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Analysis of Carbonated Biosorbents Application in Heavy Metal Removal from Synthetic Wastewater

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ABSTRACT

Purpose: This study aimed to analyze the effects of removal of hexavalent Chromium using carbonated almond green hulls. In the present study, derived carbon from almond green hulls of zonal district of Iran were used to remove hexavalent Chromium from Synthetic wastewater.

Materials and Methods: The effects of pH (2-10), Adsorbent dose (2-24 g/L), Cr (VI) concentration (10-100 mg/L), Contact time (1-60 min) and temperature (5-50°C) were studied. The experimental data fitted well to Langmuir isotherm ($R2 = .853$; maximum adsorption capacity 1.90 mg/g). At the end, to assess hexavalent Chromium, Spectrophotometer UV/VIS Spectrometer T80+ at 540 nm wavelength was used.

Results: The findings of the present study revealed that hexavalent Chromium removal was highly dependent on the pH. Surprisingly it was understood that due to limited space in the adsorbent, the increase in the initial hexavalent Chromium density caused the removal efficiency to decrease.

Conclusion: Carbonated almond green hull does efficiently remove hexavalent Chromium from industrial water wastes.

Keywords: heavy metals; hexavalent chromium; adsorption; wastewater; carbon, biosorbents.

INTRODUCTION

Hexavalent chromium or Cr(VI) is the most dominant heavy metal in the natural environment, and is highly toxic even when present at negligible concentrations (50 g L^{-1}) in water bodies.[1] Being an anion, Cr(VI) is highly mobile and enters the soil environment easily posing a tremendous risk for groundwater contamination. Cr (VI) has catastrophic health effects on the human body which include respiratory diseases, skin ulceration, nasal irritation and lung cancer.[2] Genotoxicity and carcinogenicity of Cr (VI) has become a serious issue leading to classification of Cr (VI) as a Group A inhalation carcinogen by United States Environ-mental Protection Agency (US EPA),[3] and Group I human carcinogen by International Agency for Research on Cancer (IARC). Due to its serious impact on environment and people's health, industrial effluents containing Cr (VI) must be treated as a rule (Grevatt 1998). The maximum permissible limit for Cr (VI) in inland water is 0.1 mg L^{-1} and 0.05 mg L^{-1} for potable water.[3,4]

The methods employed for the removal of Cr (VI) from aqueous solutions, include chemical oxidation–reduction, ion exchange, electro dialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis, chemical precipitation and adsorption.[5] Most of these methods suffer from drawbacks such as high capital and operational costs and problems in the disposal of the residual metal sludges.[6] Many studies

have appeared on the development of low-cost activated carbon adsorbents produced from cheaper and readily available materials in the literature.[7] Activated carbons with their large surface area, micro porous character and chemical nature of their surface have made them potential adsorbents for the removal of heavy metals from industrial wastewater.[6]

Adsorption is a highly effective process which has many applications and is regarded as a cost-effective and efficient method for the removal of heavy metals from aqueous media.[8] Different materials can be used in the adsorption process such as powder and granular activated carbon, ash, bentonite and kaolinite clay. Activated carbon is one of the most effective substances used for the removal of chromium.[9]

A number of studies for removal of Cr (VI) have been reported using adsorbents like activated groundnut husk carbon,[10] coconut shell activated carbon,[11] coconut shell, wood and dust coal activated carbons,[12] sawdust carbon,[13] sawdust and used tyres carbon,[14] rice husk carbon,[15] hazelnut shell carbon[16] and almond shell carbon[17] and so on.

According to the Institute of Standards and Industrial Research of Iran, the maximum permissible level of chromium in drinking water is 0.01 mg/l (ISIRI, 1053).[18] Standards and regulations regarding the disposal of industrial wastewater are becoming increasingly strict. On the other hand, because of the development of different industries and extensive use of metals, new, efficient and low cost methods for the treatment and removal of pollutants especially Cr (VI) should be adopted.[19]

Sahranavard and colleagues carried out a research entitled *Biosorption of Hexavalent Chromium Ions from Aqueous Solution Using Almond Green Hull as a Low-Cost Biosorbent*.[20] The almond green hull used in that study was 400µm in size. The distictive features of the present study are the thickness of almond hull, its mesh size and the use of carbon obtained from burning of the almond green hull.[20] Hasar and Cuci investigated hexavalent chromium, zinc and nickel removal using activated carbon obtained from almond shell.[2-23] However, the present study has used carbon obtained from almond green hull as biosorbents and has shown an acceptable removal percentage without spending on activated carbon production.[21-23] Ahmadpour and colleagues,[24,25] Doulati and colleagues,[26] and Homem[27] used almond shell for the removal of heavy metals, Direct Red 80 dye and amoxycillin, while in the present study, Cr (VI) removal has been carried out using almond green hull.

In this study it is hypothesized that resultant carbon of Almond green hull efficiently removes Chromium (VI) from synthetic wastewater. This research is examining the effects of different factors like exposure time, pH, chromium initial concentration, adsorbent dose, temperature and adsorbent type on adsorption process in terms of the removal of Cr (VI) from aqueous media.

MATERIALS AND METHODS
Preparation of Adsorbent

Almond green hull was obtained from a local fruit field in the eastern part of Iran (Birjand). The sorbent was washed thoroughly several times with deionized water to get free of any dust or pollution and was dried in room normal temperature for some days. Then, dried sample was burnt and then turned into carbon in a furnace (F6000) at 700°C. Finally, the burnt hull was ground and sieved (in two ranges of 2< to <4 mm) and stored in special containers. The elements and morphology of the adsorbents' structure were analyzed using SEM and EDX micrographs.

The chemicals needed in the present study are made by the German company of Merck and the used devices are: pH meter for pH measurement, pH -meter 765 made in German climatic company, shaker made by IK company by which the sample contaminated water with Cr (VI) are combined with adsorbents and the digital KERN balance made in Germany to weigh all the solid chemicals. The Incubator shaker, model Aerotron made by Sweden Infors Company was also used to change the temperature. To even the samples, watman 125mm paper was used.

Reagents and Solutions

At first, one mill molar of Cr (VI) stock solution was prepared. This solution was made by the dissolve of 2.827gr, of $K_2Cr_2O_7$ purity degree of 95%, made by the German Merck in 1 liter of distilled water (APHA, etal 2005). To make the standard solution ready for experimentation, the stock solution was attenuated. In each step, the experiment was triplicated.

Adsorption Experiments

Batch adsorption studies were performed at different pH (2, 4, 6, 8, and 10), sorbent dose (2, 4, 8, 16 and 24 g/L), initial metal-ion concentration (10-100 mg/L), contact time (1, 2, 3, 5, 15, 30, 45, 60 min), temperature (5, 10, 20, 40 and 50°C), and particle size (mesh No. 5 and 10) to obtain the equilibrium data. All experiments were performed in triplicate and the average results were reported. In each experiment, 25 cc of the sample solution (with certain density and dose of carbonated of Almond

Green Hulls) was mixed in 25± 1 °C in shaker with 300 turns/min. After step stage and exposing various doses of carbonated almond green hull to different concentrations of Cr(VI) separately, the solutions containing adsorbent were filtered through Whatman filter paper no. 42 (125 mm). Cr (VI) concentrations in the solutions were determined by the standard colorimetric method[28] with 1, 5-diphenylcarbazide in acetone. Then, equilibrium Cr (VI) concentration was determined using the method 3500-Cr B by a T80+ UV/VIS Spectrophotometer at a wavelength of 324.8nm (λ = 540).[29]

The amounts of Cr (VI) removal yield (%R) and the adsorption equilibrium capacity (q_e) according to the changes in absorbent dose and chromium concentration were calculated using the following equation. Each experiment was carried out two times and the mean was reported.

$$q_e = \frac{V}{M} \times (C_{in} - C_{out}) \qquad (1)$$

Where q_e is equilibrium adsorbed metal (mg/g adsorbent) on the carbonated Almon green hull, V is the solution volume (L), W is the amount of sorbent (g), and Cin and Cout (mg/L) are the initial and final Cr (VI) concentrations of the solution, respectively. The Cr (VI) percent removal (%) was calculated using the following equation:

$$\%R = \frac{(C_{in} - C_{out})}{C_{in}} \times 100 \qquad (2)$$

Mechanism and Isotherm Analysis

The pH_{zpc} is an important property of adsorbent. This parameter determines the surface behavior of adsorbent. The electrical neutrality of the adsorbent surface is indicated by pH_{zpc} at a particular pH value. In this study, in order to determinepH_{zpc}, NaCL solution was used and the pH was adjusted in the ranges 2-10 using NaOH and HCL solution.

The IR Spectra of adsorbent were measured Fourier Transform Infrared spectrophotometer (AVATAR, 370 FT-IR) to elucidate the functional group presenting on the surface carbonated Almond green hull before and after contact with Cr (VI) solution. Furthermore, the morphology of the sample was determined by scanning electron microscopy (SEM). The existence of metal ion on the surface of adsorbent was determined using EDX.

The abilities of three widely used isotherms, the theoretical Langmuir, Freundlich and Temkin isotherms, to model the adsorption equilibrium data were examined.

RESULTS
Effect of pH

The pH of solution has a significant effect on the adsorption of chromium. As pH increased, the adsorption of Cr (VI) gradually decreased (**Figure 1**). The surface charge of adsorbent can be determined using pH_{zpc}. At pH values below pH_{zpc} (isoelectric point) the surface charge will be positive and pH>pH_{zpc} while at values above this the surface charge will be negative (**Figure 2**).

This study carried out on the removal of Cr (VI) revealed that pH of solution has a significant effect on the anion absorption. That is, when pH increases (in the range of neutral to alkaline values), absorption of aqueous chromium ions significantly decreases. This can be clearly observed for both adsorbents (carbon obtained from Almond green hull). Removal percentage of the carbonated Almond green hull at pH = 2 is 33% and at pH 10 is 9/74%.
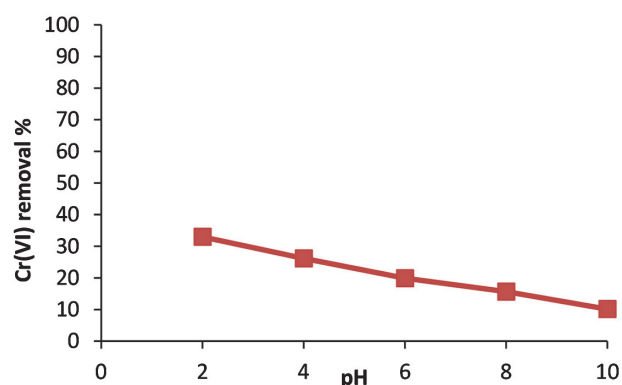

Figure 1. The effect of solution pH on the removal efficiency of Cr(VI)
(Absorbent dose: 8 g/lit; the initial concentration of chromium: 20 mg/lit; exposure time: 60 min; temperature: 25ºC; stirring speed: 300 rpm)
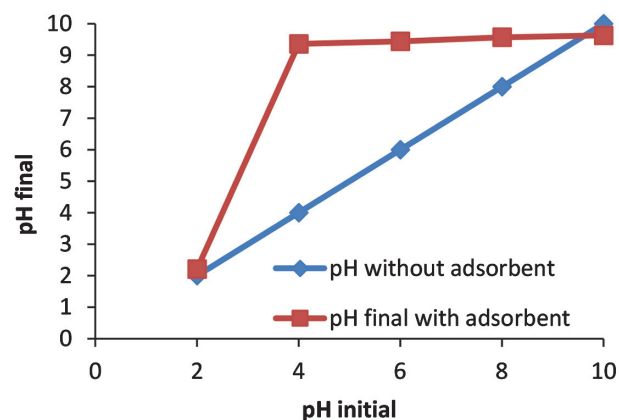

Figure 2. Results of determining pH_{zpc} carbonated Almond green hull

Effect of Adsorbent Dose

Figure 3 and **Figure 4** show the obvious effects of absorbent dose on the removal efficiency of Cr (VI). As shown in **Figure 3**, increasing carbonated Almond green hull adsorbent dose from 2 g/lit to 24 g/lit causes the removal efficiency to increase at first and then decrease. The optimum adsorbent dose is 4 g/lit for carbonated Almond green hull.

It can also be seen in **Figure 4** that there is an inverse correlation between the equilibrium adsorption capacity (q_e) and the removal percentage of chromium. Keeping the other factors constant are the experiments done to find the optimum Cr concentration in which maximum adsorption occurs.

The effects of the initial concentration of chromium, exposure time, and temperature are presented in **Figure 5**, **Figure 6**, and **Figure 7**, respectively.
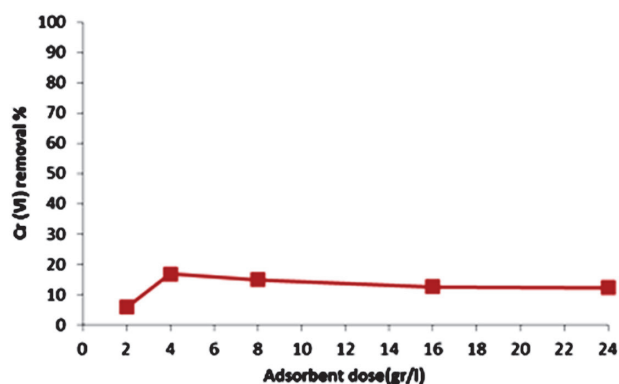

Figure 3. The effect of the dose of carbonated Almond green hull on the removal of Cr (VI)
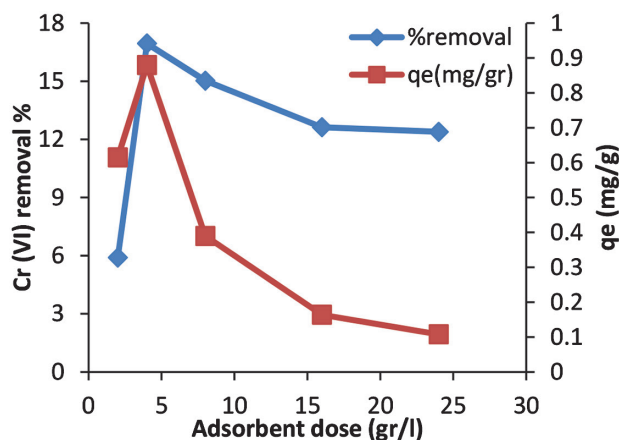

Figure 4. The comparison of the effect of changes of adsorption equilibrium capacity and absorbent dose on the removal of Cr (VI).
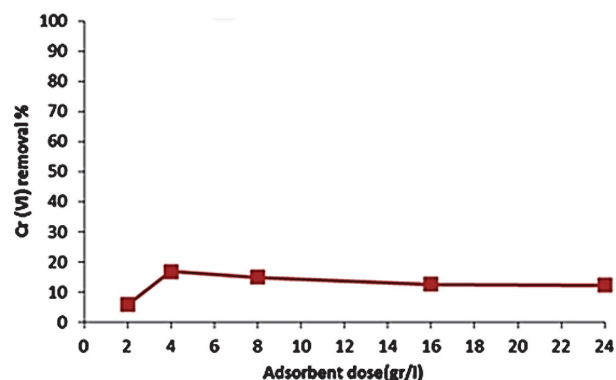(Concentration = 20 mg/lit, temperature = 25°C, pH = 2)

Figure 5. The effect of the initial concentration of chromium on the removal efficiency of Cr (VI).
(pH = 2; absorbent dose: 4 g/lit; exposure time: 60 min; temperature: 25 ºC; stirring speed: 300 rpm)
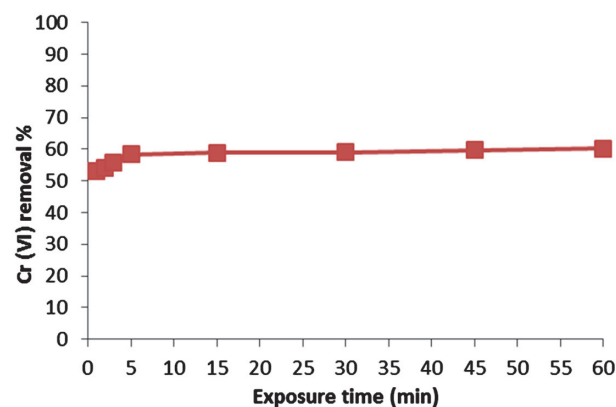

Figure 6. The effect of exposure time on the removal efficiency of Cr (VI).
(pH = 2, absorbent dose: 4 g/l, the initial concentration of chromium: 20 mg/lit; temperature: 25 ºC; Stirring speed: 300 rpm)
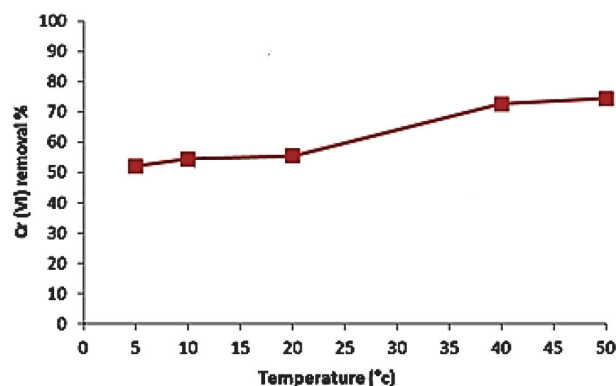

Figure 7. The effect of temperature on the removal efficiency of Cr (VI) byadsorbent
(pH = 2; absorbent dose: 4 g/lit; the initial concentration of chromium: 20 mg/lit; exposure time: 60 min; stirring speed: 300 rpm)

Adsorption Isotherm

Adsorption isotherms are useful to describe absorption capacity in order to facilitate evaluating the feasibility of the application of this process and analyzing

and designing absorption program.[30] In this study, equilibrium adsorption of chromium has been modeled using Langmuir and Freundlich and Temkin isotherms at constant temperature (25± 1 °C) and different adsorbent doses.

Langmuir Isotherm Model

The Langmuir isotherm is based on the monolayer adsorption of chromium ions on the surface of adsorbent sites and is expressed in the linear form in Eq. 3.[31]

$$\frac{C_e}{x/m} = \frac{1}{KV_m} + \frac{C_e}{V_m} \tag{3}$$

Where Ce is the equilibrium solution concentration, x/m the amount adsorbed per unit mass of adsorbent, m the mass of the adsorbent, Vm the monolayer capacity, and K is equilibrium constant related to the heat of adsorption by Eq. 4:

$$K = K_0 \times \exp\left(\frac{q}{RT}\right) \tag{4}$$

Where q is the heat of adsorption.

FreundlichIsotherm Model

The Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in linear form in Eq. 5:[31]

$$\log \frac{x}{m} = \log k_f + \frac{1}{n} \log C_e \tag{5}$$

Where K_f and $1/n$ are Freundlich constants related to adsorption capacity and intensity of adsorption, and other parameters are the same as in the Langmuir isotherm. The term log(x/m) can be plotted against logCe with slope $1/n$ and intercept $\log K_f$.

TemkinIsotherm Model

Temkin isotherm is based on the assumptions that the heat of adsorption of all the molecules in the layer would decrease linearly with the increase in coverage of adsorbent due to adsorbent–adsorbate interactions and that the adsorption is characterized by a uniform distribution of binding energies. Temkin isotherm is represented by the following equation:

$$\frac{x}{m} = \left(\frac{RT}{b}\right)\ln A + \left(\frac{RT}{b}\right)\ln C_e \qquad \frac{RT}{b} = B \tag{6}$$

$$q_e = \frac{RT}{b}\ln(A_t C_e)B = \frac{RT}{b_r}$$

Where b is the Temkin constant related to heat of sorption (J/mol), A the Temkin isotherm constant (L/g), R the gas constant (8.314J/mol/K), and T is the absolute temperature (298 K).

The information obtained from isotherm modeling is summarized in **Table 1**. The results revealed that the R_2 of the Langmuir isotherm was greater than the other diagrams, indicating that the Langmuir isotherm better represented the adsorption of Cr (VI) on these two adsorbents.

The effects of adsorbent properties are presented in (**Figures 8-10**).
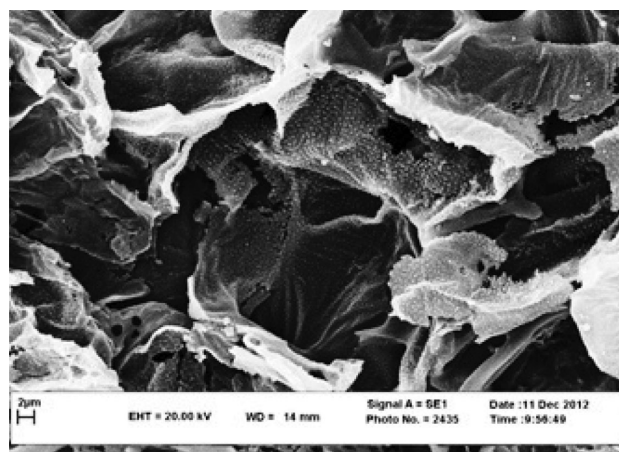


(A)
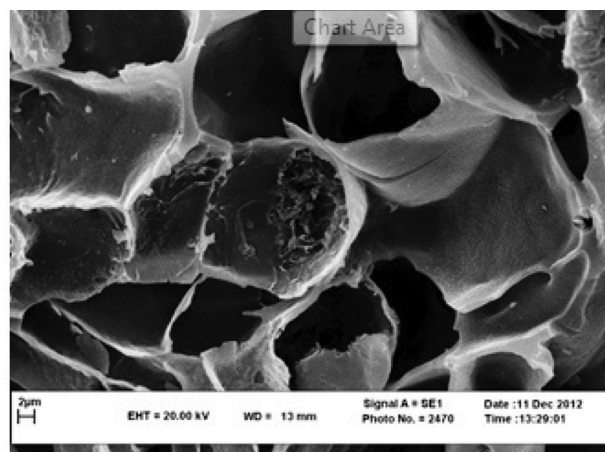
(B)

Figure 8. Micrograph of the almond green hull adsorbent using a Scanning Electron Microscope (SEM). (A) adsorbent before contact with chromium at 5 kx magnification. (B) adsorbent after contact with chromium at 5 kx magnification

Table 1. Parameters of linearized Langmuir, Freundlich and Temkin isotherms for adsorption of chromium (VI) onto carbonated Almond green hull.

	Temkin			Freundlich			Langmuir		
	Ln A	B(RT/b)	R2	Log Kf (L/mg)	N	R2	Kl(L/mg)	qmax(mg/g)	R2
Adsorbent	0.8949	1.485	0.184	1.200	0.4894	0.154	0.0767	1.901	0.853

(A)   (B)
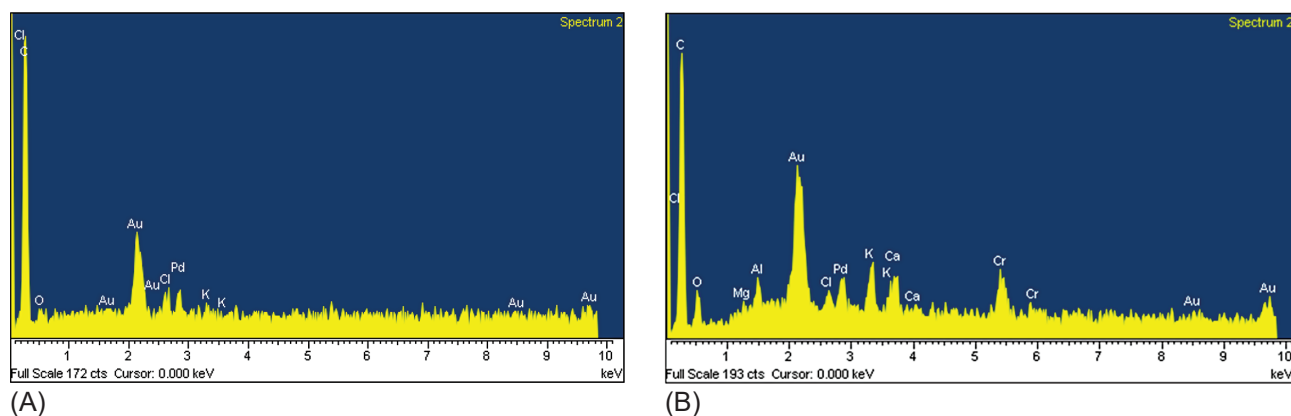
Figure 9. EDX photo of carbonated almond green hull. (A) adsorbent before contact with chromium. (B) adsorbent after contact with chromium
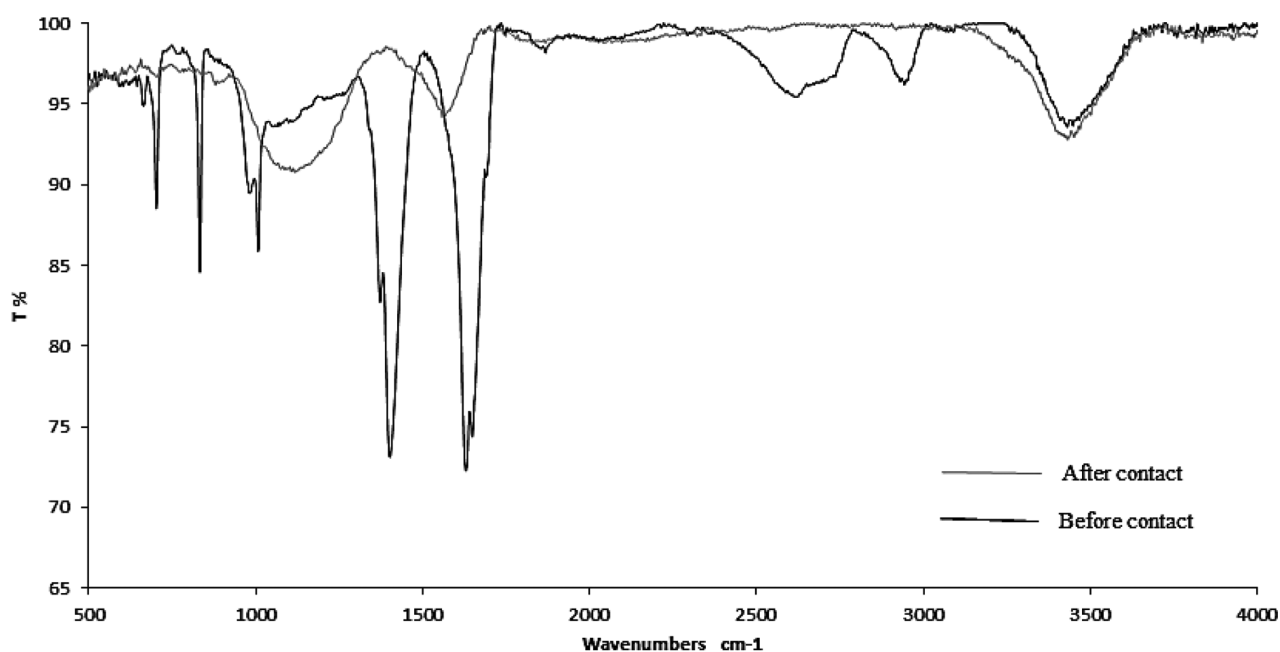
Figure 10. FTIR spectra of the adsorbent

DISCUSSION

pH changes can affect chromium adsorption because it determines the chromium ion species and adsorbent surface charge. That means if the adsorbent surface charge is positive, more anions and electrostatic interactions will occur. Therefore, pH of solution, besides, effects on Cr ions species and continually adsorption process.

At pH≤ 2 and lower values, Cr (VI) is dominantly in the form of $HCrO^{-4}$ and $Cr_2O_7^{-2}$. Because of its low free energy of adsorption, $HcrO^{-4}$ which composes the most part is effectively absorbed. On the other hand, adsorbent surface charge is negative at high pH values and the dominant ions are CrO_4^{-2} and $Cr_2O_7^{-2}$. So, the adsorption of anions through electrostatic attraction is decreased. Considering the increase in adsorption at low pH values and the fact that potassium dichromate has

been used and chromium ions exist in the form of CrO_4^{-2}, $Cr_2O_7^{-2}$ and $HcrO^{-4}$, an explanation for the decrease in adsorption at higher pH values is as follows: according to Le Chatelier's principle, at low pH values, because of low concentration of OH^- ions in the solution, the OH^- groups on the adsorbent tend to move toward the solution. As a result, positive ions will be created on the adsorbent which start adsorption and by increasing pH, the concentration of OH^- groups rises so the OH^- groups on the adsorbent do not tend to release. Therefore, there are less positive sites and adsorption will decrease. In other words, at pH values under pH_{zpc} (zero point of charge (adsorbent surface charge is positive and thus readily available for the adsorption of Cr (VI) anions. However, at pH values above pH_{zpc}, adsorbent surface charge is positive and adsorption of Cr (VI) anions decreases. Furthermore, at higher pH values hydroxyl ions increase in the solution and compete with chromium ions for the active sites. So, chromium adsorption decreases.[20] Since the adsorbent pH_{zpc} is in the range of 2, a decrease in adsorption efficiency in alkaline conditions is reasonable.

Our results are in agreement with those of Mossaviand colleagues,[32] Song Wong and colleagues,[33] and Nadeem and colleagues.[28]

According to the obtained results, as it is shown in **Figure 3**, by increasing adsorbent dose, removal percentage first increases and then decreases again. After repeating the experiments for several times, it was revealed that by increasing adsorbent dose, pH increases and thus removal percentage decreases. This may be explained by the fact that the furnace heat which turned the adsorbent into ashes has weakened alkaline functional group bonds. After being stirred in chromium solution for an hour, these bonds are broken and alkaline functional groups dominate acidic ones. Thus, solution pH becomes alkaline and the removal percentage decreases.

It can also be seen in **Figure 4** that there is an inverse correlation between the equilibrium adsorption capacity (q_e) and the removal percentage of chromium.

As shown in **Figure 6**, the removal efficiency decreases as the initial concentration of Cr (VI) increases that is increasing concentration from 10 mg/lit to 100 mg/lit decreases removal yield. **Figure 6** demonstrates that by increasing Cr, its removal percentage in the solution decreases. This is due to the limited number of active sites on the adsorbents which are saturated in high concentrations. When chromium initial concentration decreases, metal ions in the solution decrease and a high percentage of ions are absorbed by the adsorbent.[23] Since what limits adsorption is solution concentration, at low

concentrations, adsorption capacity has a small role in chromium removal efficiency. On the contrary, surface area has a more important role in chromium adsorption at higher concentrations. This can be due to the increase of Cr (VI) ions to be absorbed by the available sites on the adsorbent surface.[11]

The studies conducted on the adsorption of aqueous heavy metal ions using different adsorbents have mostly investigated the effect of metal initial concentration on ion adsorption. In most cases, they have come to the conclusion that increasing metal concentration in the solution decreases removal efficiency. Song Wong and colleagues[33] and Shirzad-Siboniand colleagues[34] did researches which demonstrated Cr (VI) removal efficiency decreases as chromium initial concentration increases.[33,34] Here adsorbent plays a more significant role. Increasing the absorbent dose from 10 g/l to 100 g/l decreased the removal efficiency.

Regarding to the illustrated results in **Figure 7** related to exposure time and removal percentage, it is obvious that adsorption is fast in the first few minutes and a steep slope can be seen in the figure which is related to physical adsorption, then the curve gets smoother which is due to mass transfer resistance. After a while, when the available sites are occupied by metal ions, repulsive forces between the bulk and the adsorbed molecules come into play and decrease the adsorption. At last adsorbent reaches saturation point. After this time, increasing the time does not increase the adsorption that is the equilibrium time after which adsorption capacity remains constant or changes little. This decrease in adsorption may be due to desorption.[28] T. Alton[35] and Taghizadeh and colleagues[36] obtained similar results to the results of this stage of study.[35,36]

Figure 8 shows that increasing temperature from 5 to 50° C increases removal efficiency of Cr (VI). Removal efficiency considerably increases by an increase in temperature. Various studies conducted on this issue demonstrated that adsorption is an endothermic reaction. Therefore, the increase in removal percentage can be attributed to the increase in adsorption reaction which is due to its endothermic nature. It can be seen that increasing temperature from 10 °C to 20 °C causes a significant increase in the removal efficiency.

According to the studies carried out by Gholamreza Moussavi,[32] increasing temperature increases absorption.[32,37] By increasing temperature from 5 to 50 removal yield increases which was from 52/71% to 71/29%.

Figure8 shows scanning electron micrograph (SEM)

of the surface of carbonated almond green hull absorbent at 5 kx magnification, before and after contact with Cr (VI), respectively. The pictures demonstrate that the absorbent are many porous. EDX photos in **Figure 9** show the existing elements in the absorbents before and after adsorption process. According to these pictures, by contacting the absorbent, chromium has been absorbed and became one of the species of the carbonated almond green hull.

The analysis of the FTIR spectra **Figure 10** indicated that a variety of functional groups at 1049, 1376, 1454, 1568, 1642, 3419 Cm^{-1} wave numbers are responsible for the removal of chromium in carbonated Almond green hull. The comparison of FTIR spectra before and after the contact with chromium shows that the peaks attributed to the functional groups present in the local adsorbent significantly decreased after being used as an adsorbent that indicates interaction between functional groups and chromium in the solution and shows the role of chemical interactions in absorption.

CONCLUSIONS

In this study, carbonated Almond green hull, which is an unavoidable waste material, is used as an inexpensive adsorbent for the removal of hexavalent chromium from aqueous solutions. The studies indicated that adsorbent is an effective, low-cost adsorbent for the removal of toxic Cr (VI) from aqueous solution. The results indicated that adsorption reached equilibrium after about 60 minutes. Chromium (VI) adsorption is severely dependent on solution pH and the obtained results suggest that the maximum Cr (VI) removal occurred at pH = 2. The best removal efficiency for absorbent happens when its concentration is 4 (gr/lit). By increasing the temperature from 5 to 50 centigrade degree, the absorbent rate increased notably. This shows that the absorption is endothermic. The SEM pictures demonstrate that the adsorbents have deep pores and a relatively smooth surface. EDX images show the existing elements in the adsorbents after being contacted with Cr (VI). According to this picture, after being contacted with the adsorbents, chromium ion has been absorbed. It should be noted that the results indicated the data fit better to the Langmuir equation than to the Freundlich and Temkin equations. The experimental results indicated that, we can conclude that carbonated Almond green hull wastes have many advantages such as having no costs and easy availability. Also due to the particularly high level, it can be converted to an effective substance for the removal of chromium and it is able to substitute, the activated carbon.

CONFLICT OF INTEREST
None declared.

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