Assessment and Treatment some of the Local Seeds then used in Removal of Heavy Metals

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Abstract: The concentrations of some heavy metals such as Pb, Cd, Cu, Cr, and Zn present in common seeds used as spices or medicinal plants (*Moringa*, *cumin, mahaleb, Fenugreek, anise* and *cress*). The seeds available at local markets in Saudi Arabia were determined using atomic absorption. The *fenugreek* and *anise* contained higher concentration of Pb (0.85 mg kg^{-1} and 0.4 mg kg^{-1}) than the recommended by FAO/WHO. The *fenugreek* sample has higher concentration of Cu (11.31mg/kg) than the recommended by FAO/WHO. The concentrations of other metals in all the samples under investigation were under the maximum permissible concentration. No risk from daily intake of the seeds under study for hazardous Pb, Cd, Cu, Cr and Zn if the human take about 20g of spices per day. But there are dangerous from *fenugreek, anise* for lead, *anise* for cadmium and *fenugreek, anise* for copper. The adsorption of selected metal ions onto ground seeds after treatment were studied under various pH. The results showed that *Moringa* seeds were capable of absorbing the heavy metals tested compared to other seeds in some wastewater samples. The percentage removal by *Moringa* seeds were 99% for lead, 97% for chromium, 91% for cadmium, 90% for copper and 74 % for zinc. Maximum percentage adsorption obtained at pH7.

[Khairia M. Al-Qahtani. **Assessment and Treatment some of the Local Seeds then used in Removal of Heavy Metals.** *J Am Sci* 2015;11(11):198-203]. (ISSN: 1545-1003). http://www.jofamericanscience.org. 21. doi:10.7537/marsjas111115.21.

Key words: Seeds, Biosorotion, Heavy metals, polluted water.

1. Introduction

Heavy metals are the most harmful of the chemical pollutants and are of particular concern due to their toxicities to humans[1]. Metals and metalloids with atomic weights ranging from 63 to 200.6 g/mole and densities greater than 4.5 g/cm^3 are stable in nature[2]. There are 59 elements classified as heavy metals and out of these five are considered to be highly toxic and hazardous heavy metals [2]. These are cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), and zinc (Zn) which are released into environment by human activities or through constituents of the earth's crust.

Cadmium pollutants in water may occur from industrial discharge and mining waste[1]. Cadmium contamination is caused by its release in wastewaters and contamination from fertilizers and air pollutants. Cadmium is more toxic than lead and chromium. Cadmium at extreme levels causes Itaiitai disease and at low levels over prolonged periods causes high blood pressure, sterility among males, kidney damage and flu disorders[3]. Hence, Cadmium removal in water using natural polyelectrolytes such as *Moringa seeds* would be an advantage[4].

Chromium is widely distributed in the earth's crust and is used in metal plating[5]. In general , food appears to be the major source of chromium intake and on the basis of guideline value, there are no adequate toxicity studies available to provide long-term carcinogenicity study[6]. In epidemiological studies, an association has been found between exposure to chromium (VI) by the inhalation route and lung cancer[7].

Copper is both an essential nutrient and a drinking water contaminant[6]. Recent studies have shown effects of copper in drinking water on the gastrointestinal tract, but there is some uncertainty regarding the long term effects of copper on sensitive populations such as carriers of the gene for Wilson disease and other metabolic disorders of copper homeostasis[6].

Lead in water arises from a number of industrial and mining sources and is the most widely distributed of all toxic metals[5]. Lead in water causes serious problems such as anaemia, kidney disease and affects the nervous system [5]. Placental transfer of lead in humans affects babies and young children absorb 4–5 times as much lead as adults[7]. The lead toxicant accumulates in the skeleton and causes adverse health effects and interferes with calcium metabolism and with vitamin D metabolism[3]. However, evidence from studies in humans show adverse neurotoxic effects other than cancer occurring at very low concentrations of lead[7]. Therefore, there is need for the removal of lead from all drinking water.

Zinc is an essential trace element found in virtually all food and potable water in the form of salts or organic complexes[7]. Zinc is found in industrial waste and used in metal plating. Therefore, sources of zinc in water are mainly from industrial discharge and natural sources[8]. The removal of zinc is important for water treatment processes in producing good quality water [9].

The Kingdome of Saudi Arabia (KSA) imports seeds used as spices and other among a lot of food stuff from overall countries. These seeds may be subjected to contamination by way or more as described above.

The objective of this work is to estimate the levels of some heavy metals i.e. lead, cadmium, cupper, chromium and zinc that may be present in some seeds used as spices and medical seeds available in local markets in Al-Riyadh region. Also, the levels of investigated metals were recommended by the International Organizations (FAO and WHO). Then, the seeds were treated to remove heavy metals, and then used as an economical and environmentally safe method for the removal of heavy metals from aqueous solution.

2. Material and methods

Seeds Samples were collected from local markets, Recognized and classified according to their English name, scientific name, and the used part of the plant (Table 1). Sample origin is not specified.

Table (1): Scientific and common names of studied seeds

Common name	Scientific name	Family	Used part
Cumin	*Cuminum cyminum*	Umbellifeae or Apiaceae	Seeds
Mahalib	*Prunus mahalib*	Labiatae	Seeds
Fenugreek	*Trigonella foenumgraecum*	Legomnoseae	Seeds
Anise	*Pimpinella anisum*	Umbellifeae or Apiaceae	Seeds
Cresson	*Lepidium sativum*	Cruciferae	Seeds
Moringa	*Moriga oleifera*	Brassic ales	Seeds

A. Assessment of heavy metals in sample: Sample preparation

Samples were cleaned and oven-dried at 80°C for approximately 12 hours before chemical analysis. The dried samples were grounded in a stainless steel mill until obtaining fine particles that pass through a 0.5mm mesh and kept dry for analysis.

Determination of metal concentration

For determination of heavy metal concentrations, a wet digestion of the dried samples was done according to the method described by Jones and Case (1990) using conc. H_2SO_4 and 30% H_2O_2 mixture. 3.5mL of 30% H_2O_2 was added to 0.5g of dry-ground sample placed in a 100ml beaker. The content of the beaker was heated to 100^0C, and the temperature was gradually increased to 250^0C, and left at this temperature for 30 minutes. The beaker was cooled and an additional 1ml of 30% H_2O_2 was added to the digestion mixture and the contents were reheated again. The digestion process was repeated more than one time until clear solution was obtained. The clear solution was transferred into 50ml volumetric flask, and completed to the mark with double distilled deionized water. A blank digestion solution was made for comparison. A standard solution for each element under investigation was prepared and used for calibration. Metal measurement was performed with a Perkin-Elmer model 2380 Atomic Absorption Spectrometer, double beam and deuterium background correction. Hollow cathode lamps of Pb, Cd, Cu, Cr and Zn were used at specific wave length of every metal. Measurements were done against metal standard solutions[10].

The daily intake (mg kg^{-1} day^{-1}) was calculated based on these suppose:

The human weight is 50kg and the human intake from seeds per day is 20g, the daily intake was calculated according to the following equation[11]:

$$DI = C\frac{20}{1000} \div 50 \quad (1)$$

Where DI is the daily intake (mg kg^{-1} day^{-1}), C is the metal concentration in seeds.

B. Treatment of sample (Biosorbent)

A samples were modified and adopted in the treatment of the biosorbent. The method described by Mubeena *et al.*[12], 80g of the biosorbent (seeds) was treated with 1600ml, 0.1M HNO_3 with continuous stirring for 2 hours to remove metals from the biosorbent and increase its surface area. Then it was washed with 500ml distilled water, this was done in thrice then the sample was then sundried for about 6 hours. After the acid treatment, the adsorbent (about 50g) was extracted with 400ml methanol to remove inorganic and organic matter from the sorbent surface. This was carried out for 2 hours 30 minutes. The adsorbent pH was adjusted to 7 using 0.1M NaOH, washed with distilled water, oven-dried for about 1 hour, kept in an airtight plastic container and put in a refrigerator at 4°C prior the analysis.

C. Biosorption Experiments: pH studies of selected metals

The influence of pH on Cu^{+2}, Pb^{+2}, Cd^{+2}, Cr^{+3} and Zn^{+2} ions biosorption was studied by introducing 0.5g of adsorbent into 250ml conical flasks containing 30ml of 15ppm metal solution. 0.1M

NaOH and 0.1M HCl were used to adjust the pH during the study. The pH range of interest was 4 - 11 and three hours was the duration of the agitation at 200rpm. After agitation, the solution was filtered using Whatman filter paper no. 42. Then they were refrigerated until the metal analysis was done. The percentage adsorption was determined using the equation below:

$$\text{Precentage adsorption} = \frac{Co - Ca}{Co} \times 100 \quad (2)$$

Where *Co* is the initial concentration of solution, *Ca* concentration of solution after adsorption. The residual metal ion concentrations resulting from these experiments were determined by using Perkin Elmer model 3110 Atomic Absorption Spectrometer.

3. Results and Discussion

A. Assessment of heavy metals in sample

Essential metal (Zn and Cu) and Heavy metal (Pb, Cd and Cr) analyses have been performed on 6 local seeds and the outcome has been presented in Table2. The values of metal concentrations were compared with the maximum permissible concentration of 20, 50, 10, 0.5 and 50 mg/kg for Cu, Zn, Pb, Cd and Cr, respectively, as recommended by WHO trace elements in human nutrition and health[13].

The lead contents of different samples are given in Table 2. As comparing with standard limit, the *Fenugreek* sample has the highest content of lead (0.85mg/kg) that far exceeds the standard level recommended by WHO 1996 (0.30mg/kg). Sample of *anise* also contained higher concentrations of lead (0.4mg/kg) than that recommended by FAO/WHO 1996. However, zero readings were obtained for *cumin, mahalib, cresson* and *moringa*. As shown in Table 2, the concentrations of cadmium of all the samples under investigation were under the maximum permissible concentration (0.05mg/kg) of cadmium (FAO/WHO 1996). The amount of cadmium was in the range 0.01mg/kg in *Cresson* and coriander to 0.006mg/kg for *Cumin*. This high level of cadmium might be due to the use of cadmium-containing phosphate fertilizers, or from the practice of growing these plants on soil amended with sewage sludge, or both. However, other samples like *moringa, fenugreek, anise* and *mahaleb* show no detectable amount of cadmium. These results may agree with what was reported earlier[14] that lead concentration in food products ranged from undetectable levels to a few mg kg^{-1} of wet weight.

Varied levels of copper concentration were found as shown in Table 2. Samples of *cumin, mahaleb* and *moringa* are almost free from copper. The rest of samples contained variable amounts of copper from 0.11 to 11.31mg/kg. As compared with the standard limit, the Fenugreek sample has the highest content of copper (11.31mg/kg) that far exceeds the standard level recommended by WHO 1996 (1.5mg/kg).

The levels of chromium are given in Table 2. Samples of *cumin, mahaleb, Fenugreek, anise, cress* and *moringa* are almost free from chromium. Varied levels of zinc concentration were found as shown in Table 2. The data shows variation in concentration of zinc for the investigated seeds. Thus zero readings was obtained for *anise*. The rest of samples contained amount in the range (8.60, 11.02, 12.40, 25.12 and 32.61mg/kg) in *mahaleb, moringa, cumin, cress* and *Fenugreek*, respectively, that far exceeds the standard level recommended by WHO 1996 (45mg/kg).

The results in Table 3 showed that no risk from daily intake of the seeds under study for hazardous Pb, Cd, Cr, Cu and Zn if the human intake is about 20g of seeds per day. But there are dangerous from *fenugreek, anise* for lead, *anise* for cadmium and *fenugreek, anise* for copper.

The minimal risk levels for hazardous Pb, Cr, Cd, Cu and Zn through oral route and has acute effect are 0.0002, 0.0001, 0.0001, 0.002, 0.02 mg $kg^{-1}day^{-1}$, respectively. Whereas the human needs from seeds is very few grams per day there is no risk from used the species under study in the food. And also, there should be thorough control for imported food stuff at customs to meet FAO/WHO recommendations and tolerable daily intake limits for heavy metals, and to avoid the passing for human consumption and prevent unknown disease.

Table (2): Elements concentrations (mg/kg) on dry weight basis of studied common seeds.

	Element(mg/kg on dry weight basis)				
Seeds name	Pb	Cr	Cd	Cu	Zn
Cumin	ND	ND	0.006	ND	12.40
Mahalib	ND	ND	ND	ND	8.60
Fenugreek	0.85	ND	ND	11.31	32.61
Anise	0.40	ND	0.002	0.32	ND
Cresson	ND	ND	0.01	0.11	25.12
Moringa	ND	ND	ND	ND	11.02
PML	0.3	0.05	0.05	1.5	45

ND: Not Detected PML: Permissible Maximum Limits (WHO standards)

Table (3): Daily intake (mg $kg^{-1}day^{-1}$) of 20g+ of metals of studied common seeds effect based on 50g of human body.

Seeds name	Element(mg/kg on dry weight basis)				
	Pb	Cr	Cd	Cu	Zn
Cumin	NE	NE	NE	NE	NE
Mahalib	NE	NE	NE	NE	NE
Fenugreek	Acute	NE	NE	Acute	NE
Anise	Acute	NE	Acute	Acute	NE
Cresson	NE	NE	NE	NE	NE
Moringa	NE	NE	NE	NE	NE
MRL	0.0002	0.0001	0.0001	0.002	0.02

NE: No Effect MRL: Minimal Risk Levels

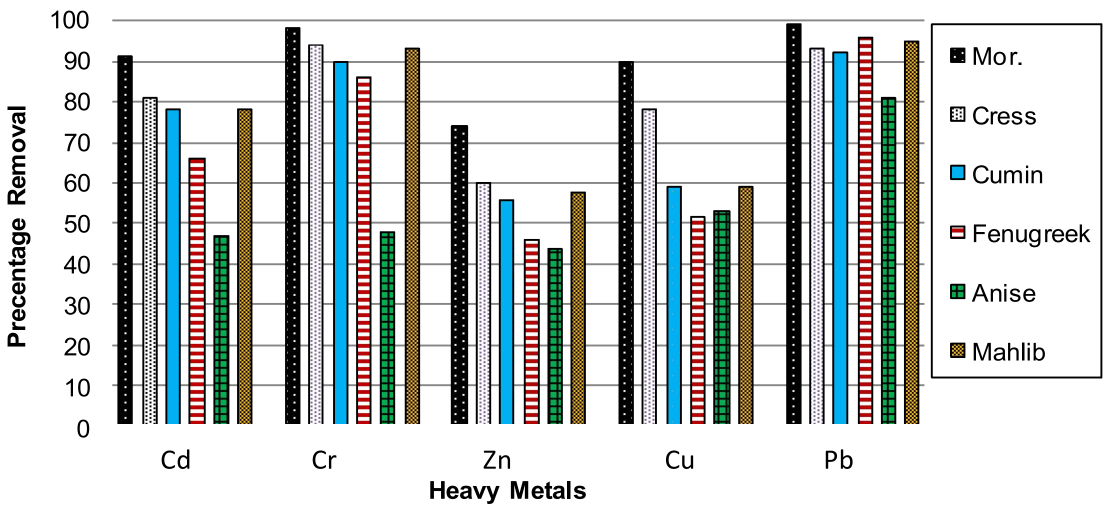

Fig. 1: Percentage removal of heavy metals using local seeds

B. Biosorption Process:

Natural compounds that can be used are starch and cellulose derivatives, protein materials and gums composed of polysaccharides[15].

In this research, *Moringa* seeds and other local seeds were investigated and their ability to aid metal removal from polluted water was investigated. Fig.1 shows that *Moringa* seeds have a high percentage removal of heavy metals compared to *cumin, mahlib, fenugreek, cress* and *anise*. *Moringa* shows more than 90% of metal removal and the highest percentage removal was achieved for chromium and lead (97% and 99%). *Mahaleb, cress* and *cumin* do not show very high percentages of metal removal while chromium, cadmium and zinc had less than 80% of metal adsorption. *Anise* and *fenugreek* show metal removal but their heavy metal removal percentages were low.

The adsorption of metals using *Moringa* is limited to the adsorption surface. This is because *Moringa* is a cationic polyelectrolyte of short chain and low molecular weight[16]. Heavy metals and solids that have high charges than *Moringa* colloidal surface will remove high percentage of metals compared to other seeds. The mechanism that brings about the adsorption of heavy metals is through the positive metal ion that forms a bridge among the anionic polyelectrolyte and negatively charged protein functional groups on the colloidal particle surface. There is formation of complexes with the heavy metals and the organic matter of *Moringa* and other seeds such as proteins. Due to its hydrophilic character, several hydrogen bonds are formed among polyelectrolyte and water molecules[17]. Polyelectrolyte coagulant aids have structures consisting of repeating units of small molecular weight forming molecules of colloidal size that carry electrical charges or ion sable groups that provide bonding surfaces for the flocs. Adsorption describes attachment of ions and molecules from seed protein by means of specific mechanisms[18].

However, adsorption is one of the processes affecting speciation, migration and biological availability of trace elements in natural water[18]. Metal ions in coagulation react with proteins and destroy them in water[19]. The *Moringa* seeds showed adsorption of metals for which the percentage adsorption for copper was about 90%, lead was about

99%, cadmium was 93%, chromium was 97%, and zinc was 73%, which were higher compared to other local seeds.

The local *Moringa* seeds did not significantly have toxic effects but aided in improving the water quality for drinking purposes. The mechanism of coagulation with the seeds of *Moringa oleifera* consists of adsorption and neutralization of the colloidal positive charges that attract the negatively charged impurities and metals in water. The results obtained in this study were comparable with the performance achieved in heavy metal removal by previous workers[4] using *Moringa oleifera* extracts.

The effect of pH on adsorption of selected ions by seeds as presented by Fig. 2 is divided into two phases. First, there is a slight increase in percent adsorption between pH 4-7. Second, the amount adsorption decreases from pH 7-11. pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction. The adsorption results agree with work done by Kanaan and Veemaraj[20-21].

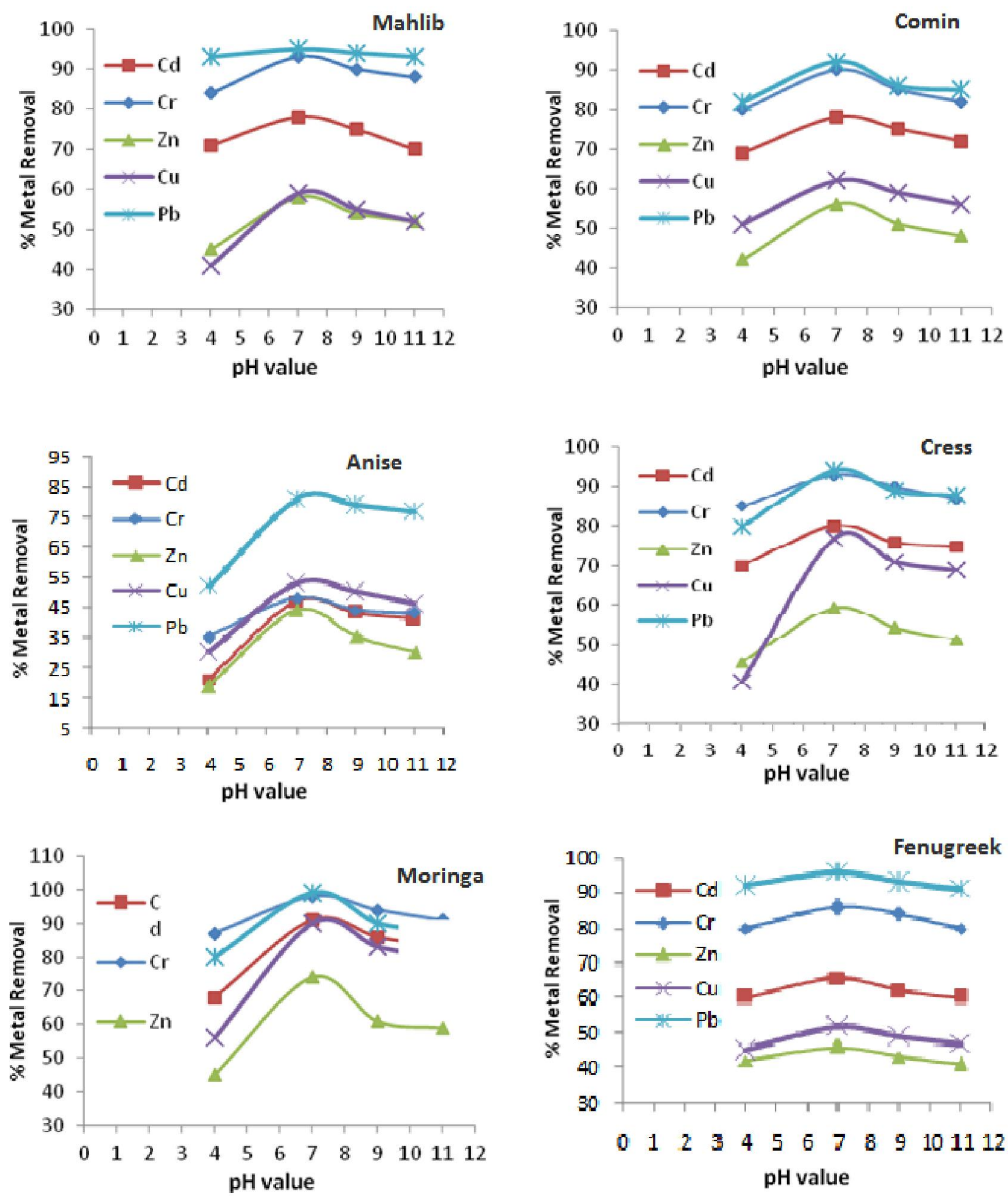

Fig.2: Removal of metal ions from aqueous solution at different pH using different seeds.

Conclusion

Data shows variation in concentration of metals for the investigated seeds. The human needs from seeds is very few grams per day there is no risk from used the seeds under study in the food.

Locally available seeds such as *Moringa*, *cumin, mahaleb, Fenugreek, anise* and *cress* were used for water purification. The data obtained showed that *Moringa* seeds were much more effective in water purification in terms of adsorption of metals. Thus, interventions to improve the quality of drinking water will provide significant benefits to the health of people in the Pacific. The use of local *Moringa* seeds as primary coagulants for clarification is useful in the production of drinking water in developing countries where purchase of other chemical coagulants are expensive and the operating costs are high for metal removal. This research will only help detect future problems of heavy metal levels in drinking water and how inexpensive natural coagulants can be used for water purification.

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11/18/2015