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Reduction of Heavy Metals Content in Contaminated Vegetables due to the Post-harvest Treatments

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HEAVY metals highly contaminated samples of potato, tomato, and cucumber were used to study the effects of washing, shelling and soaking (in vinegar 5% for 5 min.) on heavy metals reduction. Heavy metal levels were determined for untreated and treated samples using Atomic Absorption Spectrophotometer and the reduction ratios of heavy metal levels were calculated. The vinegar (acetic acid) effect could be due to its effect on the pH value that influences the solution chemistry of the heavy metals such as hydrolysis, complexation by organic and inorganic ligands, redox reactions, precipitation and the adsorption availability of the heavy metals. For potato, the results revealed that washing and shelling have removed high ratio of heavy metals, however the reduction was not sufficient to decrease the levels of Pb and Cd to be within the MRLs. While soaking in vinegar in addition to washing and shelling of potato has led to a significant decrease in Pb and Cd concentrations being lower than the MRLs. For tomato and cucumber, the Cd element was not detected after washing of both vegetable kinds. Lead level in tomato was significantly decreased to the MRLs values when washed and shelled, while Pb level in cucumber was still higher than MRLs.

Keywords: Vegetables, Washing, Soaking, Heavy metals, Household processing.

Introduction

Vegetables are important food for human health since they have beneficial role in body growth. The main functional constituents of vegetables are protein, carbohydrates, vitamins and minerals. Also, the phytochemicals, such as antioxidant, are found in most vegetables [1]. Although vegetables have several health benefits, but they may contain some chemical hazards especially heavy metals [2].

The main sources for vegetables contamination by heavy metals are contaminated soil, polluted air, pesticides, fertilizers and irrigation by wastewater. Heavy metals can be taken up by vegetables through adsorption from a contaminated soil or by surface deposition from a polluted air [3].

Consumption of vegetables contaminated by heavy metals may cause gastrointestinal cancer [4], pancreas cancer [5], hypertension [6], liver dysfunction [7], lung fibrosis [8], and kidney diseases [9]. As vegetables are mostly consumed after household treatments, so it is necessary to understand the effect of those treatments on the levels of heavy metals. In this respect, Sattar et al. [10] studied the levels of Cd, Hg, As, Cr and Pb in vegetables before and after washing by household chemicals. They found that washing by acetic acid 10% was more effective for heavy metals removal than tap water, acetic acid 5%, sodium chloride 5% and sodium chloride 10%.

Suruchi and Jilani [11] studied the effect of washing by de-ionized water on heavy metals removal from vegetables (spinach, methi and coriander) collected from Agra city, India. The reduction ratios of Pb were 21, 14 and 11(%) for spinach, methi and coriander, respectively. Meanwhile, reduction ratios of Cd were 21, 13 and 31(%) for spinach, methi and coriander, respectively.

In addition, Sattar et al. [12] studied the effect of washing by tap water, radish solution (4 or 8 %) and ginger solution (4 or 8 %) on the removal of heavy metals (Ar, Cd, Cr and Pb) in some vegetables (cauliflower, spinach, okra and brinja). They disclosed that washing of vegetables by ginger solution (8%) had the highest removal for heavy metals than the other methods. Therefore, the aim of this study was to investigate the effect

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of household processing; including washing, shelling, and soaking in vinegar on heavy metal levels in highly contaminated vegetables (potato, tomato and cucumber) of our previous study [2].

Experimental

Materials and methods

Household processing for vegetables.

Washing by tap water and soaking in vinegar solution (5%) for 5 min. were applied to the whole fruits of potato, tomato, and cucumber. However, shelling was only applied to potato. Heavy metals concentrations were determined before and after the tested treatments, and ratios of reduction were calculated.

Heavy metals analysis

Five grams of a vegetable sample were accurately weighed and dried in an oven at 105°C, then ashed in a muffle furnace at 550° C. The ash was dissolved using 1 ml HCl conc. then transferred by de-ionized water to complete the volume of 25 ml [13]. The ash suspension was filtered through an ashless filter paper Whatman No. 42 then determined by Atomic Absorption Spectrophotometer (Agilent Technologies 200 Series AA) at the Central Laboratory, National Research Centre. The determination condition such as preparation of standard solutions, specific wave length for the metals, slit width, detection limits and calculation of metal concentration were applied according to Abdel-Rahman et al. [2].

Statistical analysis

Results were subjected to one-way analysis of variance (ANOVA) of the general liner model (GLM) using SAS [14] statistical package. The results were the average of three replicates ($p \leq 0.05$).

Results and Discussion

The levels of Pb in all untreated vegetables were above the maximum residue limits (MRLs) according to European Commission [15] as shown in Fig. 1. The level of Cd was above MRLs of European Commission [16] only in untreated potato. Meanwhile, concentrations of Cu and Ni in all untreated vegetables were below MRLs of Codex [17] and WHO [18], respectively. Chromium was only detected in cucumber and was less than MRLs set by WHO/FAO [19].

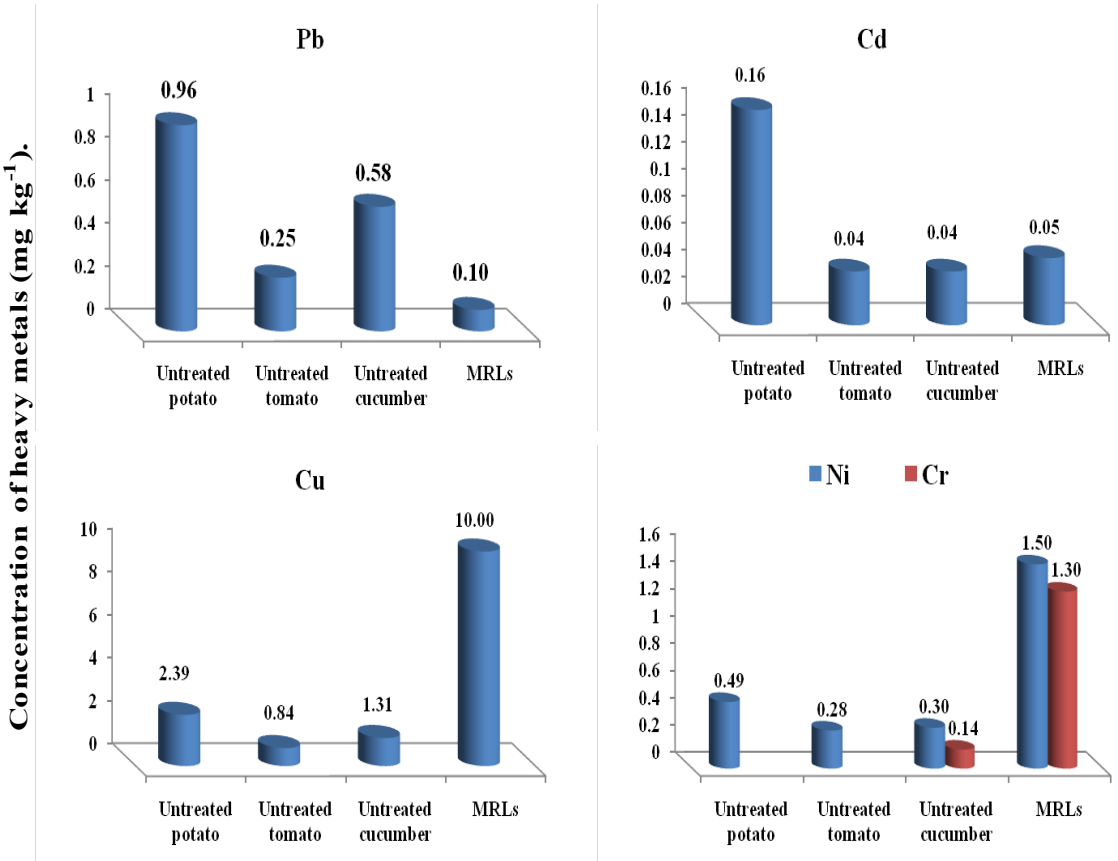

Fig. 1. Concentrations of heavy metals (mg kg^{-1}) in untreated vegetables as compare with MRLs.

The effect of washing, shelling and soaking (in vinegar 5% for 5 min.) on heavy metals removal in potato samples are summarized in Table 1. The results revealed that heavy metals of washed potato were decreased by 46, 38, 31 and 53 (%) for Pb, Cd, Cu and Ni, respectively with significant differences between untreated and washed samples. The washing process was more effective on Ni level in potato.

Shelling of potato following the washing process gave a synergetic effect in the reduction effect on Pb, Cd, Cu and Ni by 84, 63, 46 and 69 (%), respectively. So, the shelling process increased the reduction ratios of heavy metals by 38, 25, 15 and 16 (%) for Pb, Cd, Cu and Ni, respectively as compared with washing process. The shelling process was more effective on Pb level in potato samples which may be return to the Pb accumulation in potato shells as direct contact with the agriculture soil [20]. The shelling process after washing was not sufficient for the reduction of Pb and Cd levels to be lower than MRLs. Significant differences were observed between heavy metals concentrations in shelled and unshelled potato samples except for Cd.

Soaking process (in vinegar for 5 min) as third process after washing and shelling increased the reduction ratios of heavy metals from 84 to 92 (%), from 63 to 81 (%), from 46 to 56 (%) and from 69 to 84 (%) for Pb, Cd, Cu and Ni, respectively. This may be return to acetic acid (vinegar) as a chelating agent for the studied heavy metals [21]. The soaking process was more effective on the reduction ratio of Cd (18%) as compare to shelled and washed potato samples, while, the reduction ratios of Pb, Cu and Ni were 8, 10 and 15%, respectively. The levels of Pb and Cd of soaked potato samples were below MRLs. No significant differences were observed between heavy metals concentrations before and after soaking except for Cu.

Regarding the effect of household processing on heavy metals residues in tomato, the results were illustrated in Table 2. It was found that the concentrations of Pb, Cd, Cu and Ni were decreased by 60, 100, 43 and 57 (%), respectively due to the washing process with high significant differences between concentrations of heavy metals in untreated and washed samples. Contamination of tomato samples by Cd may be attributed to surface

TABLE 1. Effect of household processing on heavy metals levels in potato samples.

Treatment	Heavy metals ($mgkg^{-1}$) in potato							
	Pb	Red.* (%)	Cd	Red. (%)	Cu	Red. (%)	Ni	Red. (%)
Untreated	$0.96^{a} \pm 0.03$	0.0	$0.16^{a} \pm 0.02$	0.0	$2.39^{a} \pm 0.05$	0.0	$0.49^{a} \pm 0.03$	0.0
Washing	$0.52^{b} \pm 0.02$	46	$0.10^{b} \pm 0.01$	38	$1.64^{b} \pm 0.04$	31	$0.23^{b} \pm 0.02$	53
Washing and shelling	$0.15^{c} \pm 0.01$	84	$0.06^{bc} \pm 0.01$	63	$1.28^{c} \pm 0.03$	46	$0.15^{c} \pm 0.01$	69
Washing, shelling and soaking	$0.08^{c} \pm 0.01$	92	$0.03^{c} \pm 0.01$	81	$1.06^{d} \pm 0.03$	56	$0.08^{c} \pm 0.01$	84
LSD	0.08		0.05		0.15		0.08	

*Red.: Reduction

Means followed by different subscripts within column are significantly different at the 5% level.

TABLE 2. Effect of household processing on heavy metals levels in tomato samples.

Treatment	Heavy metals ($mgkg^{-1}$) in tomato							
	Pb	Red.* (%)	Cd	Red. (%)	Cu	Red. (%)	Ni	Red. (%)
Untreated	$0.25^{a} \pm 0.03$	0.0	$0.04^{a} \pm 0.01$	0.0	$0.84^{a} \pm 0.04$	0.0	$0.28^{a} \pm 0.02$	0.0
Washing	$0.10^{b} \pm 0.01$	60	<d.l	100	$0.48^{b} \pm 0.03$	43	$0.12^{b} \pm 0.01$	57
Washing and soaking	$0.04^{b} \pm 0.01$	84	<d.l	100	$0.22^{c} \pm 0.02$	74	$0.03^{c} \pm 0.01$	89
LSD	0.09		0.03		0.14		0.06	

*Red.: Reduction <d.l.: below the detection limit.
Means followed by different subscripts within column are significantly different at the 5% level.

deposition from polluted air [3]. So, Cd was not detected in tomato samples after washing process. Meanwhile, Pb in washed tomato samples was equal to MRLs as 0.1 mg kg^{-1} [15].

Reduction ratios of heavy metals in tomato samples were increased after soaking (in vinegar for 5 min) as 84, 74 and 89% for Pb, Cu and Ni, respectively. Soaking, as a second process, had an additional effect on the reduction of Pb, Cu and Ni as 24, 31 and 32 (%), respectively. Interestingly, the Pb level of tomato samples after soaking process has been decreased to be lower than MRLs. As well as, significant differences were observed in the concentrations of Cu and Ni between the washed and soaked samples of tomato, however no differences for Pb concentrations were observed between the two processes.

Concerning the cucumber samples, it can be noticed from the result in Table 3 that the levels of Pb, Cd, Cu, Ni and Cr in washed samples were decreased by 79, 100, 63, 30 and 43(%), respectively with significant differences between untreated and washed cucumber. Soaking of washed cucumber in vinegar increased the reduction ratios of Pb, Cu, Ni and Cr as 81, 71, 53 and 57 (%), respectively. So, the additional effects of soaking process on the reduction ratios of Pb, Cu, Ni and Cr were 3, 8, 23 and 14 (%), respectively with no significant differences between its levels in washed and soaked cucumber except for Cu. Levels of Pb in washed and soaked cucumber were slightly over the MRLs, while Cd was not detected after washing process.

Cucumber contains higher levels of biopolymers (such as cellulose, hemicellulose and lignin) than tomato and potato. These biopolymers have many functional groups (carboxyl, hydroxyl, amino, phosphate, and carbonyl) which can act as binding sites for heavy metals [22]. This explains the decrease of total reduction ratios of Pb and Ni in cucumber samples as compared with potato and tomato samples. Also, Cr was only detected in cucumber samples before and after treatments. Meanwhile, Cr was not detected in untreated potato and tomato samples as previously mentioned in our previous study [2]. On the other hand, total reduction ratio of Cu in potato samples was lower than in tomato and cucumber samples, and this may be due to the high levels of combined Cu with potato tissues as naturally [23].

Washing as a practice is easy and effective in most household treatments for vegetables before eating [24]. As the common source of contamination by heavy metals may be attributed to aerial deposition and adhere to vegetables. So, the washing process by water mechanically removes the deposited particles from the vegetable surface [25-27]. Also, Fernandez et al. [28] reported that metals from anthropogenic sources are mainly found in a water soluble form. So, the significant differences between heavy metal concentrations in washed and untreated vegetables suggest that heavy

TABLE 3. Effect of household processing on heavy metals levels in cucumber samples.

Treatment	Heavy metals ($mgkg^{-1}$) in cucumber									
	Pb	Red.* (%)	Cd	Red. (%)	Cu	Red. (%)	Ni	Red. (%)	Cr	Red. (%)
Untreated	$0.58^{a} \pm 0.03$	0.0	$0.04^{a} \pm 0.01$	0.0	$1.31^{a} \pm 0.02$	0.0	$0.30^{a} \pm 0.03$	0.0	$0.14^{a} \pm 0.01$	0.0
Washing	$0.12^{b} \pm 0.01$	79	<d.l	100	$0.48^{b} \pm 0.02$	63	$0.21^{b} \pm 0.01$	30	$0.08^{b} \pm 0.01$	43
Washing and soaking	$0.11^{b} \pm 0.01$	81	<d.l	100	$0.38^{c} \pm 0.01$	71	$0.14^{b} \pm 0.01$	53	$0.06^{b} \pm 0.01$	57
LSD	0.09		0.03		0.08		0.09		0.05	

*Red.: Reduction <d.l. : below the detection limit.

Means followed by different subscripts within column are significantly different at the 5% level.

metals can reach the studied vegetables by aerial deposition and dissolve in water. These results are in agreement with those obtained by Sing [29] who reported that, about 75 - 100% of Pb and Cd and 27 - 55% of Cu were reduced, when the vegetable samples were washed by a clean tap water.

Also, the reduction of heavy metals in vegetables by vinegar (acetic acid) could be due to the change of pH value. The pH value of a solution influences the solution chemistry of the heavy metals such as hydrolysis, complexation by organic and inorganic ligands, redox reactions, precipitation, the speciation and the adsorption availability of the heavy metals [30].

Conclusion

The levels of Cu, Ni and Cr in untreated vegetables were below the maximum residue limits (MRLs). Meanwhile, the Pb levels in all untreated vegetables were above the MRLs and the level of Cd was higher than the MRLs only in untreated potato. The highest ratios of heavy metals reduction in vegetables were achieved by the washing process. The heavy metals in potato were decreased by 46, 38, 31 and 53 (%) for Pb, Cd, Cu and Ni, respectively and by 60, 100, 43 and 57 (%) as the same order in tomato. Also, the ratios of heavy metals reduction in cucumber after washing process were 79, 100, 63, 30 and 43 (%) for Pb, Cd, Cu, Ni and Cr, respectively. The potato shelling as a second process after washing was not satisfied to decrease the levels of Pb and Cd to MRLs, but their levels were below MRLs after soaking as the third process. Level of Pb in tomato was equal to MRLs after washing and was below MRLs after soaking. Meanwhile, level of Pb in cucumber was slightly over the MRLs after washing and soaking processes. Finally, levels of Cd in tomato and cucumber were not detected after the washing process.

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خفض محتوى العناصر المعدنية الثقيلة فى الخضروات الملوثة خلال معاملات ما بعد الحصاد

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فى الدراسة الحالية تم إستخدام عينات من البطاطس والطماطم والخيار ذات مستوى عال من التلوث بالعناصر المعدنية الثقيلة لدراسة تأثير معاملات الغسيل والتقشير والنقع (فى خل ٥ ٪ لمدة ٥ دقائق) على تقليل مستوى العناصر المعدنية الثقيلة فى الخضروات. وقد تم قياس تركيز العناصر المعدنية الثقيلة فى العينات قبل وبعد المعاملات باستخدام جهاز الإمتصاص الذرى، ثم تم حساب نسب الإختزال فى التركيزات المبدئية للعناصر نتيجة تأثير المعاملات المدروسة. ويعمل الخل (حامض الخليك) على تغيير الأس الهيدروجينى للوسط والذى بدوره قد يؤثر على الخصائص الكيميائية لذوبان العناصر المعدنية الثقيلة مثل خاصية التحلل المائى، خاصية تكوين معقدات مع الروابط العضوية والغير عضوية، خاصية الترسيب، تفاعلات الأكسدة والإختزال وكذلك خاصية إتاحية الإدمصاص للعناصر المعدنية الثقيلة. بالنسبة للبطاطس، فقد أظهرت النتائج أن عمليات الغسيل والتقشير قد أدت إلى إزالة نسبة كبيرة من العناصر المعدنية الثقيلة ولكنها لم تكفى لخفض مستويات الرصاص والكادميوم إلى ما دون الحدود القصوى المسموح بها. بينما أدت عملية نقع البطاطس المغسولة والمقشرة فى الخل إلى خفض مستويات كلا من الرصاص والكادميوم إلى ما دون الحدود القصوى المسموح بها. أما بالنسبة للطماطم والخيار، فقد لوحظ عدم ظهور عنصر الكادميوم بعد عملية الغسيل. ومن الجدير بالذكر أن عمليات الغسيل والنقع قد أدت إلى خفض مستويات الرصاص فى الطماطم إلى ما دون الحدود المسموح بها، بينما لم تنجح فى خفض نسبته فى الخيار إلى الحدود الآمنه.