J. Pesticides. 44(8):347-351.

Liu WS, Zhu Z, Zhang XM (2010). Study on removing organophosphorus pesticide residues from vegetable with four rinsing method (in Chinese). Modern Food Science and Technology. 26, (12):1395-1398.

Liu Y, Wang G, Zhang XH (2002). Method for removing pesticide residues in vegetables (in Chinese). Chin. J. Public Health Eng. 1(2):101-103.

Riederer AM, Lu C ((2012). Measured versus simulated dietary pesticide intakes in children. Food Addit Contam Part A Chem Anal Control Expo Risk Assess. 29(12):1922-37.

Su MQ, Yang BC, Cheng MH (2003). Advance in researches of the efficacy and synthetic utilization of garlic (in Chinese). Acta Agriculturae Boreali-Occidentalis Scinica. 12(4):151-156.

Sun XD (2005). Damage, type and reason of over-standard for pesticide reside in vegetable and its control measure (in Chinese). Guizhou Agricultural Science. 33(6):99-100.

Wu M (2010). Over standard pesticide: Land mine embedded in dinning table?. Ecological economy. 7(227):22-27.

Xue KB (1994). The role of washed- rice water (in Chinese). Hebei Agricultural Science and Technology. 1:37.

Zhang S, Xu MY, Cao K (2008). Pesticide residues in vegetables home-removal technology research (in Chinese). Journal of Anhui Science and Technology University. 22(5):6-9.

Zhou SF (2009). Licorice mung bean soup in the treatment of Aconitum kusnezoffii poisoning. JETCM. 18(3):382-383.