

Novel Adsorption Method for Contaminated Water by Wild Endemic Almond: *Amygdalus scoparia*

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Many of the water systems keep ecosystems thriving and feed a growing human population have become stressed. Water pollution especially heavy metal contamination is a major global problem and it is leading to deaths and diseases. In this study the potential of wild endemic almond: *Amygdalus scoparia* shell was assessed for adsorption of heavy metal ions such as Pb²⁺, Ni²⁺, Cr⁶⁺ and Cr³⁺ from aqueous solution. *A. Scoparia* fruits were collected in July 2014 from Sirmand Mountains near Hadji-Abad County, Hormozgan province and the mountains in Gnow protected area, Bandar-Abbas, Hormozgan province in Iran, respectively. Analyzing of Pb, Ni and Cr (III) and Cr (VI) concentrations performed using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). Adsorption capacity of Cr (VI), Cr(III), Pb and Ni onto modified almond shells by phosphoric acid was investigated in a batch system by considering the effects of various parameters like contact time, initial concentrations, pH, temperature, adsorbent dose and particle size. The adsorption was pH solution dependent and the maximum adsorption was observed at solution pH of 3.23. Moreover, contents of different heavy metals in the contaminated water showed significant ($p < 0.05$) and positive correlation with contents of Pb ($r = +82$ to $r = +96$), Cr⁶⁺ ($r = +74$ to $r = +94$), Cr³⁺ ($r = +84$ to $r = +98$), Ni ($r = +33$ to $r = +42$) in the wastewater and *A. Scoparia* modified shell, respectively. The amounts of Cr (VI) adsorbed increased significantly with increase in dose of *A. scoparia* adsorbent ($p < 0.05$) and their contact time ($p < 0.05$). The results of this study revealed that *A. scoparia* can accumulate high level of lead, Chrome (VI) and (III) in a short time and their uptake rate by plant is significantly affected by their concentrations in the contaminated water ($p < 0.005$). A contact time of 48 hours by almond shell was found to be optimum and 87.1% Cr (VI), 89.8% Cr(III), 84.4% Pb and 48.1% Ni was removed. Experimental results showed that low cost bio-sorbent was effective for the removal of pollutants from aqueous solution.

Key words: *Amygdalus scoparia*, Contaminated Water, Adsorbent, Removal of Heavy Metals.

Nowadays one in seven people on our planet, lack access to safe drinking water. More than 40 percent of the planet's population will be living in areas of "severe" water stress and around

768 million people do not have access to a safe, reliable source therefore water pollution has become to a major global problem and it is leading worldwide cause of deaths and diseases. Pollution of the biosphere with toxic metals has accelerated dramatically since the beginning of the Industrial Revolution¹⁻³. Wetland is a water environment which has considerable scientific, economic and

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social values. They are the habitats of various organisms contributing to the gene cache of microbes, plants and animals on the earth. However, nowadays the pollution and degradation of the wetlands are increasing dramatically⁴. Marine animals can accumulate metals through sea water, suspended particles, sediments and food chains⁵. Permanent contaminants such as metals may be transferred to higher levels in the food chain through environmental expansion. Behavior of trace elements in various weathering environments is dramatically different. In world soil neutral or alkaline weathering environments, U, V, Mo, and Zn have high mobility, while Mn, Pb, Ba, Be, and Bi have low mobility, and Cu, Co, Fe, Ni, Th, Y have very low mobility. Otherwise, in reducing environment conditions As, Ba, Be, Bi, Cd, Co, Cu, Mo, Ni, Pb, Se, Th, U, Zn, V, and Y have a very low degree of mobility⁶. Trivalent chromium occurs widely in nature and is an essential nutrient required by the human body to promote the action of insulin in body tissues. Chromium as a pure metal has no reported human or environmental toxicity effects. Both acute and chronic toxicity of chromium are mainly caused by hexavalent chromium compounds (Cr VI). Hexavalent chromium is considered the most hazardous of all forms, and in welding fume it is a suspected human carcinogen. DNA damage in welders has been associated with hexavalent chromium exposure⁷. This is consistent with the classification of hexavalent chromium as a human lung carcinogen⁸.

Many agricultural by-products such as almond and other fruit or nut shells are available and have low cost. Almond (*Rosaceae* family) with wide applications in pharmaceutical, oleo chemicals, food and cosmetic industries is considered as a pleasant nut throughout the world. Other than the regular almond, there are more than thirty wild or partially cultivated almond species in the world of which twenty species have been reported in Iran⁹. Iran is the main center for distribution of genus *Amygdalus*. L. *Amygdalus* is one of the most problematic genera in family *Rosaceae* and taxonomy of this genus like many other genera in this family with numerous problems because of high degree of variation in morphological conditions¹⁰. (Khatamsaz 1993). It shows high degree of variation within one species, high hybridization inter species and high

homoplasmy under ecological conditions¹¹.

As Iran is one of the richest countries in the world as regards genetic resources of medicinal and wild unknown plants that some of them are export¹². We have studied on potential ability of *Amygdalus* specie as this endemic specie found in some parts of Iran especially in south regions due to accumulate Chrome and Nickel as the major concern in wetland pollution.

MATERIALS AND METHODS

Study of Area

Almond in areas with warm, dry summers and cold winters and short fall grows well. Distribution Almond mountain areas in Zagros foothills of khuzestan begins and in altitudes 600 to 1500 meters above sea level is located (Figure 1). Around the city of Dezful, Izeh, Baghmalek, Masjed Soleiman and Haftgol abundant of almond can be seen [13]. The Izeh fault zone is a transverse fault zone with dextral strike slip (and some reverse component) in the Zagros Mountains (Iran). It causes some structural deformations. This fault zone is acting as eastern boundary of Dezful Embayment and forms subsidence of the embayment¹³. The Type of regional climate is related to the dry forests and minimum temperature of 18.11 °C and the average temperature of 23 °C and the maximum temperature are 48.5 °C.

Shell samples were washed several times with deionized water and dried (sun or mechanical). The adsorbents were then ground in a blender and stored for further use. All reagents and chemicals were used of analytical reagent grade and were obtained from standard sources.

Phosphoric acid, activated carbon, potassium dichromate and other chemicals were obtained from standard sources.

Characteristics of wastewater

To move forward on chemicals management, a project has been done in Pharmaceutical faculty in Tehran-Iran which has 20 laboratories in chemical and toxicological laboratories whose area of work are divided into two types of educational and research. The research has focused on comprehensive environmental management of the poisonings and exposure to toxic and hazardous chemicals especially Lead, Nickel and Cr (III) and Cr (VI). The

wastewater of inorganic research laboratory was collected during 2 weeks in summer 2015. The samples were collected *ten days before the experiment*. They were in sterile plastic bottle and were transported to laboratory and kept in 25 °C.

Experimental design and Chemical analysis

The shell part of *A. scoparia* was soaked in phosphoric acid 2% for 24 hours and then dried at 80 °C in an oven for 24 hours [6,7, 25-29]. Dry parts were then ground and passed through standard steel sieves (72 mm mesh size). The fine powder was used without washing or any other physical or chemical treatments. The amount of adsorbent was kept constant as 0.5 gram in all the combinations. Adsorbent was added to 100ml waste water contained heavy metal solutions. The sorption studies were carried out at 25 ±1 °C till 60 hours and in every 10 hours they were studied. A metal and biomass free blank was used as control. The mixtures were filtered through filter paper (pore diameter 11µm) and metal concentrations were determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

Metal removal (%) at any instant of time was determined by the following equation:

$$\text{Heavy metal removal (\%)} = (C_i - C_f) / C_i \times 100$$

Where, C_i and C_f represent initial and final metal concentration (mg/L) at any instant of time, respectively

Shell samples after being used as adsorption and wastewater treated samples after being objected by *A. scoparia* modified shell were studied with concentrated HNO_3 and H_2O_2 , due to find out the potential of adsorbing heavy metals. The digested solution was filtered and then analyzed for Pb, Ni and Cr (III) and Cr (VI), concentration using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) (Varian 730-ES Axial ICPOES: USA).

pH of wastewater samples before and after being treated by *A. scoparia* adsorbent were determined. The pH of samples was measured by potentiometer (Inolab, Weilheim, Germany) after calibration using standard buffers pH 6.0 and 9.0. The pH was recorded after the pH meter provided final reading.

Statistical analysis

The values reported here are means of six values. Data were tested at different significant levels using student t-test to measure the variations

between the wastewater parameters before and after treated by *A. scoparia* modified shell with wastewater. One way analysis of variance (One-ANOVA) was used for data analysis to measure the variations of metal concentrations using SPSS 22.0 software (SPSS Inc, IBM, Chicago, IL).

RESULTS

The mean ±SD values of various physico-chemical and heavy metal characteristics of control (untreated waste water) and treated wastewater are presented in Table 1. The results revealed that wastewater contained significant quantity of nutrients like Na^+ , K^+ , Ca^{2+} , Mg^{2+} , TKN, PO_4^{3-} , SO_4^{2-} and heavy metals such as Cd, Cr, Cu, Fe, Mn, Pb and Zn. These are very important parameters that lead to water and soil contamination. The values of various wastewater characteristics like TDS (2860.00 mg L⁻¹), BOD (1450.30 mg L⁻¹), COD (3225.00 mg L⁻¹), Ca^{2+} (650.90 mg L⁻¹), TKN (420.70 mg L⁻¹), Cu (10.36 mg L⁻¹), Fe (16.84 mg L⁻¹), Mn (6.67 mg L⁻¹), Pb (9.64 mg L⁻¹), Zn (18.66 mg L⁻¹), SPC (7.68×10⁸ SPC ml⁻¹) and MPN (8.69×10⁵ MPN 100 ml⁻¹) were recorded beyond the prescribed BIS standards of irrigation water (Table 1). The higher TDS in the wastewater is likely due to the occurrence of fecal matter while the more BOD and COD are associated with the presence of higher biodegradable organic waste in the wastewater. The higher number of SPC and MPN in the wastewater are the indicator of fecal pollution and pathogens. TKN and PO_4^{3-} were also recorded higher in the wastewater and are associated with eutrophication of aquatic ecosystems. Therefore, various parameters clearly indicated that the wastewater was highly rich in plant nutrients, heavy metals and contagious.

Chemical analysis

Experimental results showed that the percentage removal Cr (VI) increases with the increasing amount of adsorbent up to 5.4 g for treated shells by phosphoric acid 2%. After this dose of adsorbent no significant change was observed, but for untreated almond shells percentage removal Cr (VI) increases with the increasing amount of adsorbent.

Metal accumulation in shells increased significantly with an increase in applied metal solution concentration in both lead (figure 2) and

Table 1. Physico-chemical and heavy metal characteristics of control (untreated wastewater) and treated wastewater by *A. scoparisa* shells after 60 hours

Parameters	Untreated wastewater by <i>A. Scoparia</i> shell	^a Treated wastewater water by <i>A. Scoparia</i> Shell	BIS for irrigation water
TDS (mg L ⁻¹)	2920.00±5.80	***180.50±3.64	1900
EC(dS m ⁻¹)	4.50±1.05	0.12±0.10	-
pH	6.92±0.55	^{NS} 6.85±0.36	5.5-9.0
BOD (mg L ⁻¹)	1450.30±7.88	***4.20±0.70	100
COD (mg L ⁻¹)	3436.00±6.00	***6.32±1.80	250
Na ⁺ (mg L ⁻¹)	286.95±4.20	***10.60±1.15	-
K ⁺ (mg L ⁻¹)	380.70±3.57	***6.33±1.40	-
Ca ²⁺ (mg L ⁻¹)	650.90±4.65	***28.95±2.30	200
Mg ²⁺ (mg L ⁻¹)	266.44±3.73	**18.76±2.65	-
TKN (mg L ⁻¹)	562.56±2.89	***33.18±3.76	100
PO ₄ ³⁻ (mg L ⁻¹)	120.68±1.28	***0.33±0.06	-
SO ₄ ²⁻ (mg L ⁻¹)	923.11±2.85	*168.94±2.80	1000
Cd (mg L ⁻¹)	2.86±0.06	***0.13±0.03	2
Cr (mg L ⁻¹)	11.24±0.02	***1.02±0.01	2
Cu (mg L ⁻¹)	10.36±1.05	**2.64±0.12	3
Fe (mg L ⁻¹)	16.84±1.15	*3.85±0.04	1
Mn (mg L ⁻¹)	6.67±1.04	***0.48±0.06	1
Ni (mg L ⁻¹)	3.18±0.02	*1.08±0.04	0.2
Pb (mg L ⁻¹)	10.47±3.28	***0.81±0.03	1
Zn (mg L ⁻¹)	24.49±1.11	*7.08±2.03	15
SPC (SPC ml ⁻¹)	8.67×10 ⁸ ±13	**1.84±×10 ³ ±3	10000
MPN(MPN100 ml ⁻¹)	9.11×10 ⁵ ±10	**2.88×10 ² ±11	5000

Mean ± SD of six values; a treated wastewater. Significant -***p>0.1 level; **p>0.01% level; *p>0.05 level; NS-not significant.

Cr (III) and Cr (VI), (Figures 3 and 4 respectively) treated groups. In Figures 2, 3 and 4 the mean contents of heavy metals are reported. The metal concentrations remained high in shells in Cr (III) and Cr (VI), treated groups, while lead metal content was higher in treated shells than untreated shells. The ratios of shells/water ratios were calculated to indicate the translocation efficiency of Pb and Cr from water to the adsorbents while for the results of nickel translocation was not significant. The Cr (III) concentrations in samples after 10, 20, 30 and 40 hours are higher in shells than Cr(VI), hence the translocation factor ratios were less than one for Cr (VI) treated samples shows that this method is highly suitable for adsorbing Cr(III) to the Cr (VI). Even though the Cr(VI), concentration of shells of Cr treated samples in 48 hours treated samples is higher compared to controls solutions, the extent of metal accumulation and uptake

efficiency of Cr(III) was lower than that of Cr(VI), in long term contaminated situation study. Most of shells in Cr (VI) samples deformed after 60 hours remaining in contaminated water. The effect of



Fig. 1. Location of *Amygdalus scoparisa* sampling collection

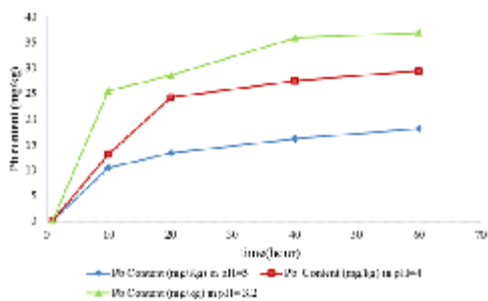


Fig. 2. The mean content of Lead (mg kg^{-1}) in *A. Scoparia* treatment groups in contaminated 100, 200 and 300 mg kg^{-1} Lead solution in the form of $\text{Pb}(\text{NO}_3)_2$ in different pH and contact times (hours)

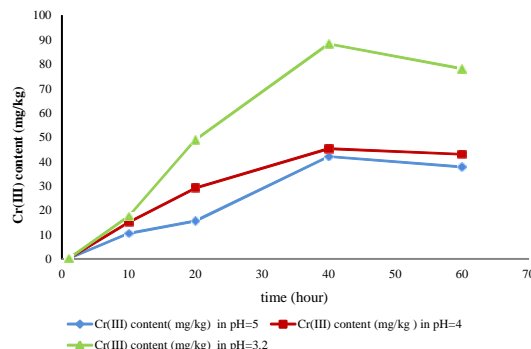


Fig. 3. The mean content of Cr(III) (mg kg^{-1}) in *A. scoparia* treatment groups in contaminated 100, 200 and 300 mg kg^{-1} chrome solution in the form of $\text{Cr}(\text{NO}_3)_3$ in different pH and contact times (hours)

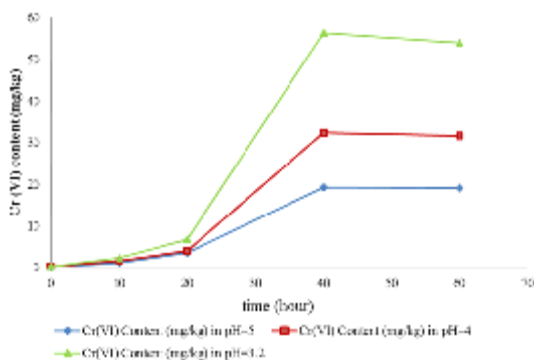


Fig. 4. The mean content of Cr (VI) (mg kg^{-1}) in *A. Scoparia* treatment groups in contaminated 100, 200 and 300 mg kg^{-1} Chrome (+6) solution in the form of $\text{Cr}(\text{NO}_3)_6$ in different pH and contact times (hours)

adsorbent dose on Cr (VI) uptake was investigated by varying the shell adsorbent dose (1, 2, 3, 4 and 6 $\text{g } 100 \text{ ml}^{-1}$) for a time interval of 0- 60 hours min (Figure-4).

DISCUSSION

The results of present study revealed adsorption capacity of Cr (VI), Cr(III), Pb and Ni onto modified almond shells by phosphoric acid was investigated in a batch system by considering the effects of various parameters like contact time, initial concentrations, pH, temperature, adsorbent dose and particle size. The adsorption was pH solution dependent and the maximum adsorption was observed at solution pH of 3.23. Moreover, contents of different heavy metals in the contaminated water showed significant ($p < 0.05$) and positive correlation with contents of Pb ($r =$

+82 to $r = +96$), Cr^{6+} ($r = +74$ to $r = +94$), Cr^{3+} ($r = +84$ to $r = +98$), Ni ($r = +33$ to $r = +42$) in the wastewater and *A. Scoparia* modified shell, respectively. The amounts of Cr (VI) adsorbed increased significantly with increase in dose of *A. scoparia* adsorbent ($p < 0.05$) and their contact time ($p < 0.05$). The results of this study revealed that *A. scoparia* can accumulate high level of lead, Chrome (VI) and (III) in a short time and their uptake rate by plant is significantly affected by their concentrations in the contaminated water ($p < 0.005$). A contact time of 48 hours by almond shell was found to be optimum and 87.1% Cr (VI), 89.8% Cr(III), 84.4% Pb and 48.1% Ni was removed. Experimental results showed that low cost bio-sorbent was effective for the removal of pollutants from aqueous solution.

According to ATSDR, current evidences indicate that Cr (VI) is a cancer agent only by inhalation. Chronic inhalation studies on mice exposed to airborne Cr (VI) suggest that Cr (VI) is an animal carcinogen¹⁴⁻¹⁵. The mice developed lung tumors from exposure to 4.3 mg m^{-3} of Cr(VI). However, a number of chronic animal studies showed no carcinogenic effects in rats, rabbits, or guinea pigs exposed to 1.6 mg/m^3 of Cr(VI)¹⁴⁻¹⁷. Thus, cancer effects on animals seem to depend on the type of animal. Eating small amounts of chromium (VI) is not harmful. However, eating or drinking large amounts in food or water can cause an upset stomach, ulcers, convulsions, and damage the kidneys and liver. This type of exposure can be fatal. There is not enough data to know if eating or drinking chromium (VI) causes cancer¹⁴⁻¹⁷. The results of this study revealed that *A. scoparia*

can accumulate high level of Chrome (VI) and (III) in a short time and their uptake rate by plant is significantly affected by their concentrations in the contaminated water ($p < 0.005$).

CONCLUSION

The present investigation shows that the almond shells are effective and inexpensive biosorbents for the removal of Cr (VI) from aqueous solutions. The removal of Cr(VI) from aqueous solutions strongly depends on the contact time, initial concentration, pH, temperature, agitation speed, absorbent dose and particle size. The amounts of Cr (VI) adsorbed increased with an increase in dose of both adsorbents and their contact time. A contact time of 48 hours was found to be optimum. The maximum adsorption capacity was obtained at solution pH of 3.2.

A contact time of 48 hours by almond shell was found to be optimum for Nickel adsorbing and 48.1% Ni was removed. Although Ni is required in minute quantity for body as it is mostly present in the pancreas and hence plays an important role in the production of insulin. EPA has recommended daily intake of Ni should be less than 1 mg beyond which is toxic¹⁷. Ni has been identified as a suspected carcinogen and adversely affects lungs and nasal cavities¹⁸.

This research conduct adsorption of heavy metals by agricultural waste and by-product and proved that this friendly method should gain more attention and research interest for the removal of heavy metals from waste water due to its surface area, adsorption capacity and plenty abundant in nature must be followed seriously.

Also, this research suggests more investigations by other genera and families of cost-effective waste agricultural products applying as adsorbents for these heavy metals and other toxic metals such as cadmium, arsenic and Mercury.

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