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Confiscation of heavy metal residues in cauliflower using washing solutions

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RESEARCH ARTICLE

Abstract

The heavy metals are a major category of globally distributed pollutants of soil and water by domestic sewage and industrial discharge. The irrigation with waste water is recognised to contribute potentially the heavy metal contents to the soil and ultimately in vegetables. The vegetables play a very vital role in maintaining the nutritional status of humans. The production of food and maintaining its quality is the foremost matter throughout the world. Heavy metals have the tendency to accumulate in cauliflower through uptake from soil, water and atmosphere. The heavy metals intake through diet causes many disorders like nervous system issues, kidney disorders, bone diseases and reproductive problems. The present project was designed to determine the mitigating impact of washing techniques on the heavy metals such as lead, arsenic, zinc and mercury in cauliflower grown under controlled field trails. The quantities of heavy metals were determined in fresh and chemically washed cauliflower with the help of Atomic Absorption Spectrophotometer. The calculated amount of these heavy metals was compared to their maximum residues limits. The results were discussed using standards statistical procedures.

Keywords: cauliflower, heavy metals, washing treatments, wastewater

1. Introduction

The vegetables being a rich source of dietary fibre, minerals and vitamins have an imperative role in human diet (Wargovich, 2000). They provide micro-nutrients like iron, magnesium 19 and 16% respectively and 9% calories of total body requirement. The vegetable have been reported to reduce the chances of diseases like cancer and cardiovascular problems. Cauliflower has high nutritional values, low fat content and contains high folic acid, dietary fibre, vitamin C and water. A lot of phytochemicals, riboflavin, ascorbic acid, carotene, folic acid and valuable minerals including calcium, phosphorous and iron are also found in cauliflower. The chemical configuration of vegetables shows high sugars content, water content, starch, protein, fat and energy in calories (Jiang *et al.*, 2003).

The heavy metals are the individual metals or metal compounds that can impact human health. In general humans come in contact with these toxic elements through ingestion (drinking or eating) or inhalation (breathing). In small amounts, some of these metals are of nutritional significance for healthy life and are referred to as the trace elements, e.g. zinc (Zn), iron (Fe), copper (Cu) and manganese (Mn). Among these Zn and Cu are necessary for vital physiological and biochemical roles and essential for sustaining health throughout life. Low Zn intake causes a variety of immunological problems while Cu shortage results in anaemia, skeletal defects and neutropenia on other the hand higher intake of Zn may result in abnormal growth and reproduction (Nolan, 2003). Living organisms usually need some of these metals at lower level as high intake may results in scarring effects (Chitmanat and Traichaiyaporn, 2010).

Generally, the contamination of heavy metals occurs due the application of fertilisers, waste water irrigation, use of metal-based pesticides, industrial emissions and transportation on crops (Agrawal and Marshall, 2003). The issue of soil contamination by heavy metals is increasing and has becomes major environmental problem in Pakistan (Bhutto *et al.*, 2009). The wastewater irrigation is the major contributor of heavy metal contents of the soil. Therefore, irrigating vegetables with such water is a very serious issue in Pakistan as these effluents are heavily loaded with harmful metals and metallic compounds (Mapanda *et al.*, 2005; Nolan, 2003). High concentrations of heavy metals were reported in vegetables from the untreated wastewater irrigated areas. The heavy metals are the principal toxic contaminant present in food supply chain (Zaidi *et al.*, 2005). In the long term deposition of heavy metals on the food stuff may lead to their persistence in critical human organs and causes disruption of several biochemical processes, thereby leading to the kidneys, nervous, cardiovascular, bone related complication. Humans are generally exposed to these toxic metals through ingestion (drinking or eating) and inhalation (breathing). Such pollutants may be ingested involuntarily through food and drink, dietetic contact to heavy metals like lead (Pb), cadmium (Cd), Zn and Cu has been acknowledged as a danger to human being health through the consumption of vegetables. When the concentration of heavy metals increases above the maximum residues limits (MRLs) they cause various types of diseases. For instance arsenic causes pigmentation and irritation of skin, polyneuritis and black foot disease, cadmium causes congenital abnormalities, dried scaly skin, loss of sense of smell, hair loss and pregnancy toxemia, mercury causes neurological signs, copper causes liver, kidney and brain damage, lead toxicity may result in bone disease, kidney damage, cardiovascular and nervous disorder, zinc can result in abnormal growth and reproduction (Kachenko and Singh, 2006).

The washing of vegetables prior to consumption not only removes debris and dirt but also expected to decrease the heavy metal and pesticide contents. Solutions of chlorine, ozonated water and strong acids have been proven effective in the removal of heavy metals and pesticides residues for vegetable washing (Pugliese *et al.*, 2004). Washing practice is very common and effective in most households as plain water is easily available while readily available chemical solutions can also be used for vegetable washing (Krol *et al.*, 2000). There was about 75 to 100% reduction in Pb and Cd and about 27 to 55% reduction in Cu and Zn contents when the vegetable samples were washed two to three times with clean tap water (Singh and Kumar, 2006).

Reduction in the heavy metal contents by washing suggests that heavy metals reach on the vegetables by aerial deposition and stick to them. The washing of vegetables with water removes particles and heavy metals deposited on the surface of vegetable mechanically (Sharma *et al.*, 2006). Another study was conducted to check the effectiveness of washing treatment in reducing the level of toxic metals in vegetables. For spinach, heavy metal reduction was found to be 21, 21, 13 and 26% for Pb, Cd, Cr and Zn, respectively, but almost unaffected for Ni for unwashed and washed samples. For coriander, concentration of Cd, Pb, Cr, Ni and Zn was decreased by 11, 31, 11, 5 and 6% and for methi reduction pattern was 14, 13, 15, 17 and 13% for unwashed and washed samples (Suruchi and Jilani, 2011).

2. Materials and methods

Vegetable sample collection

Cauliflower samples were collected from self-grown, supervised field. One kg sample of cauliflower was obtained at the point of optimum maturity. The samples were instantly shifted to the laboratory of National Institute of Food Science and Technology, for subsequent analysis.

Sample preparation

The collected vegetable samples were reduced to appropriate size by using knife to facilitate the analysis. The study was designed with different washing treatments by using tap water and following concentrations of chemical solutions in water along with one unwashed sample in Table 1.

After solution preparation vegetable sample were soaked in solution for ten minutes for washing purpose. The washed vegetable was blended by using commercial blender to make homogeneous paste of pulp and juice. The vegetable samples (three replicates of each washing treatment) were kept in hot air oven at 70-80 °C till complete dryness. The dried vegetable samples of different parts of vegetables were ground into a fine powder (80 mesh) using a commercial blender and stored in polyethylene bags for analysis.

Table 1. Washing treatment plan for mitigation of heavy metals.

Reagents	Concentrations (%)	Treatment
Unwashed	–	T_1
Tap water	–	T_2
Chemical solutions		
Reddish	5	T_3
	10	T_4
Sodium carbonate	5	T_5
	10	T_6
Hydrogen peroxide	5	T_7
	10	T_8
Lemon	5	T_9
	10	T_{10}
Citric acid	5	T_{11}
	10	T_{12}

Sample digestion

The powdered vegetable sample (0.5-1.0 g) was taken into a Pyrex beaker; 10 ml of concentrated HNO_3 was added in it and kept overnight without heating. It was then heated on a hotplate and after evaporation near to dryness, the sample was cooled and 5 ml $HClO_4$ was added and heated again. After digestion was complete, the sample was filtered into a clean volumetric flask and diluted to 50 ml with double de-ionised water (Nwajei, 2009).

Preparation of standards

The standard solutions (5, 10, 15 and 20 mg/kg) of all the metals (Hg, Pb Zn and As) were prepared from the stock standard solutions containing 1000 mg/kg in distilled water.

Determination of metals

The heavy metals Hg, Pb, Zn and As in unwashed, tape water, chemically washed, dried and digested vegetable samples were determined by using a Varian GTA 120 AA 240 Graphite Atomic Absorption Spectrophotometer (Varian, Santa Clara, CA, USA; Horwitz, 2006). The data obtained was analysed and represented using standard statistical procedures, i.e. completely randomised design as described by Steel *et al.* (1997).

3. Results

The concentrations of Hg, Pb, Zn and Ar were analysed in different samples of cauliflower grown under controlled field trial at the stage of optimum maturity. The results of undertaken studies are presented and discussed in this section. The results indicates Hg, Pb, Zn and Ar concentration in cauliflower was significant as shown in Table 2, 3, 4 and 5, respectively. The concentration of heavy metals in unwashed vegetable samples were higher than samples subjected to different washing treatments and all treatments exceeded the MRL value set by FAO for Hg (0.03 mg/kg), Pb (0.3 mg/kg), Ar (0.1 mg/kg) except Zn (9.4 mg/kg). The different washing techniques resulted in varying degree of Hg reduction in vegetables (Table 2). Out of all the washing treatments, highest heavy metal reduction was observed in T_{12}, i.e. 10% citric acid solution reduced the Hg contents to 21% in cauliflower as compared to unwashed sample. Contrarily minimum reduction was observed in T_1, i.e. tap water which resulted in only 5% reduction in Hg concentration in cauliflower. The reduction pattern of Pb by T_{12}, i.e. 10% citric acid was 24 in cauliflower (Table 3). Similarly unwashed samples of cauliflower were found to be heavily contaminated with Zn and Ar. The tap water reduces the Pb, Zn and Ar contents by 6, 17 and 3% in cauliflower. Again T_{12}, i.e. 10% citric acid was found to be more effective in all the vegetables to reduce Pb, Zn and Ar contents as shown in the Table 3, 4 and 5.

Table 2. Mean ± standard deviation (SD) and percentage reduction of mercury in cauliflower.[1]

Treatment	Mean ± SD (mg/kg)	Percentage reduction (%)
T_1	0.0306 ± 0.0008^{a}	
T_2	0.0293 ± 0.0003^{b}	5
T_3	0.0274 ± 0.0008^{cd}	11
T_4	0.0251 ± 0.0007^{e}	18
T_5	0.0276 ± 0.0008^{cd}	10
T_6	0.0252 ± 0.0004^{e}	18
T_7	0.0282 ± 0.0006^{bc}	8
T_8	0.0271 ± 0.0004^{d}	12
T_9	0.0269 ± 0.0005^{d}	12
T_{10}	0.0242 ± 0.0009^{ef}	21
T_{11}	0.0265 ± 0.0009^{d}	14
T_{12}	0.0242 ± 0.0006^{f}	21

[1] See Table 1 for explanation of the treatments. Means followed by the same superscript letter are not significantly different ($P<0.05$).

Table 3. Mean ± standard deviation (SD) and percentage reduction of lead in cauliflower.[1]

Treatment	Mean ± SD (mg/kg)	Percentage reduction (%)
T_1	0.4310 ± 0.0089^{a}	
T_2	0.4052 ± 0.0023^{b}	6
T_3	0.3841 ± 0.0045^{d}	11
T_4	0.3623 ± 0.0024^{f}	16
T_5	0.3718 ± 0.0019^{e}	14
T_6	0.3531 ± 0.0019^{g}	18
T_7	0.3934 ± 0.0059^{c}	9
T_8	0.3760 ± 0.0017^{e}	13
T_9	0.3706 ± 0.0040^{e}	14
T_{10}	0.3405 ± 0.0035^{h}	21
T_{11}	0.3550 ± 0.0043^{g}	18
T_{12}	0.3276 ± 0.0014^{h}	24

[1] See Table 1 for explanation of the treatments. Means followed by the same superscript letter are not significantly different ($P<0.05$).

Table 4. Mean ± standard deviation (SD) and percentage reduction of zinc in cauliflower.[1]

Treatment	Mean ± SD (mg/kg)	Percentage reduction (%)
T_1	6.5753±0.0133^{a}	
T_2	5.4530±0.0190^{b}	17
T_3	5.1908±0.0107^{d}	21
T_4	4.4006±0.0019^{g}	33
T_5	5.0610±0.0195^{e}	23
T_6	4.0089±0.0008^{j}	39
T_7	5.3255±0.0109^{c}	19
T_8	4.3357±0.0103^{h}	34
T_9	4.5324±0.0118^{f}	31
T_{10}	3.3532±0.0168^{k}	49
T_{11}	4.2027±0.0028^{i}	36
T_{12}	3.1591±0.0177^{l}	52

[1] See Table 1 for explanation of the treatments. Means followed by the same superscript letter are not significantly different (P<0.05).

Table 5. Mean ± standard deviation (SD) and percentage reduction of arsenic in cauliflower.[1]

Treatment	Mean ± SD (mg/kg)	Percentage reduction (%)
T_1	0.1361±0.0066^{a}	
T_2	0.1317±0.0017^{ab}	3
T_3	0.1280±0.0015^{bcd}	6
T_4	0.1217±0.0018^{def}	11
T_5	0.1255±0.00314^{bcd}	8
T_6	0.1171±0.0053^{f}	14
T_7	0.1307±0.0011^{abc}	4
T_8	0.1247±0.0012^{cde}	8
T_9	0.1218±0.0036^{def}	11
T_{10}	0.1151±0.0032^{fg}	15
T_{11}	0.1186±0.0007^{ef}	13
T_{12}	0.1089±0.0084^{g}	20

[1] See Table 1 for explanation of the treatments. Means followed by the same superscript letter are not significantly different (P<0.05).

4. Discussion

Results obtained in the recent study showed that the heavy metal residues reduced significantly when the vegetables were subjected to different washing treatments. Washing of cauliflower with different treatments declined the Hg residues varying from 5 to 21%, Pb from 6 to 24%, Zn from 17 to 52% and Ar from 3 to 20% in cauliflower. Highest reduction was found in Zn followed Pb, Hg and Ar. The heavy metal Zn showed highest reduction due to its physiochemical properties and dissolving power as compared to other heavy metals. The samples collected from supervised fields showed that when the cauliflower samples containing heavy metal residues beyond the MRL were subjected to washing treatments, the level of heavy metal residues decreased to the limit falling below the MRLs. The variation in reduction of residues of heavy metals during washing operation was observed in the present study which might be due to differences in the behaviour of washing treatments because of nature of chemicals. The present result indicate that acidic solution that is citric acid shown highest reduction of heavy metals residues as it works as a chelating agent, thereby making the heavy metal residues unavailable. The salt solution that is sodium carbonate also reduced the amount of heavy metal residues significantly. The lemon extracts showed more reduction of heavy metal residues as compared to reddish extracts. The acidic detergent solution was more effective in the elimination of the Zn, Pb, Hg and Ar under investigation than salt solution and biological extracts. The vegetables play vital role in maintaining the nutritional status of humans. The accumulation of heavy metals in vegetables uptake from soil, water and atmosphere. The intake of heavy metals through diet leads to several disorders such as kidney damage, nervous disorder, bone disease and tubular growth. The uptake of metals in vegetables from contaminated soil by absorbing them as well as from deposits on the vegetable parts exposed to the air from polluted environments. In the research project spinach was grown and samples were obtained at the stage of optimum maturity to assess the concentration of heavy metals in unwashed, tape water and chemically washed vegetable.

The recent study results are in conformity with the previous findings of Krol *et al.* (2000) who found that the residues of different heavy metals that is Pb and Cd were declined significantly during vegetables washing. The results obtained from the present study are also fairly in agreement with the findings of Singh and Kumar (2006). The heavy metals have the tendency to deposit in vegetables and intake of toxic metals can cause severe complications in humans and animals. The consumption of vegetables loaded with heavy metals such as Cd, Pb or even Cu and Zn are reported to cause cancer. There are already published works related to the incidence of gastrointestinal cancer (Turkdogan *et al.*, 2002). The heavy metals that is Pb, Hg and Cr were found to be accumulated in the shoot and roots of plants at low, medium or high levels (Adeyeye, 2005). The leafy vegetables uptake much higher levels of toxic metals as compare to other vegetables because of their more exposure to environmental pollution. The results of present study are also in conformity with the findings of Sharma *et al.* (2006) who found that leafy vegetables were more contaminated with Cd (0.09 μg/g) and the minimum concentration (0.002 μg/g) was in cucurbit vegetables. Our results also showed that maximum concentration (0.15

μg/g) of Pb was found in the coriander and the minimum concentration (0.001 μg/g) in root/tuber of sugar beet. The Pb reduction pattern in this study was parallel to the investigation carried out by Singh and Kumar (2006) to estimate the heavy metal load of unwashed and washed vegetables in peri-urban, Delhi. In addition, Suruchi and Jilani (2011) also reported the same reduction pattern of Cd in spinach, okra and brinjal, exposed to different degrees of pollution in Agra, by washing with tape water. The Ar is a toxic element and the humans may get exposure to Ar through drinking water obtained by wells bored into Ar contaminated areas or through contaminated water by agro-chemical waste or industrial effluents. Al-Chaarani *et al.* (2009) also reported the arsenic reduction by washing the vegetable with tape water but it was slightly higher than that in the present study.

5. Conclusions

It should be mentioned that the heavy metal residues in cauliflower was found in varying concentrations. The waste water is the single major contributor of heavy metals accumulation in soil and vegetables. The washing of cauliflower with tap water and different household chemicals solutions not only removes the dirt and dust particles but also reduces the heavy metals significantly. The difference between washed and unwashed vegetables with regard to heavy metal concentrations suggests that heavy metals reaches on the vegetables by aerial deposition and adhere to them. The washing treatments mechanically remove the heavy metals deposited on the surface of the vegetables. On the basis of present study, it is strongly recommended that vegetables must not be grown with sewerage water and vegetables must be washed carefully before cooking to decrease the risk of intaking heavy metals.

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