

The removal of Cr(VI) from aqueous solution by almond green hull waste material: kinetic and equilibrium studies

Negin Nasseh, Lobat Taghavi, Behnam Barikbin and Ali Reza Harifi-Mood

ABSTRACT

The discharge of industrial effluents containing hexavalent chromium into the environment can be very harmful to living things. Therefore, prior to effluent discharge into the environment, hexavalent chromium should be removed from contaminated water and especially from wastewaters. In the present work, almond green hull powder (AGHP) was investigated for the removal of hexavalent chromium from wastewater. The effects of pH (2–10), adsorbent dose (2–24 g L⁻¹), Cr(VI) concentration (10–100 mg L⁻¹), contact time (1–60 min), and temperature (5–50 °C) were studied. All the experiments were performed in triplicate and average results were reported. The surface morphology, pore volume and size, pH of zero point charge (pH_{ZPC}) and surface functional groups of AGHP were characterized. Isotherm and kinetic evaluations were also conducted in the present study. The results revealed that the adsorption of Cr(VI) by AGHP was an adsorbate, adsorbent, and temperature dependent process that was favorable under acidic conditions. Furthermore, AGHP absorbed over 99% of chromium from the solutions containing 10–100 mg L⁻¹ of Cr(VI) based on the Freundlich model. In summary, hexavalent chromium was not found in almond kernel. Biosorption onto AGHP is an affordable and economical adsorption process for treating Cr(VI)-laden industrial wastewater.

Key words | adsorption, almond green hull, almond kernel, biosorption, hexavalent chromium, industrial wastewater

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INTRODUCTION

The discharge of heavy metals into aquatic ecosystems has become a matter of concern over the last few decades (Mane & Bhosle 2012). They are extremely toxic elements which can seriously affect plants and animals and cause a large number of afflictions (John Babu *et al.* 2012). Increased knowledge about toxicological effects of heavy metals on the environment is well recognized and therefore, the search for different methods to reduce water pollution is inevitable (Vinodhini *et al.* 2010). The major sources of heavy metal contaminant ions are the industrial effluents.

Due to their persistence in nature, it becomes essential to remove them from wastewaters (Klimmek *et al.* 2001). Inorganic micro-pollutants are of considerable concern because they are non-biodegradable, highly toxic, and have possible carcinogenic effects (Cimino & Caristi 1990; Pehlivan & Altun 2008).

Cr(VI) is a common pollutant introduced into natural waters from a variety of industrial wastewaters including those from textile dyeing, leather tanning, electroplating, and metal finishing industries (Aadli *et al.* 2010). Chromium was discovered in 1797 by the French chemist Louis Vauquelin. It was named chromium (Greek Chroma, 'color') because of many different colors found in its compounds. Chromium is the Earth's 21st most abundant element (about 122 ppm)

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and the sixth most abundant transition metal. The principal chromium is ferric chromite, FeCr_2O_4 , found mainly in South Africa (with 96% of the world's reserves), Russia, and the Philippines. Less common sources include crocoite, PbCrO_4 and chrome ochre, Cr_2O_3 . The gem stones emerald and ruby owe their colors to traces of chromium. Chromium occurs in 2^+ , 3^+ and 6^+ oxidation states but Cr^{2+} is unstable and very little is known about its hydrolysis (Mohan & Pittman 2006). Chromium usually exists in both trivalent and hexavalent forms in aqueous systems. The other two oxidation states of chromium have different chemical, biological, and environmental characteristics (Hongqin *et al.* 2011). Cr(III) is relatively insoluble and is required by microorganisms in small quantities as an essential nutrient trace metal, while Cr(VI) is of great concern because of its toxicity. Cr(VI) has been reported to be a primary contaminant to humans, animals, plants, and microorganisms and it is known to be carcinogenic (Rengaraj *et al.* 2007).

The hydrolysis of Cr(III) is complicated. It produces mononuclear species: $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_4^-$, neutral species $\text{Cr}(\text{OH})_3$ and polynuclear species: $\text{Cr}_2(\text{OH})_2$ and $\text{Cr}_3(\text{OH})_4^{5+}$. The hydrolysis of Cr^{6+} produces only neutral and anionic species, predominately CrO_4^{2-} , HCrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ (Mohan & Pittman 2006).

The methods employed for the removal of Cr(VI) from aqueous solutions include chemical oxidation–reduction, ion exchange, electrodialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis, chemical precipitation and adsorption (Rengaraj *et al.* 2007). Most of these methods suffer from drawbacks such as high cost, operational costs, and problems in the disposal of the residual metal sludges (Ahmadpour & Doosti 2011). Many studies have been conducted on the development of low-cost activated carbon adsorbents produced from cheaper and readily available materials (Omri & Benzina 2013). Activated carbons with large surface area, microporous character and chemical nature of their surface are potential adsorbents for the removal of heavy metals from industrial wastewater (Ahmadpour & Doosti 2011).

A number of studies on the removal of Cr(VI) have been reported using adsorbents like activated groundnut husk carbon (Periasamy *et al.* 1991), coconut shell activated carbon (Babel & Kurniawan 2004), coconut shell, wood and dust coal activated carbons (Modrogoan *et al.* 2011),

sawdust carbon (Kadirvelu *et al.* 2000), sawdust and used tyres carbon (Hamadi *et al.* 2001), rice husk carbon (Bishnoi *et al.* 2004), hazelnut shell carbon (Demirbas *et al.* 2009), almond shell carbon (Demirbas *et al.* 2008), and so on.

In the present study, an agricultural waste material, almond green hull, was examined as an economical sorbent for the removal of Cr(VI) ion from aqueous solutions. Almond trees are abundant in the world, especially in Iran. Almond hull is an agricultural crop residue that cannot be used by animals and is usually burnt. The annual production of almond (with hard shell) is about 108,000 tonnes in Iran. Almond green hull is estimated to be about 0.25–0.6 wt% of whole almond fruits depending upon their various types. Therefore, about 36,000–160,000 tonnes of this waste material, generated in the agricultural sections of the country, can be used for Cr(VI)-laden industrial waste water treatments annually. To the best of the authors' knowledge, this material has not been used before for this kind of application. Utilization of almond green hull not only provides a low cost and easily available sorbent for the removal of heavy metals such as Cr(VI), but it could also help in environmental pollution control (Ahmadpour & Doosti 2011).

MATERIALS AND METHODS

Preparation of adsorbent

Almond green hull was obtained from a local fruit field in the eastern part of Iran (Southern Khorasan). The sorbent was washed thoroughly several times with deionized water to be free of any dust or pollutant and was dried at room temperature for some days. Then, the dried sample was powdered and sieved (in two ranges of $2 <$ to < 4 mm).

In order to identify the surface characteristics of adsorbent, a LEO 1450 VP (Zeiss, Germany) was used for scanning electron micrograph (SEM) analysis and an AVATAR 370 FT-IR was used for Fourier transform infrared spectroscopy (FTIR).

Reagents and solutions

The chemicals used were made by the German company Merck. The devices used were pH meter 765 (German

Climatic Company), shaker (IK Company), by which the sample, water contaminated with Cr(VI), was combined with the adsorbents, and a digital balance (KERN, Germany) to weigh all the solid chemicals. The incubator shaker, model Aerotron (Infors Company, Sweden) was also used to change the temperature. To make the samples even, Whatman 125 mm paper was used.

In this study, the stock solution of Cr(VI) was prepared by dissolving a known quantity of potassium dichromate ($K_2Cr_2O_7$) in deionized water. The stock solution was further diluted to obtain the required concentrations of Cr(VI) solutions. 1.0 N sodium hydroxide (NaOH) and 1.0 N hydrogen chloride (HCl) were used for pH value adjustments (APHA 2005).

Batch 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⁻¹), initial metal-ion concentration (10–100 mg L⁻¹), 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 the experiments were performed in triplicate and the average of the results was reported. In each experiment, 25 mL of the sample solution (with certain density and dose of almond green hulls by screens of 5 and 10) was mixed at 25 ± 1 °C in a shaker with 300 turns min⁻¹.

Cr(VI) concentrations in the solutions were determined by the standard colorimetric method (Nadeem et al. 2006) with 1,5-diphenylcarbazide in acetone. Metal concentration of the solution was analyzed with UV/VIS spectrometer T80⁺ at $\lambda = 540$ nm and also the concentration of Cr(VI) ions were calculated from the change in metal concentration in the aqueous solution before and after equilibrium sorption by using the following equation:

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

where q_e is equilibrium of metal adsorbed (mg g⁻¹ adsorbent) on the AGHP, V is the solution volume (L), M is the amount of sorbent (g), and C_{in} and C_{out} (mg L⁻¹) are the initial and final Cr(VI) concentrations of the solution,

respectively. The Cr(VI) removal percentage (%) was calculated using the following equation:

$$\text{Cr(VI)Removal(\%)} = \%R = \frac{(C_{in} - C_{out})}{C_{in}} \times 100 \quad (2)$$

Kinetics, mechanism and isotherm analysis

The adsorption isotherm studies were carried out by varying the Cr(VI) initial concentrations from 10 to 100 mg L⁻¹ at fixed volume (100 mL), AGHP dose (4 g L⁻¹), pH (2), optimum uptake time (60 min), and room temperature. The results were analyzed by Freundlich, Langmuir and Dubinin–Radushkevich (D-R) isotherm models. The experiments of batch kinetic adsorption by AGHP were carried out by mixing 4 g L⁻¹ of AGHP with 20 mL Cr(VI) solution at pH = 2 and contact time 1–60 min. The data were fitted to the pseudo first order equation, pseudo second order equation, and the Weber and Morris model. All the experiments were repeated five times and the average values reported.

RESULTS AND DISCUSSION

Characteristics of AGHP before and after biosorption

Figures 1–3 show the SEM of the surface of biosorbent, existing chemical elements (EDX), and operational groups in the biosorbent before and after contact with Cr(VI), respectively.

Since almond kernel used in this study was continuously exposed to Cr(VI) through irrigation, there was a possibility that hexavalent chromium existed in almond kernels in the area. Fortunately, Cr(VI) ion was not seen in SEM and EDX analysis.

Figure 1 is a SEM micrograph of the local almond green hull biosorbent at 2.5 k× magnification. It shows that the adsorbent has deep pores and a relatively smooth surface. Figure 2 is an EDX image that shows the existing elements in the adsorbent after coming into contact with Cr(VI). According to this figure, after being in contact with the adsorbent, chromium was absorbed.

The analysis of the FTIR spectra (Figure 3) indicated that a variety of functional groups at 771, 820, 1,043,

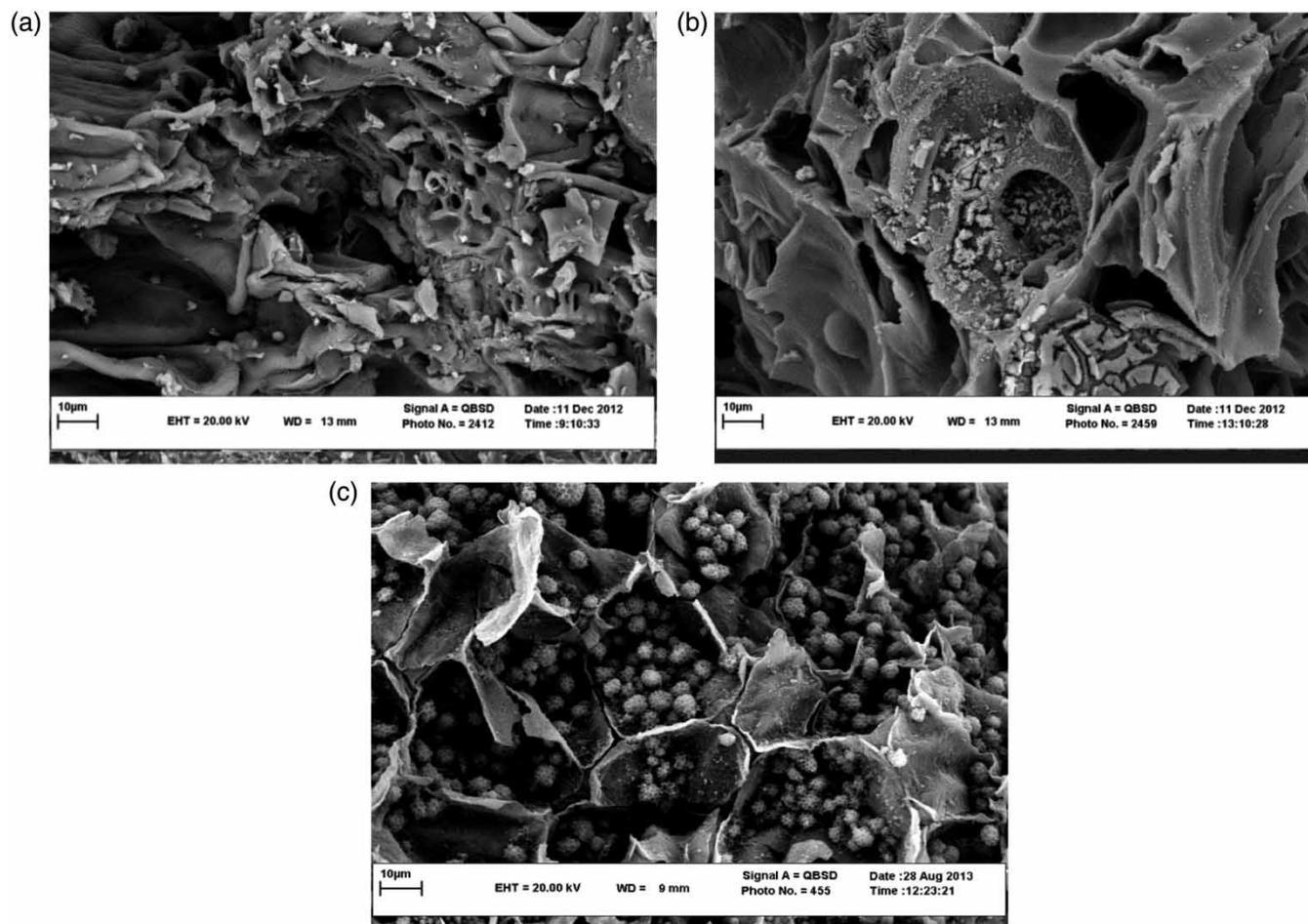


Figure 1 | SEM images of AGHP and kernel (a) before contact, (b) after contact, (c) almond kernel.

1,443, 1,283, 1,608, 2,923, 3,419 cm^{-1} wave numbers are responsible for the removal of chromium in AGHP. It means that the most part removed is attributed to C=O (1,608), O-H (3,421), C-H (2,923), and N-H (1,443) groups. The comparison of FTIR spectra before and after contact with chromium shows that the peaks attributed to the functional groups present in the local AGHP significantly decreased after being used as an adsorbent, which indicates interaction between functional groups and chromium in the solution and shows the role of chemical interactions in absorption.

Effect of pH

Since the pH of the aqueous solution affects the surface charge of the adsorbents as well as the degree of ionization

and speciation of different pollutants, the solution pH can have a significant effect on the adsorption of chromium. As pH was increased from 2 to 10, the removal efficiency decreased from 99.96 to 99.67 (Figure 4). Figure 5 shows the electrical neutrality of the adsorbent surface.

The initial solution pH is one of the most important factors that controls the process of Cr(VI) adsorption Ajmal et al. 2001; Mohan et al. 2001. Figure 4 shows Cr(VI) adsorption at different pH values. It also shows that Cr(VI) removal efficiency increases at lower pH values and noticeably decreases at a higher pH. According to this figure, the maximum removal of Cr(VI) was achieved at $\text{pH} = 2$ and after that the removal efficiency dropped significantly at $\text{pH} = 4$ and then remained relatively constant. At the optimum pH for absorption, Cr(VI) exists in solution in these two forms: $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- . The dominant form of Cr(VI)

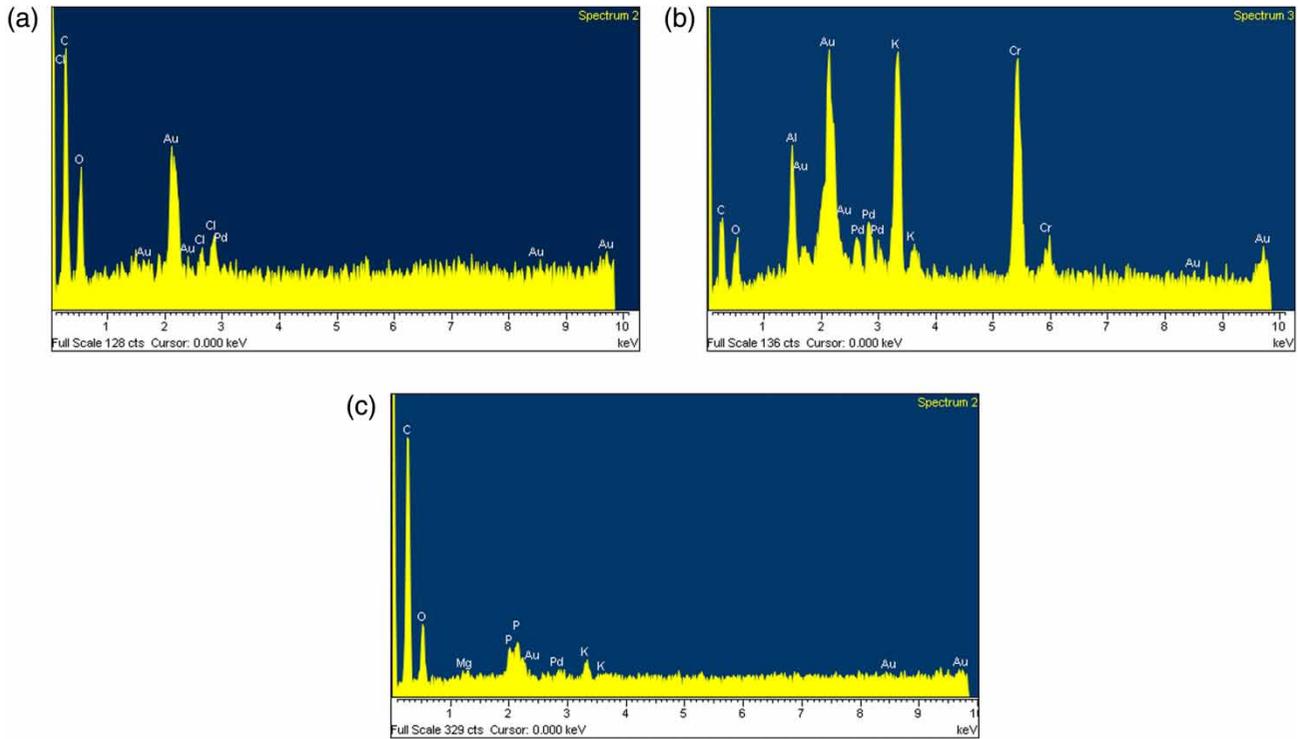


Figure 2 | EDX images of the AGHP and kernel (a) before contact, (b) after contact, (c) almond kernel.

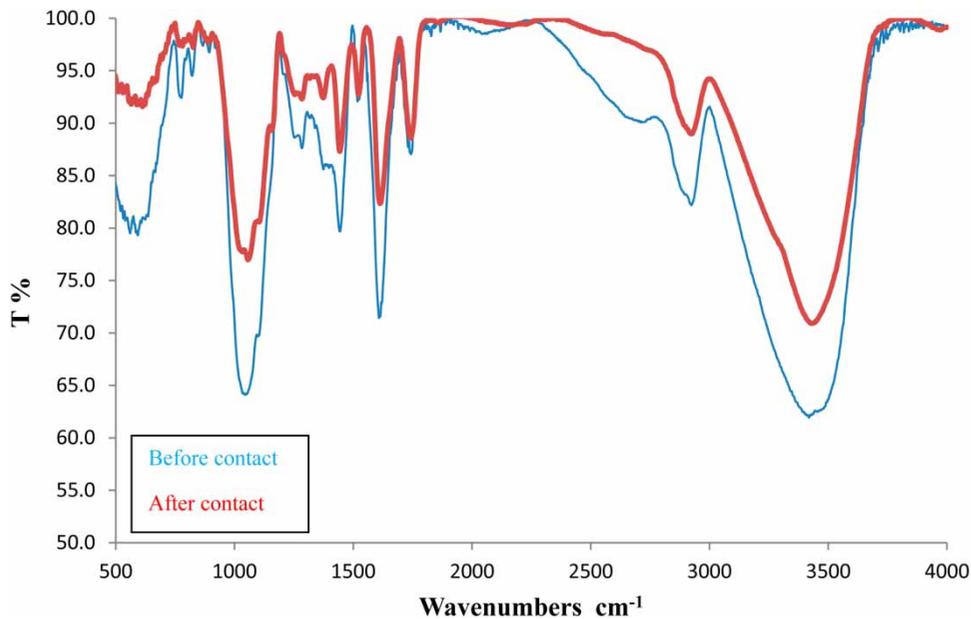


Figure 3 | FTIR spectra of the adsorbent.

with an acidic pH value is HCrO_4^- , which is released through hydrolysis of the dichromate ion $\text{Cr}_2\text{O}_7^{2-}$. The effluent concentration of $\text{Cr}_2\text{O}_7^{2-}$ increases with increasing pH.

At pH values lower than pH_{zpc} (the zero point charge of the adsorbent), the adsorbent surface is positively charged and therefore suitable for the sorption of Cr(VI) anions

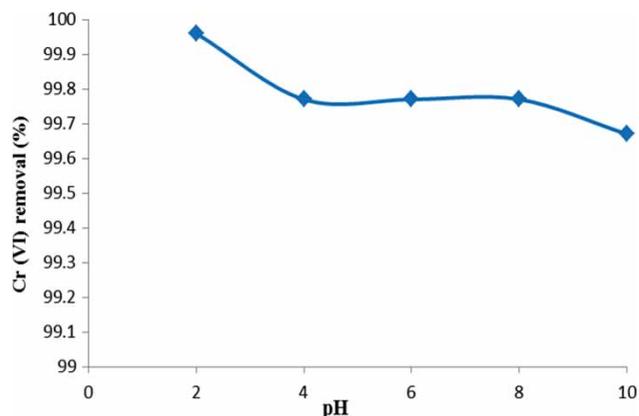


Figure 4 | The effect of solution pH on Cr(VI) removal by adsorption onto AGHP. Adsorbent dose: 8 g L^{-1} ; initial concentration of chromium: 20 mg L^{-1} ; contact time: 60 min; temperature: $20 \text{ }^\circ\text{C}$; stirring speed: 300 rpm.

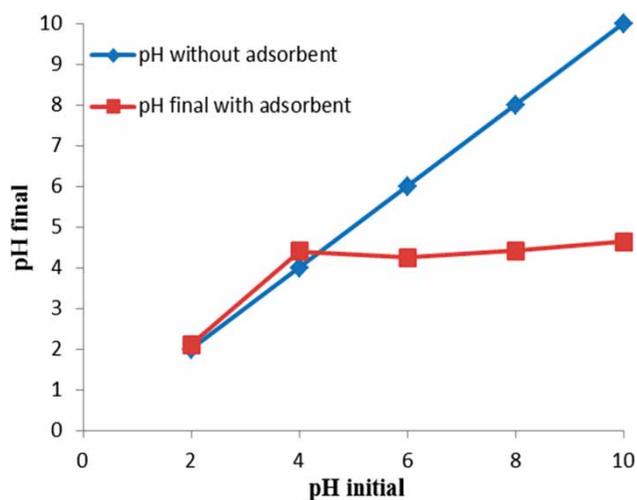


Figure 5 | The pH_{zpc} of modified AGHP.

(Figure 5). At pH values above pH_{zpc} , the adsorbent surface is negatively charged and thus the adsorption of anions is decreased. Furthermore, at higher pH values, hydroxyl ions are increased in the solution and compete with chromium ions for the adsorption sites, thus, adsorption of chromium is decreased.

Since pH_{zpc} values of the used adsorbents are about 2, a decrease in removal efficiency under alkaline conditions is reasonable.

Mossavi & Barikbin (2010) and Song wong et al. (2009) studied chromium removal using pistachio hull and carbon produced from walnut shells, and determined the optimum pH to be 2 for adsorption Song wong et al. 2009; Mossavi

& Barikbin 2010). In a study with the title 'Biosorption of Cr(VI) onto the litter of natural trembling poplar forest', the optimum pH of 2 was reported (Murat 2001).

Effect of AGHP dose

Figure 6 shows the effect of adsorbent dose on the removal efficiency of Cr(VI). As shown in the figure, increasing the adsorbent dose from 2 g L^{-1} to 24 g L^{-1} resulted in the removal efficiency increasing from 99.76 to 100%. As shown in Figure 6, as the adsorbent dose is increased, removal efficiency increases. It can also be seen in Figure 7, that there is an inverse correlation between the equilibrium adsorption capacity (q_e) and the removal percentage of chromium.

The optimum concentration of adsorbent is 2 g L^{-1} which resulted in 99/97% efficiency (Figure 6). Increasing adsorbent dose increases the sorbent site and therefore increases the total number of active sites for chromium uptake. The results of this study also conform to the results obtained by most researchers on the removal of Cr(VI) from aqueous solution by adsorption onto activated carbon (Klimmek et al. 2001). Likewise, in another study on the adsorption of chromium from aqueous solution of treated sawdust carried out by Garg et al. (2004), it was concluded that increasing adsorbent dose increases removal efficiency. The optimum dose (2 g L^{-1}) was determined for this adsorbent. Equilibrium adsorption capacity (Figure 7) was also calculated according to the adsorbent dose and chromium concentration changes as this optimal dose met environmental standards for discharge of effluent.

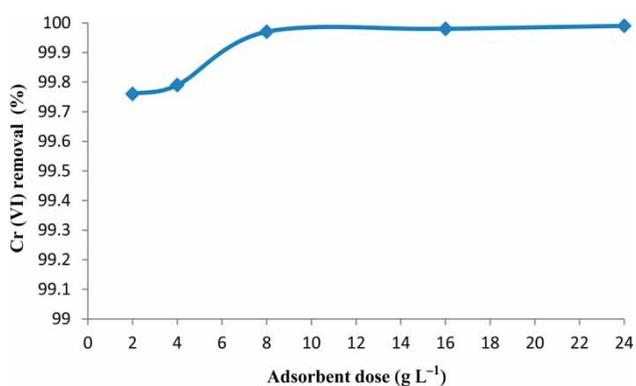


Figure 6 | The effect of adsorbent dose changes on the Cr(VI) removal. $\text{pH} = 2$; initial concentration of Cr: 20 g L^{-1} ; contact time: 60 min; temperature: $25 \text{ }^\circ\text{C}$; stirring speed: 300 rpm.

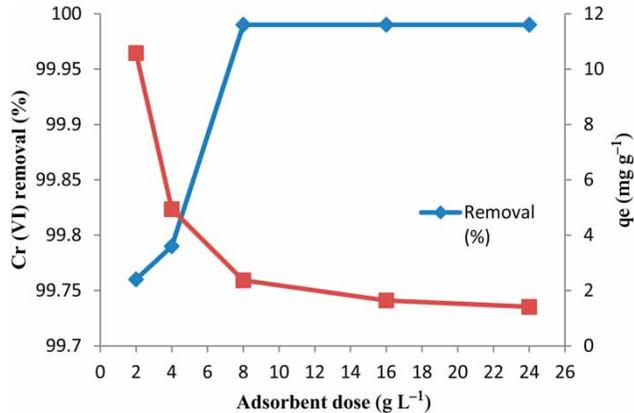


Figure 7 | Comparison of the effect of equilibrium adsorption capacity and adsorbent dose changes on the Cr(VI) removal. pH = 2; initial concentration of chromium: 20 mg L⁻¹; contact time: 60 min; temperature: 25 °C; stirring speed: 300 rpm.

The initial concentration of chromium

According to Figure 8, the removal efficiency remained constant as the concentration increased to 60 mg L⁻¹ then dropped from 99.75 to 95.90% when the initial concentration reached 100 mg L⁻¹.

Chromium removal is increased by increasing concentration to 60 mg L⁻¹ and then drops (Figure 8). This is due to the limited number of active sites on the sorbents which are saturated in high concentrations. The current results conform to the studies conducted by Wang *et al.* (2009) on the removal of Cr(VI) using walnut hull (Song Wong 2009). Similarly, in a study on Cr(VI) adsorption from aqueous solution by sawdust activated carbon, Karthikeyan *et al.* (2005) observed that increasing Cr(VI) concentration decreased removal efficiency (Karthikeyan *et al.* 2005).

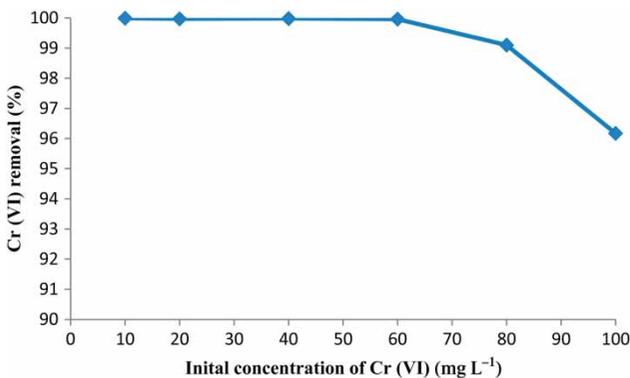


Figure 8 | The effect of the initial concentration of chromium on the removal efficiency of Cr(VI). pH = 2; adsorbent dose: 2 g L⁻¹; contact time: 60 min; temperature: 25 °C; stirring speed: 300 rpm.

Effect of contact time

It can be seen in Figure 9 that as contact time increased from 1 to 60 min, 99.75% removal efficiency reached 99.94% while the initial concentration of Cr(VI) was 20 mg L⁻¹.

According to the figure, removal efficiency increased from 99.75 to 99.94 at the initial concentration of 20 mg L⁻¹. The environmental standards were achieved within the first few minutes.

Figure 9 shows Cr(VI) removal efficiency at different contact times. According to the results, the optimum time for the absorption of Cr(VI) by AGHP adsorbent is 60 min at which adsorption efficiency reached 99.94%. However, the bulk of adsorption takes place within the first few minutes. 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 slope becomes low which is due to mass transfer resistance. After a while, when the available sites are occupied by metal ions, repulsive forces come into play between the bulk and the adsorbed molecules and reduce adsorption (Montazeri *et al.* 2010; Pashazanousi & Raeisi Kord 2010). At last, biosorbent reaches saturation point. After this time, increasing the time does not increase adsorption, that is, the equilibrium time after which adsorption capacity remains constant or changes a little. This decrease in adsorption may be due to desorption (Alowitz & Scherer 2002). Similar findings were reported by Mossavi & Barikbin (2010) and Khareshi & Saedi (2011).

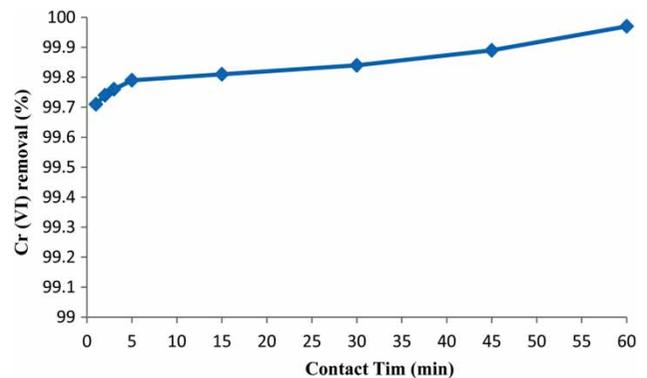


Figure 9 | The effect of contact time on Cr(VI) removal. pH = 2; adsorbent dose: 2 g L⁻¹; initial concentration of chromium: 20 mg L⁻¹; temperature: 25 °C; stirring speed: 300 rpm.

Effect of temperature

Figure 10 shows that increasing temperature from 5 to 50 °C increases removal efficiency of Cr(VI) from 75.71 to 100%.

The last parameter investigated in Cr(VI) removal experiments was temperature (Figure 10). The results indicated that removal efficiency increased with an increase in temperature. This can be attributed to the increase in the movement and convection of adsorbent particles as a result of increase in temperature. Dundar et al. (2011) worked on the biosorption of Cr(VI) onto the litter of natural trembling poplar forest and determined 45 °C and 150 min as the optimum temperature and time for reaching equilibrium (Murat 2001).

Adsorption isotherm

Adsorption isotherms are useful for describing absorption capacity in order to facilitate the evaluation of the feasibility of the application of this process and to analyze and design absorption systems (Nadeem et al. 2006). In this study, equilibrium adsorption of chromium was modeled using Langmuir, Freundlich, and D-R isotherms at constant temperature (25 ± 1 °C) and different adsorbent doses.

The information obtained from isotherm modeling is summarized in Table 1. The results revealed that the R^2 of Freundlich isotherm was greater than that of the other models, indicating that the Freundlich isotherm represented the adsorption of Cr(VI) onto AGHP better. The Freundlich model is based on monolayer adsorption on heterogeneous

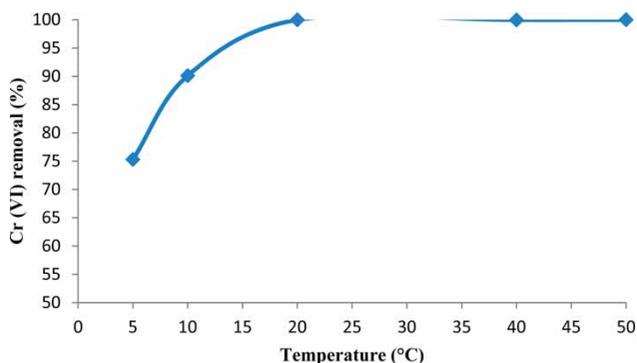


Figure 10 | The effect of temperature on the Cr(VI) removal. pH = 2; adsorbent dose: 2 g L⁻¹; the initial concentration of chromium: 20 g L⁻¹; contact time: 60 min; stirring speed: 300 rpm.

Table 1 | Results of Cr(VI) biosorption isotherms equations

| Isotherm | Unit | Information |
|----------------------------|--|---|
| Langmuir model | | $C_e/q_e = 1/K_L q_{\max} + C_e/q_{\max}$ |
| Plot | - | (C_e/q_e) vs. C_e |
| Fitted model | - | $C_e/q_e = 0.0008 + 0.0945C_e$ |
| q_{\max} | mg g ⁻¹ | 10.58 |
| K_L | L mg ⁻¹ | 117.65 |
| R^2 | - | 0.925 |
| $R_L = 1/1 + K_L C_i$ | | |
| Freundlich model | | $Lnq_e = Ln K_f + 1/n Ln C_e$ |
| Plot | - | Lnq_e vs. $Ln C_e$ |
| Fitted model | - | $Lnq_e = 1.5602 + 0.4756Ln C_e$ |
| K_f | (mg g ⁻¹ (L mg ⁻¹) ^{1/n}) | 36.3245 |
| N | - | 2.10 |
| R^2 | - | 0.9895 |
| Dubinin-Radushkevich model | | $Lnq_e = Ln q_m - K_{DR}\epsilon^2$ |
| Plot | - | Lnq_e vs. ϵ^2 |
| Fitted model | - | $Lnq_e = 2.5665 - 0.15$ |
| K_{DR} | mol ² (kJ ²) ⁻¹ | 0.15 |
| $E = 1/\sqrt{2K_{DR}}$ | kJ mol ⁻¹ | 2.58 |
| R^2 | - | 0.9803 |

surfaces with heterogeneous adsorption energies. In the Freundlich model, with the increase of K_f , if the value of n is close to 1, the heterogeneity of the surface is less critical and if n is close to 10 it will be more important.

The D-R isotherm is based on heterogeneous surfaces. In this isotherm, it is assumed that the decline in adsorption energy is against the assumed logarithmic condition in the linear form of the Freundlich equation. In this model, the interactive effects between adsorbent and adsorbate are considered indirectly and, therefore, because of these interactive effects, adsorption energy of all molecules in sorption layers decreases linearly. Based on the result of the D-R model (Table 1), the amount of free energy in Cr(VI) adsorption by AGHP is 2.58 kJ mol⁻¹. A value of E less than 8 kJ mol⁻¹ indicates that physical adsorption is the dominant process under the experimental conditions, thus, the adsorption of Cr(VI) by AGHP occurs by a mechanism of physical sorption.

Biosorption kinetics

One of the most critical factors in designing an adsorption system (for determining contact time and reactor configurations) is the prediction of absorption process rate which is controlled by the system kinetics. Biosorption kinetics is dependent on the physicochemical characteristics of the adsorbent which affects the absorption mechanism. In order to analyze kinetic mechanism, biosorption constants can be calculated using the Lagergren equation, the pseudo first order model (Lagergren 1989), the Weber and Morris model and pseudo second order (Ho & McKay 1999). The linear form of the pseudo second order equation is:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

where q_e is the amount of Cr(VI) adsorbed at equilibrium (mg g^{-1}), q_t is the amount of Cr(VI) adsorbed at time t (mg g^{-1}), and K_1 is the first order equilibrium rate constant min^{-1} . Plotting $\log(q_e - q_t)$ against t in laboratory conditions, a straight line is obtained which can be used to determine the rate constant K_1 and correlation coefficient R^2 values (Lagergren 1989).

The linear form of the pseudo second order equation can also be written as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where q_e is the amount of Cr(VI) adsorbed at equilibrium (mg g^{-1}) and K_2 is equilibrium rate constant of the second order kinetics model (mg(g min)^{-1}). t/q_t against t determines rate constant K_2 and R^2 values (Ho & McKay 1999). K_1 , q_e , and R^2 (correlation coefficient for the first order kinetic model) and K_2 , q_e , and R^2 (correlation coefficient for the second order kinetic model) values are obtained and are presented in Table 2. According to the results, the data obtained through the process of biosorption of chromium using AGHP conform to and follow the pseudo first order kinetic model ($R^2 > 0/99$).

To quantitatively compare the applicability of each model, a normalized standard deviation (Δq) was calculated as follows:

$$\Delta q = (\%) = 100 \sqrt{\frac{\sum [(q_{\text{exp}} - q_{\text{cal}})/q_{\text{exp}}]^2}{n - 1}} \quad (5)$$

where n is the number of data points and q_e is the adsorbent capacity at the equilibrium experimental ($q_{e,\text{exp}}$) and equilibrium calculated ($q_{e,\text{cal}}$) conditions, respectively. Since Δq represents agreement between the experimental and the predicted data points, it provides a numerical measure to interpret the goodness of fit of a given mathematical model to the data (Argun et al. 2007).

The calculated R^2 values (correlation coefficient) by linear regression for the studied kinetics are shown in Table 2.

According to the obtained R^2 values in Table 2, it can be observed that adsorption process in this equation follows the

Table 2 | Results of Cr(VI) biosorption kinetic modeling

| Model | Pseudo first order equation | Pseudo second order equation | Weber and Morris model |
|---|-------------------------------------|---------------------------------------|-------------------------------|
| Equation | $\ln(q_e - q_t) = \ln q_e - k_1 t$ | $t/q_t = (1/k_2 q_e^2) + t/q_e$ | $q_t = k_{id} t^{0.5} + C$ |
| Plot | $\ln(q_e - q_t)$ vs. t | t/q_t vs. t | q_t vs. $t^{0.5}$ |
| Concentration | 20 | 20 | 20 |
| Fitted model | $\ln(q_e - q_t) = -3.585 - 0.013 t$ | $t/q_t = 0.203 + 0.094 t$ | $q_t = 0.002 t^{0.5} + 10.09$ |
| R^2 | 0.854 | 0.980 | 0.896 |
| Constant | $k_1 = -0.013 \text{ min}^{-1}$ | $k_2 = 0.0435 \text{ mg(g min)}^{-1}$ | $k_{id} = 0.002$ |
| Calculated q_e ($q_{e,\text{cal}}$) | 0.028 mg g^{-1} | 10.64 mg g^{-1} | - |
| Experimental q_e ($q_{e,\text{exp}}$) | 10.123 mg g^{-1} | 10.123 mg g^{-1} | - |
| Δq % | 2.80% | 0.72% | - |

Table 3 | Comparison of maximum adsorption capacities of Cr(VI) in various adsorbents with and without activation

| Sorbent | q_{\max} (mg g^{-1}) | Reference | Sorbent | q_{\max} (mg g^{-1}) | Reference |
|----------------------|--------------------------------------|------------------------------|--------------------------------|--------------------------------------|---------------------------------|
| AGHP | 10.123 | Present study | Rice husks | 0.6 | Sumathi & Naidu (2005) |
| Almond shell | 3.40 | Pehlivan & Altun (2008) | Rice straw | 3.15 | Gao <i>et al.</i> (2008) |
| Almond shell carbon | 10.6 | Dakiky <i>et al.</i> (2002) | Almond shell | 2.40 | Mohan <i>et al.</i> (2005) |
| Walnut | 2.28 | Tunali <i>et al.</i> (2005) | Oil cake from Jatropha | 0.63 | Garg <i>et al.</i> (2007) |
| Walnut shell | 8.01 | Pehlivan & Altun (2008) | Sugar cane bagasse | 13.4 | Altundogan <i>et al.</i> (2007) |
| Hazelnut shell | 8.28 | Mohanty <i>et al.</i> (2005) | Maize cob | 13.8 | Park <i>et al.</i> (2008) |
| Coconut shell carbon | 20.0 | Alaerts <i>et al.</i> (1989) | Coal | 6.78 | Gao <i>et al.</i> (2008) |
| Palm pressed fibers | 14.0 | Alaerts <i>et al.</i> (1989) | Oak pine | 0.47 | Park <i>et al.</i> (2008) |
| Sawdust | 1.5 | Arica & Bayramoglu (2005) | Spent activated clay | 1.42 | Weng <i>et al.</i> (2008) |
| Beech sawdust | 16.1 | Kapoor & Yang (1989) | AC derived from coconut shells | 1.38 | Mohan <i>et al.</i> (2005) |

pseudo second order model. Furthermore, it is also supported by the fact that K_2 coefficient is larger than K_{1d} and K_1 .

Comparison of almond green hull with other adsorbents

The adsorption capacity of Cr(VI) onto almond green hull was compared with several low cost adsorbents and they are shown in Table 3. The adsorption capacity of Cr(VI) on AGHP is calculated as 10.123 mg g^{-1} at $\text{pH} = 2$ and room temperature. Almond green hull in the present study possesses reasonable adsorption capacity in comparison with other sorbents.

CONCLUSION

In this study, the feasibility of using almond green hull as a biosorbent for the removal of Cr(VI) from industrial wastewaters was investigated. Adsorption reached equilibrium after about 60 min. Cr(VI) adsorption was severely dependent on the solution pH and the obtained results suggest that the maximum Cr(VI) removal occurred at $\text{pH} = 2$. According to the results, increasing the temperature from 5 to 50°C increased adsorption noticeably which proves that it is an endothermic reaction. AGHP can remove

hexavalent chromium at a concentration of 80 mg L^{-1} , adsorbent dose of 2 g L^{-1} , $\text{pH} = 2$, contact time of 60 min, stirring speed of 300 rpm and at room temperature, with the removal efficiency of 99.94%.

The obtained results indicate that almond green hull can be used as an effective, low cost, and easily available biosorbent for hexavalent chromium removal from wastewater.

Pseudo second order and Freundlich models fit the kinetic and equilibrium experimental data, respectively.

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