Investigation of the possible presence of Cr (VI) in almond kernel and its reduction from aquatic solution using almond green hull

Negin Nasseh¹, Lobat Taghavi², Behnam Barikbin³*, Maryam Khodadadi³, Hadigheh Dorri³

¹Young Researchers and Elites Club, Science and Research branch, Islamic Azad University, Tehran, IR Iran.
²Department of Environment and Energy, Science and Research Branch, Islamic Azad University, Tehran, IR Iran
³Social Determinants of Health Research Center, Birjand University of Medical Sciences, Birjand, IR Iran

*Corresponding author: Behnam Barikbin, Social Determinants of Health Research Center, Associate Professor, Department of Environmental Health Engineering, Faculty of Health, Birjand University of Medical Sciences, Birjand, IR Iran Tel: +985632381251, Fax: +985632440450, Email: B_barikbin@yahoo.com

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Abstract

Background: Heavy metals are the most important factors of environmental pollution that are accumulated in soil and plant through irrigation and taking these contaminated herbs by human and animal ultimately hurt community health and cause various diseases including cancer. This study was done to determine the chromium (VI) in almond kernel and investigate almond green hull adsorption to remove this metal from the aqueous solutions.

Methods: In this study, the concentration of hexavalent chromium in Birjand almond kernel using SEM and EDX imaging is investigated and its adsorption rate by almond green hull of the area through aqueous solutions was determined by changing the contact time, concentration, pH, adsorbent dose and the temperature. Chromium concentration was determined according to standard method by colorimetric method and using a UV / VIS spectrophotometer at 540 nm.

Results: This study showed that irrigating agricultural land of this district does not cause the accumulation of hexavalent chromium in almond kernel. Removal of hexavalent chromium is also highly dependent on pH of the solution so that, the results indicate a high removal at pH=2. Also, with increasing adsorbent dosage, contact time and temperature, the removal rates increased and because of the limited sites in the adsorbent, by increasing the initial concentration of chromium, the removal efficiency decreased.

Conclusions: Cr (VI) was not observed in almond kernel, although almond green hull removes this metal effectively from aqueous solutions.

Keywords: Adsorption; Aquatic Solution; Hexavalent Chromium; Almond Green hull; Almond kernel

1. Introduction

One of the important contaminating sources is heavy metals, was entrance to water resources across various methods is one of the serious environmental and health problems of the human being. Stability of heavy metals in the environment and their entrance to food chain and their accumulation properties cause incidence of acute and chronic effects in humans and other living creatures (1). Heavy metals are abundantly found as naturally occurring compounds and enter water cycle through various processes such as geochemical processes. Furthermore, usage of heavy metals in human life along with extraction of these elements from inorganic minerals have caused a significant amount of these metals to enter the environment and especially the flow of surface and groundwaters (2).

Heavy metals cause imbalance in living creatures especially human beings through various mechanisms and develop a wide range of complications and disorders in all organs. Among the most important complications and disorders caused by them are carcinogenicity, affecting the central and peripheral nervous system, effect on the skin, effect on the hematopoietic system, effect on the cardiovascular system, damage to the kidneys, and accumulation in the tissues. So far among heavy metals, lead, mercury, and cadmium have led to disastrous events
and have been considered as history in toxicology books. Metal ions are essential for many biological processes including respiration and growth. On the other hand, accumulation of essential metals including zinc and copper or toxic nonessential metals such as cadmium and mercury is dangerous. Some genetic disorders or nongenetic diseases are caused by deficiency or accumulation of heavy metals. For example, shortage of copper develops serious diseases such as Alzheimer's, Parkinson's, Menks Syndrome, and Wilson Syndrome. Deficiency of zinc also causes several syndromes including Accrodermatitis. Cadmium (II) is a nonessential metal and unlike copper and zinc it is toxic even at very lower concentrations. Among contaminations caused by industrial cadmium is Itai-Itai disease (3).

Chromium is an essential rare element for human. Trivalent chromium plays a key role in human nutrition and its deficiency causes cardiovascular problems, metabolic disorders, and diabetes. However, if the amount of trivalent chromium used by human exceeds the normal value, it adversely affects the human health and causes skin itching, for example (4).

Hexavalent chromium is very dangerous for the human, especially for those who work in steel and textile industry and it is more dangerous. This type of chromium has various effects on the human health. Typically, chromium compounds can be found in leather products. This compound causes severe allergies in people, such as itching. When one breathes this type of chromium, the nose is stimulated and nose bleeding occurs. Other diseases caused by hexavalent chromium are itching, peptic ulcer, problems in respiratory system, deficiency in the immune system, kidney and liver damage, changes in genetic compounds, lung cancer, and even death in some cases (5). The dangers caused by chromium on human health are dependent on its oxidation state. Based on the national toxicology program of the US (NTP) and the list associated with it, trivalent chromium and its resulting compounds have no carcinogenic effects on experimental animals. However, the results obtained from NTP regarding hexavalent chromium and its resulting compounds demonstrate substantial evidence regarding the carcinogenicity of this chemical element on experimental animals. These compounds are calcium chromate, chromium trioxide, lead chromate, strontium chromate, and zinc chromate. The international agency of cancer (IAC) has classified chromium and the compounds of trivalent chromium in the list of the third group (i.e. a group of elements that are not carcinogenic) (6).

Therefore, considering the hazards of accumulation of this heavy metal in the human body and, treating it from drinking water which is one of the important sources of entrance of this heavy metal into the human body, various methods including chemical deposition, reverse osmosis, electro dialysis, ultrafiltration, and ion exchange have been investigated for removing chromium by various researchers. These processes are mostly costly and their operation requires experts (7).

Absorption is a very effective process with various uses and is considered an economic and efficient method today for removing heavy metals from drinking water. In comparison with chemical methods, this method is effective at most 70% for removing heavy metals. However, what distinguishes this method over other methods is its flexibility, in expansiveness and availability, being environmentally friendly, reusability and recoverability, and high absorption rate and power. Overall, adsorption is the process of accumulation of compounds at the interface between two phases. Active carbon is one of the most effective compounds that is used for removing hexavalent chromium and as its recovery is costly, researchers have always been seeking for new adsorbents (8). Therefore, the practical objective of implementing this plan is to use inexpensive materials and compounds including Green almond shell wastes, which have found various uses thanks to fast and considerable removal of most heavy metals.

So far, numerous studies have been conducted regarding removal of hexavalent chromium using inexpensive adsorbents in Iran and other countries of the world. For example, in a research application of biological adsorption process by pomegranate kernel powder in removing hexavalent chromium from aqueous environments was investigated. The results indicated that by increasing the mass of the adsorbent and contact time, the removal efficiency increased, while increase in the pH and initial concentration of the chromium leads to diminished removal efficiency. According to the results, the best removal efficiency has occurred at an acidic pH and adsorption had reached equilibrium within 120 min. The obtained results showed that the pomegranate kernel powder is a suitable natural adsorbent for removing hexavalent chromium (9). The results of the research called investigation of removal of eczema and chromium using harmel powder from...
aqueous environments indicate that the greatest removal of hexavalent chromium occurred at pH=1.5 and the optimal dose of the adsorbent was obtained to be 10 g/L due to the limited active sites in the adsorbent, with the increase in the initial concentration of chromium, the removal efficiency decreased and with prolongation of contact time and increase in the mixing rate, the removal efficiency grew (10). A group of researchers tried to remove hexavalent chromium from aqueous environments using holly modified sawdust. In this study, changes in pH, contact time, adsorbent dose, and initial concentration of hexavalent chromium were examined in a batch system. The results obtained from the experiments suggested that the removal efficiency of hexavalent chromium diminished with increase in pH and initial concentration of chromium. Overall, the results showed that holly modified sawdust can be used as an effective and inexpensive method for removing hexavalent chromium from aqueous solutions (11).

Similarly, another research titled removal of hexavalent chromium using newspaper was performed. In this study, the greatest removal of the metal occurred at the concentration of 50 mg/L and the high removal capacity of chromium ion was observed at 60°C within 5 h. in this study, newspaper was introduced as a very good adsorbent for removing hexavalent chromium (12). Another researcher performed a study called equilibrium and kinetic studies of removal of chromium (VI) ion by peanut skin in the form of a green approach. In this study, the effects of the solution pH, initial concentration of the metal ion, mixing rate, and contact time were investigated. Removal of metal ions was dependent on their physiochemical properties and concentration of the adsorbent. The greatest removal happened at pH=2 (13). The powder of needle-like pine fruits was another adsorbent which was used for removing hexavalent chromium from aqueous solutions. The results of this research showed that the adsorption process is highly influenced by the final pH of the solution (14). In 2012, Zozeli et al performed a study regarding usage of agricultural wastes of citrus skin in removing cadmium and chromium from aqueous solutions. The results demonstrated that the maximum removal efficiency of cadmium and chromium by modified orange and sour orange shortcut skin is over 64.99%. The optimal pH for removing cadmium and chromium by the modified orange skin adsorbent is 9 and 5.8, respectively, while by sour orange it is nine (15). Furthermore, through adsorption on a strong basic anion resin, attempts have been made to remove hexavalent chromium from aqueous solutions. In this study, removal of hexavalent chromium was examined through adsorption on a strong basic anion resin with changing pH, contact time, initial concentration of the adsorbent, and initial concentration of the hexavalent chromium in a batch system. The results revealed that the removal efficiency of hexavalent chromium decreased with increase in the pH and initial concentration of the chromium (16). Considering usage of almond green hull as a bioadsorbent, Nasseh et al (1392 (1)) used almond green hull for Ghaen Region and its resulting ash to remove hexavalent chromium. In this research, it was found that hexavalent chromium removal had a significant increase with the decrease in artificial wastewater from pH (pH=2). Furthermore, with the increase in contact time and temperature, the removal percentage increased and due to the limited sites in the adsorbent, with the increase in the initial concentration of chromium, the removal efficiency diminished. Further, with the increase in the adsorbent dose, the removal percentage increased in the bioadsorbent, while in the carbon resulting from it, it first increased and then decreased (17). In another study, attempts were made to study removal of hexavalent chromium using almond variety green hull from Mahiroud region, one of the dependencies of RazaviKhorasan province with a very soft and thin material and with a granulation of 10. The results of that study also indicated that almond green hull is also able to remove these heavy-metal when compared with other bioadsorbents used in other studies with an acceptable efficiency, despite being thin and feeble (18). Almond green hull used in this research has different influential factors (including material, thickness, and granulation), with those of the one used in the research by Nasseh et al. therefore, the aim of this study is to investigate application of inexpensive and available bioadsorbent of almond green hull of Birjand city with granulation of 10 with a material with medium thickness) with different granulation and a material between two varieties mentioned in the references to solve the problem of existence of hexavalent chromium in some of the aqueous solutions of this province, where it is naturally found in them. The effect of a number of influential factors such as the adsorbent’s dose, initial concentration of the metal in the solution, adsorption pH, i.e. contact time, temperature, and material of the adsorbent.
is also investigated. Furthermore, another distinctive aspect of this paper with other papers is that in addition to investigating the level of adsorption of hexavalent chromium using a bioadsorbent, the probable extent of accumulation of hexavalent chromium metal in almond kernel of this region was also studied.

Chromite mine is located some kilometers away from Birjand city, the capital of southern Khorasan province, which introduces chromium heavy-metal into the waters of this region naturally. Therefore, the residents of this region have an unhealthy water to drink. Furthermore, farmers also use these waters for irrigation of agricultural lands. Therefore, over time chromium enters vegetation and agricultural crops and in turn the food chain of the residents of this region. On the other hand, almond is one of the native plants of this province, which can be found across various parts of it and is considered the commercial and economic product of the region. The farmers of this region separate its green hull following fruit harvesting from the trees and liberate it as waste in the environment. This causes both contamination and ruins the beauty of the environment. As various studies have confirmed high levels of hexavalent chromium in the water of this region (4), in this research first the extent of adsorption of this heavy-metal in almond kernel was investigated and then using the bioadsorbent of its green hull, chromium was removed from aqueous solutions of the region. Moreover, by preparing EDX and SEM images, the extent of existence of hexavalent chromium in almond kernel and its green skin before and after the adsorption was examined.

2. Methods

2.1. Preparation of almond kernel to investigate the extent of accumulation of hexavalent chromium in it:

The almond of Birjand region was harvested in the harvesting season from the trees. Next, its green and wooden skin was peeled off and the almond kernel was beaten by a glass Mortar. After minimizing its fat level (the fat of the kernel causes damage to the imaging device and development of error in it) by the laboratory, the extent of accumulation of hexavalent chromium in it was examined using SEM and EDX device.

2.2. Preparation of the adsorbent:

In the harvesting season of the almond fruit from the tree, its green skins were collected from the region and after washing with distilled water at room temperature, they were dried for 1 week such that their humidity would be completely removed. Following this stage, the dried skins were crushed and using ASTM standard sieve with a mesh size of 5, they were granulated and the adsorbents that passed through the sieve were collected.

Further, the morphology and elements present in the structure of the adsorbents were also investigated concurrently by EDX and SEM devices in the central laboratory of Mashhad Ferdowsi University.

2.3. Preparation of the solution:

To prepare hexavalent chromium solution with different concentration, potassium dichromate with a purity degree of 95% made by Merck, Co was used. First, 1000 mg/L of chromium solution was prepared by adding 2.827 g potassium dichromate (K₂Cr₂O₇) to a 1000-ml volumetric balloon using double distilled water. Next in every stage the chromium solution with the intended concentrations was prepared by adding a certain amount of the just prepared solution (1000 mg/L) to 1000 ml of double distilled deionized water in a volumetric balloon. For example, to prepare hexavalent chromium 20 mg/L solution, 20 ml of the initial fabricated solution (1000 mg/L) was withdrawn by bubble pipette and then added to 1000-ml volumetric balloon and until reaching this volume, double distilled water was employed.

2.4. Adsorption experiments:

All of the adsorption experiments except for the stage of investigating the effect of changes in temperature on the removal percentage were performed at 25±1°C and the pH of the solution was adjusted using pHmeter (pH-meter 765, Calimatic Co, Germany) using HCl and NaOH 0.1 N solution. In every stage, a certain and precise amount of the adsorbent was added to the samples and mixed using a shaker device (KS260, IK Co, Germany) at 3000 rpm within a certain period of time. The effect of different parameters, the initial pH of the solution within the range of 2-10 (2, 4, 6, 8, and 10), the amount of the adsorbent (2-24 g/L) (2, 4, 6, 8, 16, and 24), 10-100 mg/L concentration (10, 20, 40, 60, 80, and 100), mixing time of 1-60 min (1, 2, 3, 5, 15, 30, 45, and 60 min), and temperature of 5-50°C (5, 10, 20, 40, and 50) was investigated using incubator shaker device (Aerotron, INFORS Co, Switzerland).
Following the preparation stages and applying different doses of almond green hull individually, with different concentrations of hexavalent chromium, the solutions containing the adsorbent were passed through a filter paper 125 mm (filter papers Whatman 42), and the final concentration of the hexavalent chromium was measured using spectrophotometer UV/Vis spectrometer T80 at the wavelength of 540 nm according to the standard method 3500-Cr B (19). The removal percentage of hexavalent chromium (R%) as well as the equilibrium adsorption capacity of the adsorbent (q_e) were calculated in investigated considering the changes in the adsorbent dose and chromium concentration. To ensure the accuracy of the results, each experiment was replicated two times and its mean was reported.

\[ R = \frac{(C_o - C_f)}{C_o} \times 100 \]  (Relation 1)

\[ q_e = \frac{V}{M} \times (C_{in} - C_{out}) \]  (Relation 2)

C_o and C_f are the initial and final concentration, respectively (mg/l)

3. Results

3.1. The effect of pH:

The pH of the solution indicated a certain effect in adsorption of chromium. With the increase in pH, adsorption of hexavalent chromium diminished significantly, such that the removal efficiency dropped from 99.92 to 87.49% (Diagram 1).

Diagram 1. The effect of solution pH on Cr(VI) removal by adsorption on Almond Green Hull. Adsorbent dose: 8 g/L; the initial concentration of chromium: 20 mg/l; contact time: 60 min; temperature: 20 °C; Stirring speed: 300 rpm.

3.2. The effect of the adsorbent dose:

Diagram 2 indicates the effect of adsorbent’s dose on the removal efficiency of hexavalent chromium. As can be observed in the diagram, with the increase in the adsorbent’s dose from 2 to 24 g/L, the removal efficiency first increased and then decreased. The optimal dose for this adsorbent is 2 g/L.

Diagram 2. The effect of adsorbent dose changes on the Cr (VI) removal. pH=2, the initial concentration of Cr: 20 gr/l, contact time: 60min, temperature: 25°CStirring speed: 300 rpm.

3.3. The effect of the initial concentration of chromium:

Considering Diagram 3, the removal efficiency decreases with the increase in the initial concentration of hexavalent chromium from 10 to 100 mg/L.

In this section, the equilibrium concentration for performing other stages of the work with artificial wastewater was chosen to be 20 mg/L.
3.4. The effect of contact time:
As can be seen in Diagram 4, with the increase in the contact time from 1 to 60 min, the removal efficiency grew from 70.64 to 99.42% with the initial concentration of hexavalent chromium as 20 mg/L.

3.5. The effect of temperature:
Diagram 5 represents the increase in the removal efficiency of hexavalent chromium from 47.25 to 99.92% with the increase in temperature from 5 to 50°C.

Diagram 3. The effect of The initial concentration of chromium on removal efficiency of Cr(VI). pH=2; adsorbent dose: 4 gr/l; contact time: 60 min; temperature: 25 °C; Stirring speed: 300 rpm.

Diagram 4. The effect of contact time on Cr(VI) removal. pH=2; adsorbent dose: 4 gr/l; the initial concentration of chromium: 20 gr/l; temperature: 25°C; Stirring speed: 300 rpm.

Diagram 5. The effect of temperature on the Cr (VI) removal. pH=2; adsorbent dose: 4 gr/l; the initial concentration of chromium: 20 gr/l; contact time: 60 min; Stirring speed: 300 rpm.
3.6. The effect of the adsorbent material:

![SEM images of Almond Green Hull & Almond Kernel](image1)

- **A**: Before contact
- **B**: After contact
- **C**: Almond kernel

![EDX photos of Almond Green Hull & Almond Kernel](image2)

- **A**: Before contact
- **B**: After contact
- **C**: Almond kernel

*Figure 1. SEM images of Almond Green Hull & Almond Kernel*

*Figure 2. EDX photos of Almond Green Hull & Almond Kernel*
4. Discussion

The present study evaluated the BSE screening behavior of housewives and the related factors using the Transtheoretical Model. Based on the findings, majority of studied women (75.8%) were in the preaction stage (i.e. pre-contemplation, contemplation and preparation) that means they had no experience of breast-examination. In a similar way, Vahedian (2015) and Pirasteh (2013) indicated that most women in their studies were in preaction phase and did not undergo any breast self-examination (19, 20). In line with our findings, the results of different studies on breast cancer screening behaviors including Charkazi (2013) and Moodi et al (2012) confirm the low performance of women in breast cancer screening behaviors (21, 22).

In the current study, the level of education was one of the factors that influenced breast self-examination so that with increasing educational level of women, also increased of BSE. Such a finding was compatible with findings by Bahrami (2015), Reisi (2011), Salimi Pormehr (2010) and Farshbaf Khalili (2009) (13-16). In Okobia’s research (2006) BSE was significantly associated with a higher education level (23). The reason for this might have been the increased awareness of BSE among women with higher education, their ability in obtaining health-related information through various media especially internet and access to facilities and services of breast cancer screening.

In the present study, there was a significant association between the family history of breast cancer and breast self-examination. Moreover, women with a positive family history of breast cancer had a better performance in BSE than the others. Bahrami’s (2015) and Farshbaf Khalili’s (2009) findings also approve this finding (13, 16). Li et al (2007) also regard the presence of a family member with breast cancer as the strongest motivation for conducting mammography and breast self-examination (24). Positive family history makes the women feel at risk for breast cancer and increases their sensitivity. As a result increased awareness of breast cancer, its prevention and early detection methods, leads to the optimal performance of this group of women.

According to our findings, there was a correlation between BSE and awareness level as confirmed by Didarloo (2016), Parsa (2011), Salimi (2010) and Dundar (2006) (15, 25-27). BSE was more frequent among individuals who were more aware of this behavior than others. This further clarifies the effect of education and awareness as two contributing factors to the test implementation. Given that the level of education was also a factor affecting the BSE behavior, high level of education was considered an effective factor in increasing the individuals’ awareness that in turn led to high performance of the women investigated.

In the present study, age and marital status had no relationship with BSE that was in consonance with findings by Bahrami (2015) and Farshbaf Khalili (2009). Because the majority of women participating in the study were married, the relatively large number of participants in this group might have had an important influence in this respect (13, 16).

Based on the results of our study, the household income was not also significantly associated with BSE. However, Khalili Farshaf (2009) showed that people who had higher levels of income had a better performance in BSE (16). Given that BSE is a cost-free way and can be learned with the least possible cost, it can be said that household income does not play a major role in BSE.

As for the fact that the Stages of Change Theory has been rarely applied in the study of BSE screening behavior, it can be seen as one of the advantages of this study. Nonetheless, the results of the study cannot be generalized to all women living in Birjand because the research only focused on housewives aged between 20-40 years, who referred to healthcare centers of the city. It is thus suggested that future studies conduct a community-level data collection to present a better analysis of breast self-examination screening behavior.

5. Conclusion

This study revealed the low performance of women concerning breast self-examination. Because data collection was conducted in healthcare centers, as one of the most important sources of health information, implementing optimal training programs in such centers is highly necessary to increase women’s awareness and performance regarding BSE.

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