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Research Article

Heavy Metal Removal from Edible Leafy Vegetable by Low Cost Novel Adsorbents: Hazelnut Shell

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Abstract Hazelnut (*Corylus avellna* L.) is one of the important nut crops in world as well as in Iran which harvesting of it mostly is done by hand / manual or mechanical raking of fallen nuts. There are some genotypes of hazelnut in Iran that their growing areas are limited to Gillan, Aredbil, Mazandaran, Golestan, Zanjan and Qazvin Provinces. Soil contamination by heavy metals, though restricted to surface horizons, based on soil texture are occluded, organically complexed, modified and specifically adsorbed based on anthropogenic sources, resulted in toxicity ramification on human health, has been in vogue as a serious environmental problem for last few decades. A laboratory study was planned due to reduction of Lead and Cadmium toxicity by a low-cost soil amendment. Hazelnut (*Corylus avellna* L.) pit shell an abundant and low cost natural resource in Iran was used to adsorbing some heavy metals from contaminated soil of vegetable farmlands I the south of Tehran. Different adsorption parameters like adsorbent dose, particle size of adsorbent and time of growing parsley vegetable were studied. Composite soil sample were collected from ten randomized farmland locations at 5 agricultural fields (each one more than 10 hectares), in Tehran county, Iran. Cultivated Leafy vegetable samples were grown under controlled similar physical conditions, including pH, light and demonized watering. Leaves, roots and soil samples were examined, analyses and studied, at various frequencies for heavy metals: Lead and cadmium contents. The results of current study revealed that biomass can accumulate significantly high levels of Cd ($p < 0.0003$) and Pb ($p < 0.005$) in a short time(10 days) from soil and their uptake rate by vegetable and edible plant is significantly affected by their concentrations in the contaminated soil ($p<0.001$). The results showed that both of lead and cadmium have a bigger decrease at 2% bio-mass concentration. Hazelnut hard shell (HHS) can decrease lead content at 87.7% and 100% cadmium content in leaves of parsley after 30 days treatment. On the comparative, parsley root reached 100% in all treatment along the decrease of lead and cadmium. In conclusion, waste of hazelnut could be a good adsorbent to remove heavy metals from soil amendments and improve the safety of vegetable and soil in the same time.

Keywords:Hazelnut shell, Detoxification, Heavy Metals, Adsorbent, Leafy Vegetable

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Introduction

Hazelnut (*Corylus avellana*) is widely used in many food productions in different states such as raw, roasted, salted, and paste form. Proteins are key components conferring favorable sensory, technological, and functional properties to hazelnut. For these reasons, the protein fraction of hazelnut has been the subject of extensive research over the last years. In addition, the complete annotation of the hazelnut proteome at the molecular level is of great interest, in particular in clinical research because hazelnut proteins can elicit even severe allergic reactions in sensitive subjects [1].

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According to statistics of FAO, in Iran more than 19500 hectares the hazelnut, 18000ton produced annually, and 923 kg is mean production for every hectare [2]. There are more genotypes of hazelnut in Iran such as *Shastak, Mahali,Karaj Shirvani,, Garche, Paeezeh, Tabestaneh, Rasmi, Pashmineh* [3]. Hazelnut oil is becoming increasingly popular in many countries and is widely used for cooking, deep frying, salad dressing, and flavoring ingredients which means a lot of hard shell of hazelnut are available around the world and have different uses in industry.

Some studies present different uses for hazelnut shell. Tomasz Hebda et al., in 2018 conducted research and analysis of selected physicochemical properties show that hazelnut shells are suitable as a raw material for the production of biofuels. Their work was to determine selected properties of hazelnut shells in terms of their suitability for energy utilized for the production of biofuels. The hazelnut shells of six varieties were analyzed. The scope of work included the determination of: specific heat, calorific value, ash content, ignition temperature, humidity and bulk density. The following varieties were used for the research: *Trapezian, Berger, Barcelonski, Weba Cenny, Catalan and Casina.* They observed that among the tested varieties of hazelnut shells the highest calorific value was observed for *Casina* (almost 18.5 MJ . kg-1), and the smallest for the Trapezian variety (over 17 MJ • kg-1) [4].

Several studies refer hazelnut shell as an efficient bio absorbent. CRUZ LOPES et al., in 2014 studied on chemical analyses and revealed that hazelnut shells are composed of lignin (30.2%), cellulose (28.9%), hemicellulose (11.3%), tannins (18.2%) and proteins (6.7%). The chemical composition of the ash (27.7% K and 16.9% Ca) makes them a possible substitute for feldspar in ceramic industry. XRD showed that hazelnut shell has cellulose I fibers with high quality crystalline (69.1%) cellulose. The delignification proved to be very effective producing a pulp almost all composed by cellulose and xylan. Hazelnut shells show a good potential for particleboard production, although only to be used in the face layer [5-6].

Various studies reported that biosorption capacities such as Pehlivan et al., in 2009 proved that, the bio-sorption of Pb2+ ions on hazelnut shells and concluded that these shells are suitable sorbents for the removal of Pb2+ ion from aqueous solution [7]. Cimino et al., in 2000 found out that hazelnut shell shows a good efficiency in removing toxic ions such as three- and hexavalent chromium, cadmium and zinc from aqueous solutions similarly to other raw cellulosic materials[8]. Another possible utilization is as a source of natural and effective phenolic antioxidants as reported by Contini et al. (2008) [9]. It can be concluded that among the studied wastes that could replace xylan, melon peel has the maximum activity followed by apple pomace and hazelnut shell. Cöpür et al. (2008) investigated the possibilities of utilizing husk and shell of hazelnut in medium density fiberboard (MDF) production [10]. The results showed that panels could be produced with a mixture of beech (Fagus orientalis L.) and pine (Pinus nigra V.) fiber (60% and 40%) with hazelnut husk up to 20% addition maintaining the minimum properties required in the standards. However in the case of hazelnut shell a maximum of 10% could be added, because at higher levels the elastic modulus and internal bond strength decreased below the acceptable level.

The recycle of some hard shells in a variety of different ways have been reported. Various nutshell powders have been tested and utilized for centuries in many countries especially in folk medicine. For example walnut shell powder could be easily purchased today and even many individuals buy it in large scale due to add it to their beauty skin products and health and cosmetics products. Nowadays the waste of food industry/agricultural materials are known valuable and ecofriendly as a result of their renewable, unique chemical composition, eco-rich availability, economical and simply organized are seem to be applicable prerogative for heavy metal remediation [11-16]. Studies proclaim that various agricultural waste materials such as rice [17] bran and husk, wheat bran, wheat husk, saw dust of various plants, bark of the trees, groundnut shells, coconut shells, black gram husk, hazelnut shells, walnut shells, cotton seed hulls, waste tea leaves, Cassia fistula leaves, maize corn cob, apple pomace , banana peel , orange peels, soybean hulls, grapes stalks, water hyacinth, sugar beet pulp, sunflower stalks, coffee beans wastes , pit/ hard shell nuts, cotton stalks etc. has been certified [18-21] . These promising agricultural waste materials could be utilized in the removal of metal ions either in their natural form or after some physical / chemical modification and treatment [16-17].

Food stuff, Soil and water resources contamination by heavy metals, specially originated from anthropogenic sources, as a result of their toxicity ramification on human health, has been known as a major and serious environmental problem for last few decades [22-25]. Notably compatible is the problem of pharmaceutical wastewater/medical waste treatment, as this wastewater contains active pharmaceutical ingredients and consists of wide range of heavy metals. In the meantime the food waste is commonly produced in all the steps of food life cycle, such as during agricultural production, industrial manufacturing, processing and distribution and even consumer-generated in the context of private households. Mostly they have monetary worth components such as phytochemicals, proteins, flavor compounds, polysaccharides, fibers, and which can be re-used as nutraceuticals and functional ingredients [12, 18-19].

The potential of food and agricultural waste to remove heavy metals from contaminated water and soil was conducted on the basis of open scientific sources [20, 27-28].

Bio-sorption is a relatively new process that has proven very promising for the removal of heavy metals from wastewater. Due to the higher affinity of the adsorbent for the adsorbate species, the latter is attracted and bound there by different mechanisms [29-30].

According to scientific research as bio-adsorbents, citrus peel and pomegranate peel deserve great attention. Pomegranate peel and orange waste usually cause environmental problems and previously studies distinguished that they have no economic value for food industries [31]. The usage of banana peel as bio-sorbent for removing Cadmium and Lead from *Oryza* sativa rice was determined by Motaghi and Ziarati [11]. The collected peel of banana was subjected to three processes: powdered after drying, heated in 450 to obtained carbon active and treated by 1% citric acid. Then three above forms were analyzed for determination sufficiency as bio-sorbent. Results of this work improved the efficiency of modified waste of banana by 1% citric acid in removing heavy metal such as Cadmium and Lead from rice. Its potential is relevance to the presence of functional groups in the agricultural waste, insomuch this functional groups have the affinity for metal complexation. The application of sour lemon peel (SPL) as bio-sorbent for removing heavy metal from *Oryza* sativa

Rice was published by Razafsha et al. in 2016 [16]. They were utilized sour lemon peel in three forms: dried powder of sour lemon peel, as activated carbon by heated the SPL in 400 and the third one treated peels by 1% v/w phosphoric acid. The samples were separately placed in plastic tank containing distilled water, salt and rinsing rice at specific pH, temperature and contact time (10, 15, 20, 30 minutes and 1 hour). Finally, the absorption of Cadmium and Lead from rice samples into sorbent (SPL powder) was measured. Based on their published data, the sour lemon peels have a good potential for adsorption Cadmium and Lead from rice, also cooking rice by soaking rinsed rice samples by NaCl 2% and sour lemon peel modified by phosphoric acid 1% at least for 1 hour had the greatest effect [16]. In slightly similar studies, the other researcher was used agricultural waste in removing heavy metals. In 2018Tavakoli-hosseinabady et al. indicated the adequate effect of apricot pit shell on detoxification of heavy metals from leafy edible vegetables [30].They were successful in removing Lead, Nickel and Cadmium from edible vegetables. In 2018, Ziarati and Hochwimmer used hard shell of domestic wild almond; *Amygdalus lycioides* and *Amygdalus wendelboi*, for removing nitrate from root and leafy vegetables such as Iceberg and Romani Lettuce, Carrot, Celery, Potato, Cabbage, Broccoli, Eggplant, Cauliflower and Chinese cabbage [32].They recommended the best efficient contact time for treated vegetables by powder of wild almond shell was 15 min, although 20 min was more worked. As well as, addition of almond shell, even different concentration of shell as adsorbent did not impress or change the sensory attributes or pH of samples. Generally, A. *lycioides* and *A. wendelboi* were more effective in decrease nitrate and nitrite contents from most vegetables in this study, particularly iceberg and Romania lettuce samples and carrot samples. In 2016 Ziarati and colleagues used the modified shell of two species of wild endemic almond (*Amygdalus lycioides* and *Amygdalus wendelboi*) as adsorbent for removal of heavy metal ions such as Ni2+, Cr6+and Cr3+from contaminated water [21].They used phosphoric acid 2% to modify the shells of wild almond. According to their finding, the removal capacity of heavy metal ions was increased with an increase in the dose of both adsorbents and their contact time, also in the case of chrome the concentration of heavy metal in water (600mg/kg of Cr(III) and also Cr(VI). Solution pH of 3.2 and 48hours contact time was the optimum condition for maximal adsorption, but in this condition *A.wendelboi* showed the optimal ability against A.*lycioides* for adsorbing heavy metal.

On the whole in adsorption process the process continues till equilibrium is established between the amount of solid-bound adsorbate species and its portion remaining in the solution. The feasibility of using an adsorbent is based on the cost of the bio sorbent has to be optimum, as they often are made from abundant or waste material. Peel of citrus and pomegranate, vegetables peel, fruit Pit shells, tea and herbal tea waste and agricultural waste mix demonstrate great potential as bio-adsorbent [12].

The increase in environmental awareness and concern led to a search for new techniques capable of inexpensive treatment of polluted wastewaters with metals. The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to bio-sorption, based on binding capacities of various biological materials. The heavy metals in the soil hazardous to humans include Lead, Mercury, Cadmium, Arsenic, Copper, Zinc, and Chromium. Aquatic organisms are adversely affected by heavy metals in the environment, though the toxicity is mainly a function of the chemistry of water and sediment composition in the surface water system. Many organisms can regulate the metal concentrations in their tissues. Fish and crustacean can excrete essential metals, such as Copper, Zinc, and Iron that are present in excess. Some can also excrete non-essential metals, such as Mercury and Cadmium, although this is usually met with less success. Bio-sorption is a relatively new process that has proven very promising for the removal of heavy metals from wastewater. The bio-sorption process involves a solid phase and a liquid phase containing a dissolved species to be sorbet. Due to the higher affinity of the adsorbent for the adsorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound adsorbate species and its portion remaining in the solution. The degree of adsorbent affinity for the adsorbate determines its distribution between the solid and liquid phases. Process acceptance is based on the cost of the bio sorbent has to be optimum, and Cost is an important parameter, as they often are made from abundant or waste material.

The main goals of this investigation is to: study on the potential of food and agricultural waste of Hazelnut hard shell as an abundant waste and active bio-adsorbent to remove heavy metals (Lead and cadmium) from contaminated soil and leafy edible vegetable.

MATERIALS AND METHODS

Sampling Methods:

Soil sampling

Composite soil sample were collected from ten randomized farmland locations at 5 agricultural fields (each one more than 10 hectares), in the south Tehran county: Robat Karim (35°29′05″N 51°04′58″E), Baghershahr (35°31′57″N 51°24′09″E), Shahr-e Ray (35°35′N 51°26′E) in Tehran Province in Iran during October 2019 to February 2020 . The soil samples were filled in several plastic bags and carried to a laboratory at the Azad University, Pharmaceutical faculty, Nutrition and Food Sciences Research Center, Tehran-Iran. The heavy metal contaminated soil samples, so collected were safely transported in clean self-sealing quart-size polyethylene freezer bag to the laboratory. The common popular edible vegetable Parsley (*Petroselinum crispum*) cultivated and hosted in 80 vases of 27 × 13 × 16 cm size and grown in the same conditions as those cultivated in leafy vegetable farmlands.

Vegetable Sampling Method

The Soil prepared from farmlands in the south of Tehran utilized as the soil of 80 studied vases in the same situation such as light, water, amount of soil, temperature and other conditions except different percentages of adsorbent were prepared. The seeds of Parsley (*Petroselinum crispum*) were being planted directly on the treated and untreated soil samples in vases. Meanwhile in 70 vases the hazelnut pit shell by 0.1%, 0.3%, 0.5%, 0.7%, 1%, 2% dry weight percentage and were mixed by soil, due to observing the effect of nut hard shell as adsorbent and in specified times of 1, 10, 20 and 30 days. Meanwhile 10 vases of seeds of (*Petroselinum crispum*) parsley were planted as blank samples in the same situation as untreated samples for comparing the potential of bio-mass adsorption in current study. All vegetable samples were watered each day by Deionized water. Cadmium and lead contents in the leaves of edible vegetable in treated and the vases as well as untreated soils were investigated. The leaves of edible vegetable samples which have been grown in these soil samples were studied by the same method according the standard protocol [32-37]. In every 10 days, Aerial parts of Parsley in companion to hard shell of hazelnut were separated in 30 days, washed by deionized water and digested by wet method according the standard protocol for determining Lead and Cadmium contents. Bioaccumulation factors (BAF-s) were calculated for heavy metal content of plant parts (mg/kg) / heavy metal content of soil (mg/kg), for the metal. All physical and chemical properties and concentrations of heavy metal in soils, before and after adding bio-mass in the growth period of cultivated Parsley were analyzed in every 10 days.

***Bio-adsorbent sampling*:**

Hazelnut (15 Kg) (ripped completely) were prepared in October 2019 from 4 gardens of two cities in the north of Iran. Rudsar (37°08′15″N 50°17′17″E) and Tarom (36°57′N 48°54′E) are famous producers of hazelnut which are both located in North of Iran. Rudsar is the biggest producer of hazelnut and the most famous area for its export. This city is situated the East of and 70 kilometers from the center of the province (Rasht). Tarom is also a big producer of hazelnut and is a County in Zanjan Province in Iran. Both of above mentioned cities are the most appropriate areas for the development and nourishment of hazelnut in Iran.

After harvesting of hazelnut, the shells are removed and then are stored in refrigerating rooms at 4ºC until the time for research is reached. In order to investigate the influence of hazelnut hard shell as an amendment on removes or decrease of chemical forms of Cd and Pb. The samples were (Fine and mixed) in Dec 2019. Particle size distribution was determined by the hydrometer method [30, 38].

Estimation of Heavy Metals in Soil and Vegetable

The existence of heavy metals: Nickel, Lead and Cadmium in the soil and leaves samples as analyzed in the form of treated by different contents of bio-adsorbent and biomass of hard shell of hazelnut (0.1%, 0.3%, 0.5% , 0.7%, 1% , 2%) and untreated soil and also vegetable samples in specified times (every ten days up to 30 days of study) by ICP-MS with wet digestion method according to AOAC protocol were thoroughly studied [33]. The detection system used for the determination of heavy metalions: Cadmium and Lead, was NexION 300X ICP-MS (Perkin-Elmer, USA) the instrumental operating conditions for the determination of the elements. [22].

The plant samples were washed in deionized water dried up (24 hrs. at 75 °C) immediately to stabilize the tissue and stop enzymatic reactions. After drying, samples were supposed to pass a 1.0 mm screen using the appropriate Wiley Mill. After grinding, the sample were thoroughly mixed and a 5 to 8 g aliquot withdrawn regarding analyses and storage. Weighed 0.5 to 1.0 g of dried aerial parts of plants, then heated at 60 C^0 which were be grounded (0.5 to 1.0 mm) and thoroughly homogenized, stabilized and placed in a tall-form beaker or digestion tube. Added 5.0 ml concentrated HNO3 (65%, Merck) and cover beaker with watch glass or place a funnel in the mouth of digestion tube and allow to stand overnight or until frothing subsides. Placing covered beaker on hot plate or digestion tube into block digester and heating it at 125°C for 1 hour. Then the digestion tube was removed and it was let out to cool. Added 1 to 2 ml H_2O_2 30% (Merck) and digest at the same temperature. Repeated heating digestion process until the solution turned clear and transparent. In soil samples added additional HNO3 as needed to maintain a wet digest. Added dilute HNO3 (10%), and deionized water to dissolve digest residue and bring sample to final volume.

All recoveries of the metal observed exceeded 95%. Cd and Pb ions' concentrations were determined in three replications by means of Varian Vista ICP-MS device. The intra-day (for samples collected during the same day) and inter-day (for samples collected during different days) precision and accuracy of the method were determined under the optimal working conditions by triplicate measurements of known Lead and Cadmium concentrations. The first standard stock solutions showed a 100.0 mg/Lit concentration of Cadmium (II) Nitrate and Lead (II) Nitrate and aqueous standard solutions were prepared from them respectively.

Statistical Methods:

All the data were analyzed using the SPSS 20 statistical software for analysis of variance using ANOVA and Duncan's least significant difference (LSD at $p < 0.05$) for statistical significance. 3 duplicates with a replicate were considered in this research, and data was reported as the mean ± standard error of the mean. The values reported here are means of five values. Each sample data was the mean of 5 subsamples. A p value of 0.05 or less was considered as statistically significant.

Results and Discussion

Some physical characteristics of hazelnut kernels, nuts and shells selected from Tarom and Roodsar samples indicated in Table 1, and model of measuring showed in Figure 1. Three kinds of specimens have been tested in the present research work [2,3].

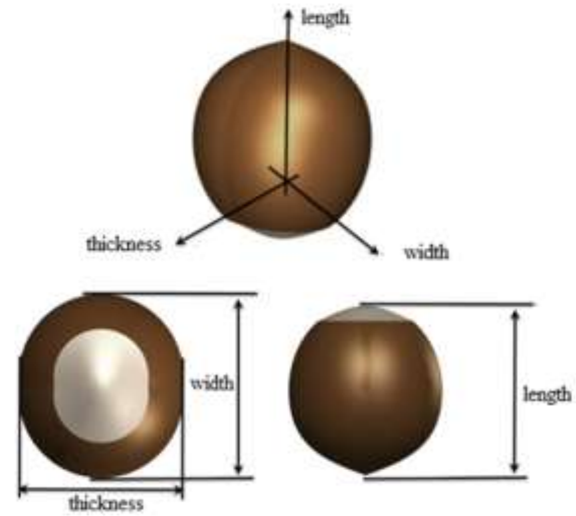


Figure 1- Reference measuring system defined along hazelnut shell and kernel.

Table 1: The diversity of nut size and weight and shell size of Persian hazelnut collected in 2019-2020 in two main hazelnut populations in the areas of Tarom and roodsar province regions (Iran)

Traits		Group	
		T*(n=30)	R*(n=30)
Nuts length (mm)	Mean	19.01	16.42
	Min	17.87	15.88
	Max	19.72	17.41
	SD	0.32	0.86
	CV(%)	2.54	2.19
Nuts diameter (mm)	Mean	16.65	15.29
	Min	13.82	12.11
	Max	18.98	19.07
	SD	1.29	1.46
	CV(%)	3.10	3.21
Shell diameter(mm)	Mean	1.84	1.45
	Min	1.22	1.24
	Max	2.48	1.76
	SD	0.26	0.18
	CV(%)	4.02	3.48

T*=Tarom,
R*=Roodsar

The mean contents of Cadmium in presence of hard pit shell of hazelnut samples are shown in table 2 in applied by different percentage and concentrations of bio-adsorbent.

The samples were analyzed by wet digestion method and standardized international protocols [33,39-47] were followed for the preparation of material and analysis of Cadmium contents and analyzed by ICP-MS in Nutrition and Food Sciences Research Center, in Pharmaceutical faculty, Tehran Medical Sciences. The data obtained from chemical analyses, mean values were calculated and are given in the table 2.

Table 2- Cadmium Content (mg/kg DW ±SE) in leaves of leafy vegetable treated by hard pit shell of hazelnut as Bio-adsorbent in comparison between untreated samples

Cd content (mg/kg DW ±SE*) in Parsley Leaves	0 day	10 day	20 day	30 day
0.1% bio-adsorbent	0.992 ±0.003	0.774 ±0.003	0.529 ±o.oo1	0.444 ±0.005
0.3% bio-adsorbent	0.967 ±0.004	0.716 ±0.001	0.518 ±0.005	0.417 ±0.003
0.5% bio-adsorbent	0.932 ±0.001	0.654 ±0.006	0.472 ±0.005	0.378 ±0.001
0.7% bio-adsorbent	0.911 ±0.005	0.621 ±0.001	0.451 ±0.004	0.313 ±0.001
1% bio-adsorbent	0.887 ±0.004	0.582 ±0.005	0.421 ±0.003	0.258 ±0.002
2% bio-adsorbent	0.871 ±0.004	0.489 ±0.004	0.389 ±0.002	ND**
untreated Samples	1.501 ±0.001	1.453 ±0.005	1.563 ±0.001	1.622 ±0.009

ND=Not detectable, SE*= Standard Error**

The effect of the concentrations/percentage in dry weight of adsorbent on the removal of Cd +2 ions by bio-mass of hard shell is depicted in figure 2, for adsorbent dose of 2% w/w. The results revealed the increasing of adsorbent doses directly significantly affected the potentially increased of cadmium removal from leafy vegetable ($p < 0.03$) which means that treated by chelation agents with the increase of the potential of bio-absorbent, removal ability of toxic heavy metal: Cadmium by biomass of Powdered hard shell. After 30 days of treatment 100% of cadmium removed from leafy vegetable ($p < 0.000$*).

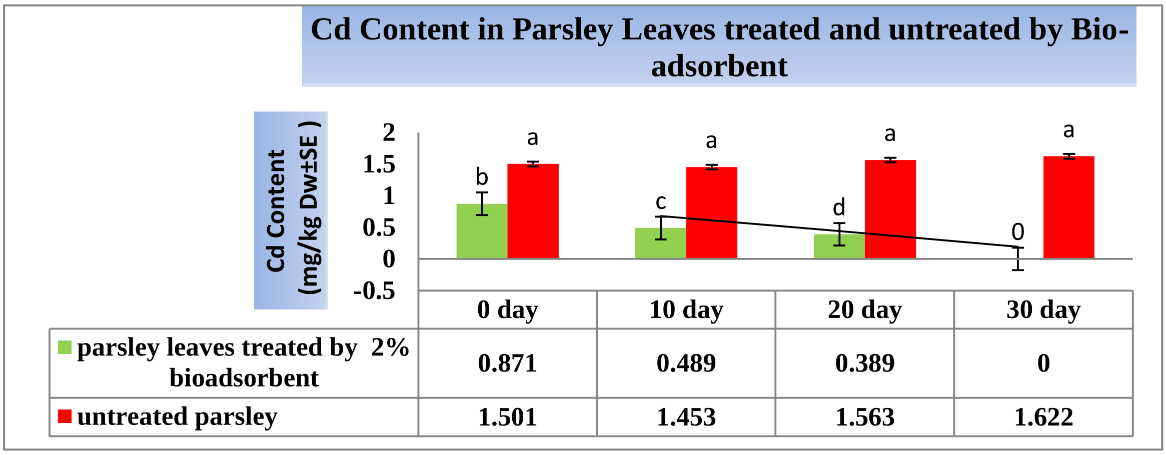
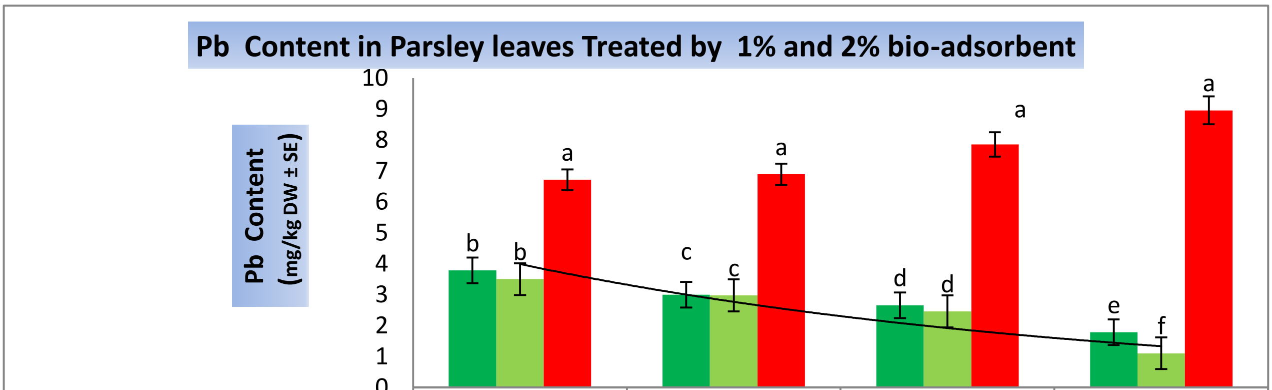


Figure 2- Effect of contact time on the removal of Cadmium from leaves of leafy vegetable, bio-adsorbent dose=2 % Hazelnut hard shell, temperature=25 ± 2 ºC.

Results in figure 3 showed significant difference in Lead up-taking by bio-adsorbent after 10, 20 and 30 days and different doses of bio-mass. The data showed that time as an efficient factor (days) have significant differentiate ($p \geq 0.01$), and the potential of taking up Pb was increased significantly not only between the first day of study but also the trend is courteously effective by 30 days study and statistic state ($p < 0.001^{***}$).

Moreover, factor of putting adsorbent in contaminated vegetable soil by Lead in the study showed significant effect ($p < 0.01$) and positive correlation with contents of Pb (r = +86 to r = +95), in the contamination of heavy metals in leaves in 10 , 20 and 30 days contact respectively. The amounts of lead adsorbed increased significantly with increase contact time ($p<0.001$).The other factor of adsorbent percentage and concentration also showed significant agent to decreasing and removal of Pb from leaves of studied Parsley edible vegetable ($p<0.001$). The data revealed that utilizing 1% and 2% bio-adsorbent of adsorbent can remove 80.1%% and 87.7% respectively of lead contents after 30 days at normal and room temperature.



	0 day	10 day	20 day	30 day
parsley leaves treated by 1% bioadsorbent	3.783	2.998	2.657	1.784
parsley leaves treated by 2% bioadsorbent	3.501	2.976	2.458	1.104
untreated parsley leaves samples	6.714	6.889	7.854	8.959

Figure 3- Effect of contact time on the removal of Lead from leaves of leafy vegetable, bio-adsorbent dose= 1% & 2 % Hazelnut hard shell, temperature=25 ± 2 ºC.

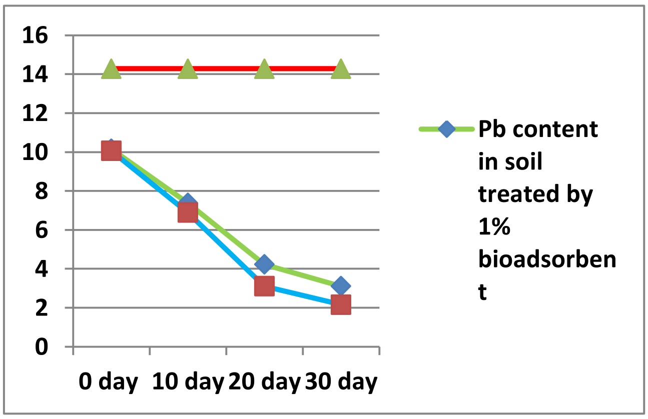


Figure 4- Effect of contact time on the removal of Lead from soil of cultivated leafy vegetable, bio-adsorbent dose= 1% & 2 % Hazelnut hard shell, temperature=25 ± 2 ºC.

Results in figure 4 in presence of 1% and 2% Hazelnut hard shell (HHS) showed significant difference in lead up -taking by bio-adsorbent after 19 and 20 and also 30 days in soil with treating and also with untreated soil samples significantly($p<0.001$). The data showed that accomplishing of treating soil samples by HHS during 10, 20 and 30 days have significant differentiate, but the potential of taking up lead was increased significantly between 0 to 10 first days of study in statistic state (p <0.000*) and in figure 5 Cadmium content in untreated sate significantly decreased to (0.811 ±0.004 mg/ kg ±SE) in presence of 1% bio-mass and (0.807 ±0.004 mg/ kg ±SE) in the first day of study while in blank and untreated soils the Cd content was 2.716 ±0.002 mg/ kg ±SE).

After 10, 20 and 30 days of study in samples treated by 2% HHS bio-adsorbent the Cd content reported: 0.389±0.004 , 0.312 ±0.002 and 0.311 ±o.oo1 (mg/kg DW ± SE) respectively that proved that biomass of adsorbent can reduce heavy metal mainly in the first days of treating. Moreover, time factor of putting adsorbent in contaminated soil by cadmium in the study showed significant effect (p <0.03) and positive correlation with contents of Cd (r = +90 to r= +93), in the contaminated soil and HHS bio-mass in 10 day contact respectively. The amounts of Cadmium adsorbed increased significantly with increase contact time (p<0.003) only till 20 days of study and after that no significant role which means probably all Ligand cleating capacity are occupied.

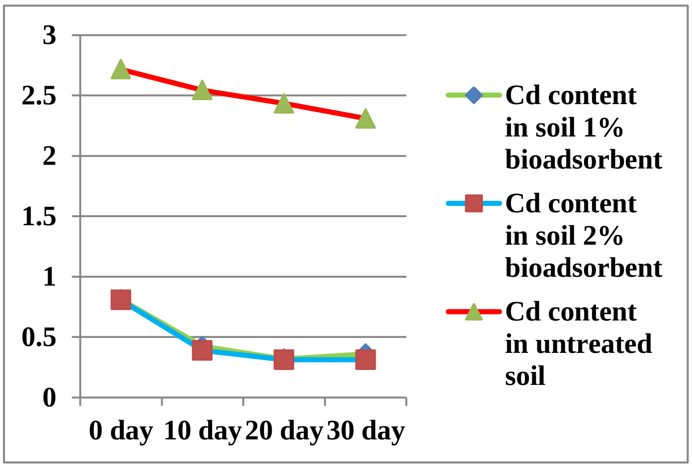


Figure 5- Effect of contact time on the removal of cadmium from soil of cultivated leafy vegetable, bio-adsorbent dose= 1% & 2 % Hazelnut hard shell, temperature=25 ± 2 °C.

Conclusion

The results of current study revealed that biomass can accumulate significantly high levels of Cd (p< 0.0003) and Pb (p < 0.005) in a short time (10 days) from soil and their uptake rate by vegetable and edible plant is significantly affected by their concentrations in the contaminated soil (p<0.001). The results showed that both of lead and cadmium have a bigger decrease at 2% bio-mass concentration. Hazelnut hard shell (HHS) can decrease lead content at 87.7% and 100% cadmium content in leaves of Parsley after 30 days treatment. On the comparative, parsley root reached 100% in all treatment along the decrease of lead and cadmium. In conclusion, waste of hazelnut could be a good adsorbent to remove heavy metals from soil amendments and improve the safety of vegetable and soil in the same time.

The present study focused on adsorption capacity of Cd and Pb, by Hazelnut hard shell as low cost adsorbent of agricultural and Food waste. The research was investigated in a batch system by considering the effects of various parameters like contact time, initial concentrations, and adsorbent dose.

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Conflicts of Interest

None of the authors have any conflicts of interest associated with this study.

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