

High Potential of *Ferulago angulate* (Schlecht) Boiss. in Adsorption of Heavy Metals

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ABSTRACT

The efficacy of various plants in eliminating different heavy metal contaminants, particularly Lead and Cadmium is a major concern nowadays due to the vast soil pollution in many countries around the world especially Iran. In this research determination of the potential ability of dried aerial parts of *Ferulago Angulara* in companion of black tea residue for cleaning up contaminated soil and their probable capability of adsorption different heavy metals (Nickel, Lead and Cadmium) was investigated. *F. Angulara* were collected in August 2015 from Kermanshah Province, Iran and samples was identified by the Herbarium of Faculty of Pharmacy, Pharmaceutical Sciences Branch, Islamic Azad University (IAUPS). The contaminated soil by Ni, Cd and Pb was put into the sites in a way that *F. Angulara* and tea leaves residue were mixed in different percentages up to 20%-20% (W/W) in examined soils individually and both of plants together in order to find the effect of companion residues in possible potential biosorption. Metal contents were detected by Atomic Absorption Spectrophotometer by wet digestion method in every 10 days during 60 days in Research Laboratory. Results indicated that the rate of heavy metals uptake by *F. Angulara* is significantly affected by the presence of dried tea leaves residues ($p < 0.003$). Tea leaves are more capable in absorbing nickel than *F. Angulara* and when we put both together in 20%-10% (tea leaves/ *F. Angulara*) the potential of taking up nickel significantly enhanced ($p < 0.01$). The Cadmium and Lead uptake rates by *F. Angulara* areal parts are significantly affected by pH and companion in the contaminated soil ($p < 0.001$). The results of this research concluded that *F. Angulara* and tea residue in the contaminated soil have suitable ability for adsorption method and removing more Lead and Nickel in pH < 7 after 20-60 days of study.

Key words: Biosorption, *Ferulago Angulara*, Tea leaves residue, Heavy metals.

INTRODUCTION

The capacity of sediments to accumulate compounds makes them one of the most important tools to assess contamination of inland aquatic ecosystems¹. Sediment quality assessments are often conducted to identify highly polluted areas that may require management action in order to protect or restore aquatic habitats². One of the major concerns of healthy soils in the environment is heavy metals which can be accumulated in

vegetables and crops grown on due to the probability of food contamination through the soil-root interface. Although heavy metals such as Nickel, Chrome, Lead, cadmium and etc are not necessary for plant growth, however they are passionately taken up and accumulated by plants up to toxic levels³⁻⁷. In public attitude, phytoremediation technology is more favorable due to its potential for cleaning up environment and the overall aesthetic perfection of the contaminated sites^{8,9}. Metallophytes are endemic plant species of natural mineralized

soils and, therefore, have developed physiological mechanisms of resistance and tolerance to survive on substrates with high metal levels¹⁰⁻¹². Since metallophytes, in general, and hyperaccumulators, in particular, are relatively rare and usually produce reduced biomass, the study of pseudometallophytes and indigenous species of contaminated soils, is of great value. Pseudometallophyte species (or facultative metallophytes) aren't specialized in metalliferous soils and have a more extensive distribution, but, due to selective pressure, are capable to survive in metalliferous soils¹³⁻¹⁹. Plants are ideal agents for soil and water remediation because of their unique genetic, biochemical and physiological features²⁰⁻²⁴. Phytoremediation requires prudent selection of resistant, preferably native plants with the greatest possible germination, growth, expansion, and root surface area²⁵. Some studies have suggested the efficacy of various plants in eliminating different heavy metal contaminants, particularly Lead and Cadmium. A few studies proved that some plants in accompany with each other can boost the potential of transition factor of heavy metals^{23, 26}.

Ferulago is a genus belonging to the Apiaceae family²⁷. It has 35 species, of which seven grow wild in Iran. *Ferulago angulata* is one of these species that are found in their natural state in Iran²⁸, basically belongs to west of Iran. Traditionally this plant was added to different products to prevent from decay as well as give them a pleasant taste. Different concentration of essential oil and extract were added to vegetable oil. Peroxide and Thiobarbituric indexes of samples were determined and compared with blanks samples (without any antioxidant and with TBHQ) showed that minimum concentration of extract for conserving of vegetable oil is about% 0.02 under excremental conditions. Extract with 0.5% concentration is more effective than TBHQ²⁹.

Ferulago species are used in folk medicine for their sedative, tonic, digestive and anti-parasitic effects²⁷⁻²⁹. Antibacterial and antifungal activities have previously been investigated for some *Ferulago* as a food preservative²⁸. *F. angulata* (referred to locally as Chavir) is a perennial shrub with the height 60-150cm³¹ that grows 1900-3200m (above sea level)³²⁻³³. The *F. angulata* have two

subspecies; subsp. *angulata* (Schlecht) that is wide spread in Turkey, Iraq and Iran, and subsp. *carduchorum* which is endemic to the Shahoo Mountains of west Iran³².

MATERIAL AND METHODS

Study Area of Plant Sampling

The aerial parts of *F. angulata* subsp. *carduchorum* were collected respectively from of Shahoo Mountains, Kermanshah province west of Iran. The voucher specimen is deposited in the herbarium of pharmaceutical Sciences Branch, Islamic Azad University, Tehran, Iran. The aerial parts were cut into pieces and air-dried for even days at room temperature (17-25°C).

Study Area of Soil Sampling

The Shahre-e-Babak covers an area of 13572 km² in the north-western part of Kerman Province, south part of Iran. The Shahre-e-Babak is located between approximately N54°23' to 55°48' and E29°49' to 31°10'. There are major anthropogenic sources of metals such as Maiduk Copper Complex and Khatoon-Abad Copper Smelter in the central and south-eastern part of the study area, respectively³³. They enter toxic metals from mining activities to their adjacent environment which has adverse effect on soil, plants, animals, and public health. It should be mentioned that, agricultural activities and animal breeding are the main job of the people in the study area. These anthropogenic sources of metals not only affect public health, but also have adverse effect on economic state of the residents due to interference with their activities. Although the Shahr-e-Baback receives considerable amount of toxic metals, there are not any deep studies about metal pollution state in the study area. Contaminated soil samples were collected from around copper smelter. Fifty soil samples (0-5 cm) were collected on August 2015 from surface of Shahr-e-Babak soil (Fig.1). Most of samples were collected adjacent to Khatoon-Abad Copper Smelter and Maiduk Copper Complexes. Also, some samples were collected from unpolluted sites (far from the major anthropogenic sources) to determine metals background. Collected samples were transferred to the laboratory in plastic bags.

At the beginning of study, soil profile characteristics were observed and recorded by a packet penetrometer (CI-700A, soil Test Inc., USA). Soil samples were mixed, homogenized and separated into three parts, 1/3 of each samples was air-dried and pass through a 2 mm sieve in order to determine p and k content, pH and electrical conductivity and particle-size distribution. The other 2/3 was passed through a 2 mm sieve without drying and 1/3 of it used to determine heavy metals concentration by Atomic Absorption Spectroscopy (AAS) after digestion with aqua-regia. The samples were analyzed by an Atomic Absorption Spectrophotometer Model AA-6200 (Shimadzu, Japan) using an air-acetylene flame for heavy metals: Pb, Cd and Ni using at least five standard solutions for each metal. All necessary precautions were taken to avoid any possible contamination of the sample as per the AOAC guidelines¹³.

Sampling method

Dried aerial parts of *Ferulago Angulara* in companion of black tea residue were separated and washed and digested by wet method according the standard protocol for measuring Cadmium, nickel and Lead. Mean values were calculated, and analysis of variance (ANOVA) and Student's t-test were performed. Bioaccumulation factors (BAF-s) were calculated for heavy metal content of plant parts (mg/kg) / heavy metal content of soil (mg/kg), for each metal.

The last port used to determine nitrate and ammonium 2M KCl extraction followed by determination using flow injection method. All the soil data are expressed on a dry basis. The soil by different pH put into 50 vases and coriander were grown in 48 examined soils and no plants were grown in two others as they have been considered as control group in soils, as the same procedure in the other reports of scientists who have investigated the effects of soil acidification on Zn and Cd phytoextraction¹⁴. As soil acidification might cause some negative side effects such as increasing solubility of some toxic metals and leaching them into the groundwater and creating another environmental risk. Therefore, at the beginning of study, we tried to control pH at the range of 5.9 up to 6.9 in samples of soils.

All samples were watered each day by tap water (Tehran tap water). The studied samples were managed by the same light situation and some circumstances in order to be compared with each other due to determine the ability of *F. angularata* in adsorbing Lead, Cadmium and Nickel from soil and its potential to avoid transferring heavy metals to coriander and keep safe the eating vegetable.

Physical and chemical properties and concentrations of heavy metals (Cadmium, Nickel and Lead,) in soils, before and after adding *F. Angulara* in companion of tea residue in the growth period of cultivated coriander were measured in every ten days. In order to assess amount of heavy metals in the soil samples, heavy metal concentrations in soils of studied vases were determined by atomic absorption spectrophotometer^{15, 34-38}.

Samples were then digested with HNO₃/HCL/H₂O₂ according to U.S.EPA 3050B test method to determination of total metals (Pb, Ni and Cd) concentrations (U.S.EPA, 1986).

Electrical conductivity

Soil suspension prepared with soil and deionized water in 1:5 ratios (10 grams of soil and 50 mL of water) was allowed to stand for one hour. Soil electrical conductivity was analyzed using a potable combo probe (Hanna Instruments).

Statistical Analysis

Mean values were calculated, and one way ANOVA using the Minitab 15.0 statistical software was used for the analysis of data in all studies. Potential of adsorbing areal parts of *F. Angulara* in the presence of tea leaves residue and without them were calculated for heavy metal contents of studied soils (mg/kg) for each metal.

RESULTS AND DISCUSSION

Chemical extraction of the soil profile before adding specified amounts of *F. Angulara* is shown in the table 1 and electrical conductivity and nitrate content in different layers is indicated in table 2 Data is averages of the profiles.

Table 1: Physical and Chemical properties of the studied soil samples before planting

Characteristic	Quantity	Characteristic	Quantity
Soil Texture	Silty Clay Loam	Sand (%)	14.3
Clay (%)	38.7	Silt (%)	47.0
Ni (mg/kg DW)	7.4356	Cd (mg/kg DW)	2.2304
Pb (mg/kg DW)	10.2331	Cu (mg/kg DW)	25.4609

Table 2. The characteristics of soil samples of Mining Area, Shahr-E-Babak, Iran, before treating by *F. Angulara*

Layer(depth cm)	pH (H ₂ O)	Electrical conductivitydS/cm 1:1	NO ₃ -Nmg/kg DW	NH ₄ -Nmg/kg DW
1 (0-20)	6.5	0.58	65.2	10.66
2 (20-40)	6.8	0.41	30.9	10.43

Results showed *F. Angulara* adsorption for all heavy metals in treated soil were affected significantly by adding black tea residue and *F. Angulara* not only affected contaminated soil and can up-take lead, Cadmium and Nickel after 10 days ($p < 0.01$) more than other studied times but also adding black tea residue have synergic effect in taking up heavy metals especially in adsorbing lead more than two other studied heavy metals. In figure 2 the treating contaminated soil trend by this plant indicates that dried *F. Angulara* areal parts in the soil which is enriched by black tea leaves can be consider as a suitable method for rescuing soil by its relatively large ratio of biomass concentration of the contaminant to soil concentration.

The rate of uptaking cadmium by areal parts of *F. Angulara* in treated soil was obviously high especially after 20 days (figure 3). The amount of Cd deposited in soils treated by both treated dried plants differed significantly ($p < 0.02$). As expected the Cd uptake rate by *F. Angulara* is significantly affected by time duration and by mixing by tea residue ($p < 0.01$) while for lead (figure 4) the p -value was less than 0.03 after 10 days being treated.

Even though the Nickel concentration in Ni treated soils in 40 and 60 days treated by *F. Angulara* and Black tea residue is higher compared to other studied times (figure 5).

The results of this research concluded that *F. Angulara* in the contaminated soil had suitable ability for adsorption heavy metals and indicated that the rate of heavy metals uptake by *F. Angulara* is significantly affected by the presence of dried plant ($p < 0.003$). Tea leaves are more capable in absorbing nickel than *F. Angulara* and when we put both together in 20%-10% (tea leaves/ *F. Angulara*) the potential of taking up nickel significantly enhanced ($p < 0.01$). The Cadmium and Lead uptake rates by *F. Angulara* areal parts are significantly affected by pH and companion in the contaminated soil ($p < 0.001$). The results of this research concluded that *F. Angulara* and tea residue in the contaminated soil have suitable ability for phytoremediation by phytoextraction method and transmitting more Lead and Nickel in pH 7 after 20-60 days of growth of plants. The synergic effect of mixing dried areal parts of *F. Angulara* by black tea residue, is referred to as the environmental friendly method for recuing contaminated soils, therefore our results showed that even the residue parts of some plants probably tolerate and adsorb more metal toxicity and are active in treating contaminated soil. Mechanisms for adsorbing toxic metals should be examined in a risk-based approach in order to determine impacts of metal speciation for other companion dried and residue plants. Regarding the results of the present study, it is recommended to study more on the



Fig. 1: The map of collecting contaminated studied soils sampling

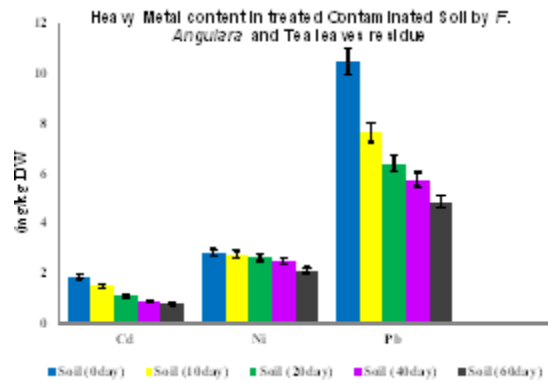


Fig. 2: Heavy metal contents in studied soils samples treated by *F. Angulata* and black tea residue during 60 days

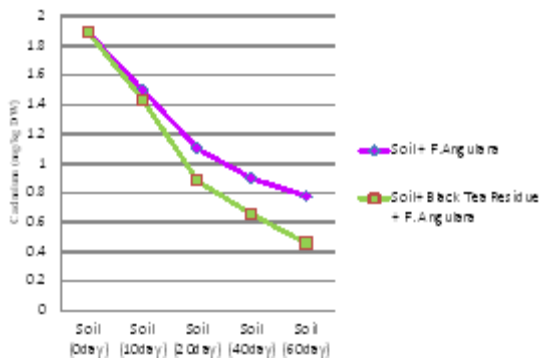


Fig. 3: Cadmium content (mg/kg DW) in *F. Angulata* areal parts added in contaminated soil in comparison to treated contaminated soil by *F. Angulata* and Black tea residue

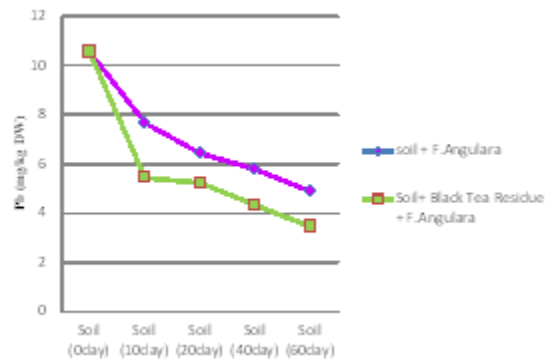


Fig. 4: Lead content (mg/kg DW) in *F. Angulata* areal parts added in contaminated soil in comparison to treated contaminated soil by *F. Angulata* and Black tea residue

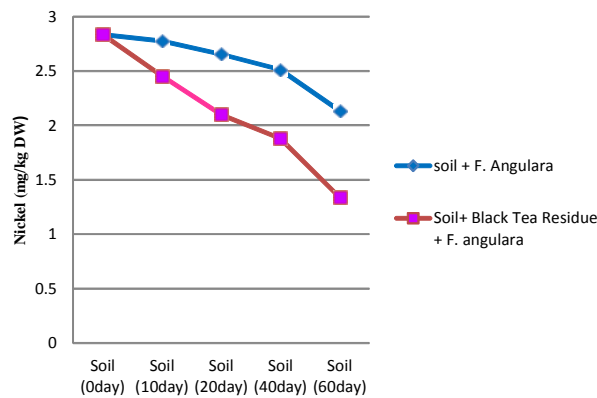


Fig. 5: Nickel content (mg/kg DW) in *F. Angulata* areal parts added in contaminated soil in comparison to treated contaminated soil by *F. Angulata* and Black tea residue

species belong to other companion plant families that have potential ability to biosorbing heavy metals more effectively.

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