



Removal of hexavalent chromium from aqueous solutions using almond green hull adsorbent magnetized by Fe_3O_4 : isotherm, kinetic and thermodynamic studies

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Received 8 September 2018; Accepted 9 June 2019

ABSTRACT

In this study, the efficiency of almond green hull magnetized by Fe_3O_4 in the removal of hexavalent chromium from aqueous solutions was investigated. Structural characteristics of this adsorbent were determined by Fourier Transform Infrared Spectroscopy (FTIR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), vibrating-sample magnetometer (VSM) and Brunauer–Emmett–Teller (BET). The parameters examined for the removal of Cr(VI) included pH (2–12), initial concentration of hexavalent chromium (10–100 mg/L), adsorbent dose (0.1–0.8 g/L), contact time (1–60 min), and temperature (5–50°C). Finally, the isotherm and kinetics of the adsorption process were investigated. The result of this study showed that removal of Cr(VI) was higher in acidic pH. By increasing the adsorbent dose, contact time, temperature and reducing the initial concentration of the pollutant, the removal efficiency increased. In optimal conditions, the maximum removal efficiency of Cr(VI) by almond green hull magnetized by Fe_3O_4 was equal to 100% and maximum adsorption capacity was 25 mg/g, (optimal conditions: pH = 2, adsorbent dose: 0.8 g/L, initial concentration of Cr(VI): 20 mg/L, time: 60 min, temperature: 50°C). The results showed that the adsorption process is more consistent with Langmuir isotherm and pseudo-second order kinetics. The thermodynamic results of the adsorption process showed that this process was endothermic and spontaneous. In summary, the adsorption process on almond green hull magnetized by Fe_3O_4 can be used as a new and efficient method in the removal of Cr(VI) from aqueous solutions.

Keywords: Hexavalent chromium; Green almond hull; Fe_3O_4 ; Isotherm; Kinetics, Thermodynamic

1. Introduction

Industrial wastewater often contains heavy metals. This wastewater is a major threat to the environment and public health if they are discharged without treatment [1]. Due to the widespread use of various heavy metals in

mine operations, battery manufacturing, electrotyping and other industries, the surrounding underground and surface water are at the risk of metal pollution [2]. These metals, which cannot be decomposed biologically, are highly toxic and they are even accumulated in very low concentrations in the food chain and in living beings [3]. To prevent the risk

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of heavy metals, prevention of these metals entering natural ecosystems is the best approach [4].

Chromium is one of the heavy metals, which is used in various industries such as metal processing, electrotyping, weaving, leather, fertilizer and is found in industrial wastewater [5,6]. The chromium in the aqueous media is found in two forms of hexavalent chromium Cr(VI) and trivalent chromium Cr(III) [7]. The hexavalent chromium has been found as $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} [3]. Different studies have shown that the hexavalent chromium Cr(VI) is 100 times more toxic than trivalent chromium Cr(III) due to high solubility in water and easy reduction [7]. The entry of hexavalent chromium into the environment threatens the health of humans due to the effects on mutagenesis, carcinogenesis, liver, kidney, and pulmonary complications [8]. The maximum level for trivalent chromium in the wastewater is 5 mg/L and for the hexavalent chromium is 0.05 mg/L [3]. Also, according to the United States Environmental Protection Agency (USEPA), the Maximum Contaminate Level (MCL) for chromium in drinking water is 0.1 mg/L, and according to the World Health Organization (WHO), European Economic Community, and Health and Welfare Canada, it is 0.05 mg/L [9,10].

So far different methods have been used for the removal of hexavalent chromium such as ionic exchange, chemical precipitation, reverse osmosis, coagulation, electrolysis, membrane process, photo catalytic degradation, chemical reduction, and adsorption [11]. Meanwhile, the adsorption has attracted the attention of many researchers since it was a simple, affordable, and effective method for the removal of heavy metal ions in low and medium concentration. Adsorption is an environmentally friendly method, which has been investigated in recent years as an effective method for the removal of organic pollutants and heavy metal ions from water and wastewater [12].

Most of the agricultural waste compounds are lignin and cellulose and other composites including functional groups such as alcohols, aldehydes, ketones, carboxylates, phenols and ethers. These groups are attached to heavy metal by substituting hydrogen ions with metal ions in a solution or giving an electron pair and forming complex with metal ions in a solution [1]. After harvesting almonds from the trees, the farmers in the Southern Khorasan Province, Iran, separate the green hulls of this native plant and leave them in the environment as waste, which in addition to pollution, disrupt the beauty of the environment.

In this study, Fe_3O_4 nanoparticles were used to improve the quality of almond green hull, due to its high surface-to-volume ratio, easy construction, easy recycling and easy separation of adsorbents [13]. The almond green hull was also used to improve its efficiency in the removal of heavy metals. Therefore, this study aimed to examine the efficiency of Fe_3O_4 nanoparticles modified with almond green hull in the removal of hexavalent chromium Cr(VI) from aqueous solutions. In addition, the isotherm and kinetics of adsorption process were evaluated.

2. Materials and methods

2.1. Chemicals and equipment

The chemicals used in this study, such as acetone, diphenyl carbazide, potassium dichromate, nitric acid

(HNO_3 65%), hydrochloric acid and sodium hydroxide, and iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were provided by Merck Company. The devices used in this study included a pH meter (765 Calimatic), a shaker (IK model KS 260) and an incubator shaker (INFORS model Aerotron). The Whatman filter and magnet were used to separate the adsorbent. In addition, the concentration of hexavalent chromium was determined by UV-Visible spectrophotometer (CE CECIL 7400). The structural characteristics of the adsorbent were determined by the following techniques: Fourier Transform Infrared Spectroscopy (FTIR) (AVATAR 370 FT-IR), energy-dispersive X-ray spectroscopy (EDX) (ZEISS, SIGMA VP-500), scanning electron microscopy (SEM) (ZEISS, SIGMA VP-500), vibrating-sample magnetometer (VSM) (VSM 7400) and Brunauer-Emmett-Teller (BET) (Quanta Chrome NOVA 2000).

2.2. Synthesis of almond green hull magnetized by Fe_3O_4

In this experimental study, the green almond hulls were provided from one of the regions of Southern Khorasan Province (called Kalateh Soleyman), Iran. The almond green hull adsorbent was rinsed properly using deionized water and dried at the ambient temperature. The samples were stored in the nylon until the experiment phase. Accordingly, the adsorbent was made by Gupta and Nayak [14]. First, 6.1 g of ferric chloride and 4.2 g of ferric sulfate was added to 100 ml of distilled water, and the solution was heated to 90°C. Then, 10 ml of 26 % ammonium hydroxide and 1 g of almond green hull powder dissolved in 200 ml of distilled water were added immediately. By adjusting the pH of solution around 10 at the temperature of 80°C, stirring was applied for 30 min; then, it was allowed to cool down at ambient temperature. The black sediment of Fe_3O_4 nanoparticles modified with almond green hull powder was collected by filtration.

2.3. Preparing stock solution and performing adsorption experiments in a batch system

To prepare Cr(VI) solutions with different concentrations during the experiment, a 1000 mg/L of stock solution of this heavy metal was used. The stock solution was prepared by solving a certain amount of Potassium Dichromate powder with a purity of 95%.

The batch experiments were carried out to determine the optimal pH (2–12), hexavalent chromium concentration (10–100 mg/L), adsorbent dose (0.1–0.8 g/L), contact time (1–60 min), and temperature (5–50°C). To perform the adsorption experiments, 0.4 g/L of Cr(VI) solution with concentration of 20 mg/L was added, then it was put on a shaker at 300 rpm for the predetermined durations. After mixing and separating the solid phase from the liquid phase, the remaining concentration of Cr(VI) was measured by a spectrophotometer at a wavelength of 540 nm. Except for the experiment phase of determining the effect of temperature variations, the room temperature was controlled in the range of 24–25°C in other phases. In all the phases of experiment, pH of the solution was adjusted using HCl and NaOH 1 and 0.1 N.

The removal efficiency of hexavalent chromium was calculated by Eq. (1).

$$R\% = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (1)$$

where C_0 is initial concentration and C_f is final concentration of hexavalent chromium (mg/L).

The adsorption capacity (q_e) was also calculated by Eq. (2).

$$q_e = \frac{V}{M} \times (C_m - C_t) \quad (2)$$

where q_e is the adsorption capacity (mg/g), V is the solution volume (L), M is adsorbent amount (g/L), C_m and C_t are initial concentration and final concentration of hexavalent chromium (mg/L), respectively [15].

To study adsorption isotherms, the experimental data were analyzed using Langmuir and Freundlich isotherm equations [Eqs. (3) and (4)]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max} K_L} + \frac{C_e}{Q_{\max}} \quad (3)$$

$$\text{Log } Q_e = \left(\frac{1}{n}\right) \text{Log } C_e + \text{Log } K_f \quad (4)$$

where Q_e is the equilibrium hexavalent chromium concentration in the solid phase (mg/g), Q_{\max} is the maximum absorbance (mg/g), k_L is Langmuir adsorption equilibrium constant (1/mg), K_f is Freundlich constant suggesting adsorption capacity, and n is a constant suggesting the adsorption intensity [16].

To study the kinetics of adsorption, the equilibrium data were examined by two common pseudo-first order and pseudo-second order kinetics models. The correlation coefficient (R^2) was considered as a measure of consistence between experimental data and two proposed models. The pseudo-first order kinetic model or equation is as follows:

$$\text{Log}(q_e - q_t) = \text{Log } q_e - \frac{K_1}{2.303} t \quad (5)$$

where q_t is the amount of absorbed material on adsorbent per time t , q_e is equilibrium time (mg/g), and K_1 is the pseudo-first order adsorption rate (1/min).

The pseudo-second-order model is as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where K_2 is the pseudo-second-order constant (g/(mg·min)). The graph t/q_t is depicted against t to obtain the velocity parameters, and the results suggest the consistency of this synthetic model with experimental data [16].

To investigate the thermodynamics of Cr(VI) adsorption by the magnetized almond green hull, Eqs. (7) and (8) were used.

$$\Delta G = -RTL \ln k_d \quad (7)$$

$$\ln k_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (8)$$

In Eq. (7), ΔG is Gibbs free energy changes, R is the universal gas constant equal to 8.314 J/mol/K, T is the temperature (K), and k_d is the thermodynamic equilibrium constant. In Eq. (8), ΔS is the standard entropy (kJ/mol), ΔH is the standard enthalpy changes (KJ/mol), and R is the universal gas constant (KJ/mol) [16].

3. Results and discussion

3.1. Characteristics of almond green hull magnetized by Fe_3O_4

The analysis of the FTIR spectra of almond green hull magnetized by Fe_3O_4 adsorbent is shown in Fig. 1. As shown, there are numerous functional groups on different wavelengths in the adsorbent at C=O (1043), O–H (3421), C–H (2923), N–H (1443), 1608 (C=N), 1549 (C=C), 1200 (C–O), 530, 629, 488 (Fe–O).

Figs. 2a and b show the SEM images of almond green hull magnetized by Fe_3O_4 before and after contact with the contaminant. As shown, the adsorbent surface has a deep porosity and hole, and hexavalent chromium is adsorbed after contact with the adsorbent and placed on the magnetic adsorbent.

Figs. 3a and b show the adsorbent EDX analysis before and after the adsorption process, respectively. As shown, the Fe^{2+} ion in the synthesized adsorbent (almond green hull magnetized by Fe_3O_4) has been shown to confirm that the synthesized adsorbent has been magnetized. In addition, the peak of chromium in EDX spectra after adsorption is observed indicating the adsorption of hexavalent chromium by almond green hull magnetized by Fe_3O_4 adsorbent from aqueous solutions.

Fig. 4 shows the magnetic moment versus magnetic field (M–H ring) at a temperature of 300 K for the adsorbent. The resulting magnetization curve showed that almond green hull magnetized by Fe_3O_4 has a proper magnetic property with magnetic saturation of 18.91 (emu/g). Accordingly, it can be concluded that the studied adsorbent is easily dispersed in water, and can be easily aggregated by the external magnetic field in a few minutes, and then can be simply dispersed with a few shakes.

Analysis of surface characteristics with BET models showed the specific surface area of almond green hull magnetized by Fe_3O_4 was 643 m^2/g .

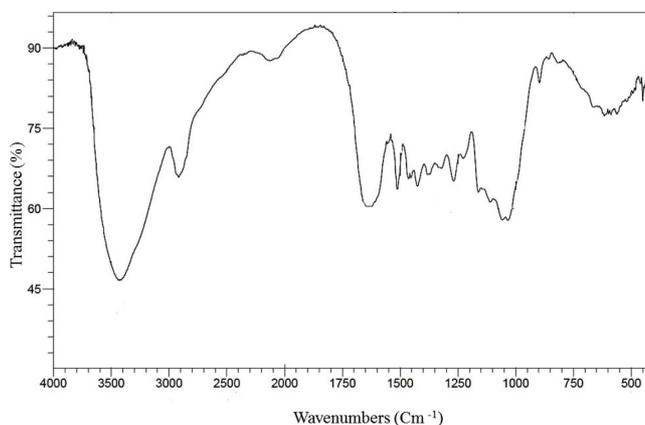


Fig. 1. FTIR analyze of almond green hull magnetized by Fe_3O_4 .

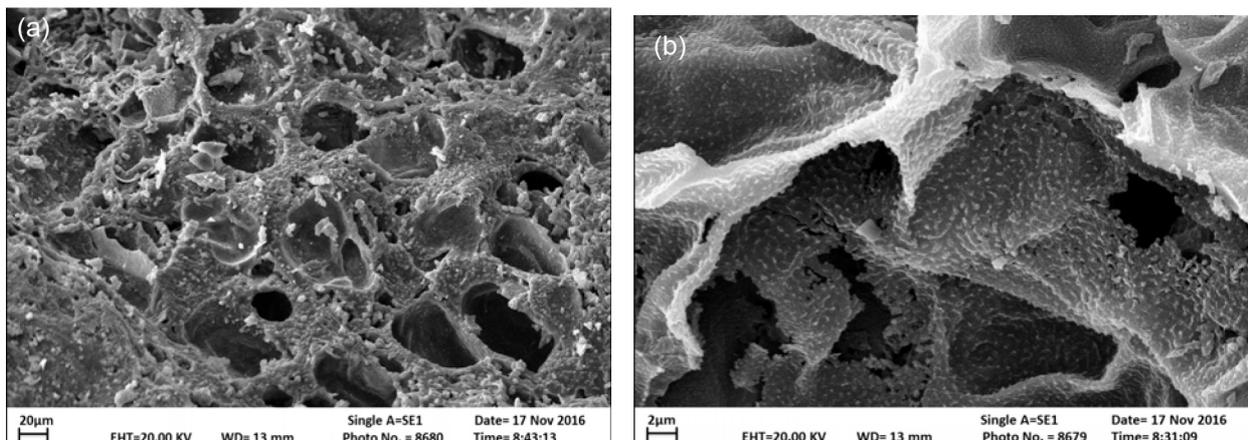


Fig. 2. SEM images of almond green hull magnetized by Fe_3O_4 a) Before adsorption b) After adsorption.

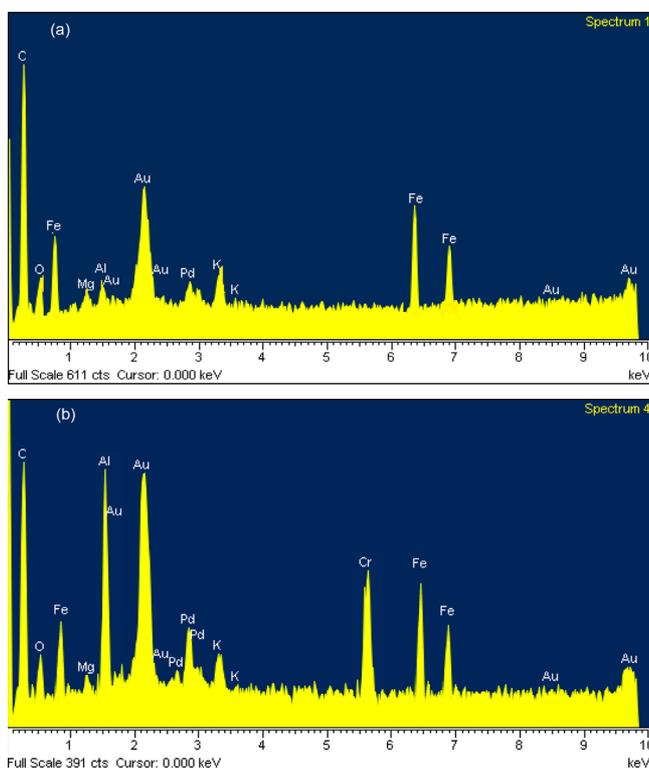


Fig. 3. EDX analyze of almond green hull magnetized by Fe_3O_4 a) Before adsorption b) After adsorption.

3.2. Effect of pH

In this stage, the effect of pH on the removal of hexavalent chromium was evaluated at pH of 2–12. Hence, Cr(VI) solution was made at a concentration of 20 mg/L, and then 0.4 g/L was added to the adsorbent and it was placed on a shaker for 60 min. Fig 5 shows the effect of pH on the removal efficiency of Cr(VI) by almond green hull magnetized by Fe_3O_4 . As shown in Fig. 5, the maximum and minimum removal efficiency of Cr(VI) was at pH 2 and 12, respectively. At pH = 2, the maximum removal efficiency of Cr(VI) was 90.84% and the maximum adsorption capacity of the almond green hull magnetized by Fe_3O_4 was 45.60 mg/g.

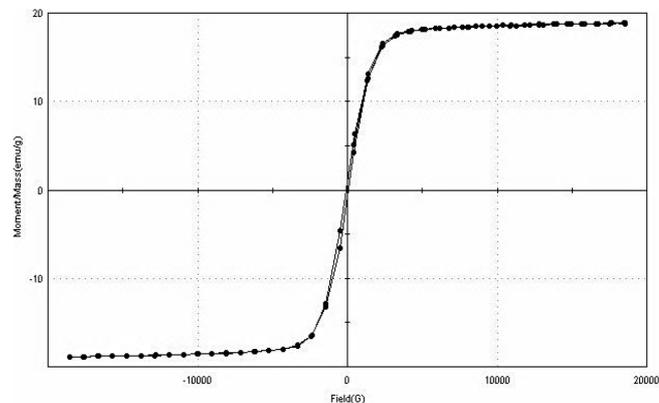


Fig. 4. VSM of almond green hull magnetized by Fe_3O_4 .

The pH variations are effective on the hexavalent chromium adsorption, since it determines the ion type of hexavalent chromium and adsorbent surface charge. This situation will also affect the reaction between adsorbent and adsorbate. Regarding Cr(VI), the dominant forms at $\text{pH} \leq 2$ are HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$, and the major component is HCrO_4^- .

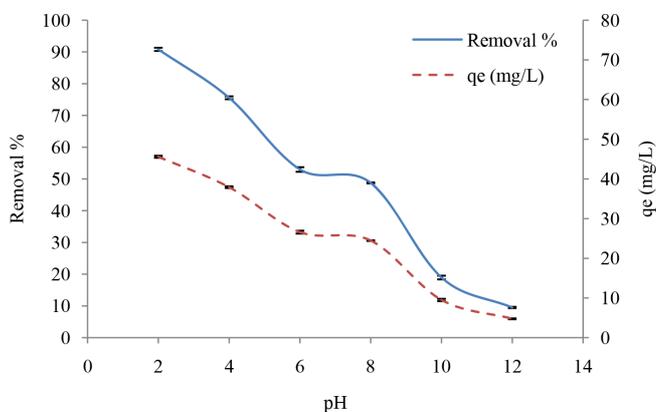


Fig. 5. Effect of pH for the removal of Cr(VI) using almond green hull magnetized by Fe_3O_4 (temperature: ambient temperature of 24–25°C, hexavalent chromium concentration: 20 mg/L, adsorbent dose: 0.4 g/L, velocity: 300 rpm, time: 60 min).

According to Fig. 5, the high adsorption of Cr(VI) in acidic pHs can be due to low concentrations of OH^- ions in aqueous environment. At these pH, OH^- groups on the adsorbent tend to move around the aqueous environment. Thus, the positive groups are created on the adsorbent which leads to the increased adsorption of Cr(VI). However, with increased pH, the concentration of OH^- groups is increased in the environment, and OH^- groups on the adsorbent have no tendency to be released. Thus, fewer positive sites are created, and the adsorption of Cr(VI) is performed at a lower rate [17,18]. Hasan et al. attempted to remove Cr(VI) from aqueous solutions using agricultural waste (maize bran). The results showed that the maximum adsorption occurred at pH = 2 [19]. Also, Hu et al. conducted a study on the removal of Cr(VI) by magnetite and emphasized the importance of pH of the environment on the removal of hexavalent chromium and maximum removal efficiency was reported pH = 2.5 [20].

3.3. Effect of adsorbent dose

Fig. 6 shows the changes in the adsorption of hexavalent chromium by almond green hull magnetized by Fe_3O_4 . As shown in this figure, by increasing the amount of adsorbent dose from 0.1 to 0.8 g/L, the removal efficiency of Cr(VI) increased from 68.54% to 99.84%. The adsorption capacity decreased with an increase in the adsorbent dose. The maximum adsorption capacity of almond green hull magnetized by Fe_3O_4 at 0.1 and 0.8 g/L was 137.63 and 25.06 mg/g, respectively.

According to Fig. 6, with increasing the adsorbent dose, the removal efficiency increased and the adsorption capacity reduced. By increasing the adsorbent dose, the contact surface between the adsorbent and hexavalent chromium increases, and there are more minor sites available at the adsorbent surface, which increases the removal efficiency [21]. The decrease in the adsorption capacity from 137.63 mg/g to 25.06 mg/g is due to the unsaturated adsorption caused by excessive adsorbent and inadequate adsorption [22]. The results of this research are also consistent with results of Dehghani et al., on the adsorption of Cr(VI) from aqueous solutions by single-wall and multi-wall carbon

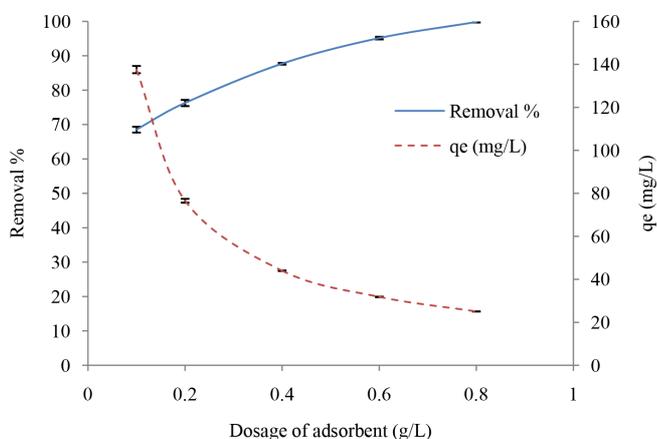


Fig. 6. Effect of adsorbent dose for the removal of Cr(VI) using almond green hull magnetized by Fe_3O_4 (temperature: ambient temperature of 24–25°C, hexavalent chromium concentration: 20 mg/L, pH = 2, velocity: 300 rpm, time: 60 min).

nanotubes. In this research, they argued that by increasing the adsorbent dose, the removal of Cr(VI) is increased due to the increase in large numbers of free adsorption sites and higher adsorbent surface [23]. Also, similar results have been reported in the study of Jiang et al. [24].

3.4. Effect of hexavalent chromium concentration

Fig. 7 shows changes in the removal of Cr(VI) in various initial concentrations. As shown, with increasing the chromium concentration from 10 mg/L to 100 mg/L, the removal efficiency decreases. The removal efficiency of Cr(VI) in these concentrations (10 mg/L and 100 mg/L) was 50.88% and 100%, respectively. In addition, the adsorption capacity of almond green hull magnetized by Fe_3O_4 is increased by increasing the concentration of Cr(VI). At 10 mg/L and 100 mg/L concentrations of Cr(VI), the adsorption capacity was 12.5 and 63.6 mg/g, respectively.

According to Fig. 7, the adsorption capacity increases by increasing the initial concentration of Cr(VI), while the removal efficiency decreases. This could be due to the fact that the higher concentration of Cr(VI) leads to an increase in driving force of the concentration gradient. This driving force reduces the inter space resistance, and as a result, it accelerates the adsorption of hexavalent chromium (VI) from solution to adsorbent [22]. In addition, the reduced removal efficiency can be due to the limited number of active adsorbent sites, which are saturated in high concentrations. By reducing the initial concentration of the solution, the amount of metal ions in the solution decreases, therefore, a high percentage of ions are absorbed into the adsorbent [25]. Therefore, at low concentrations, the removal rate of Cr(VI) is less than the sites on the adsorbent surface, but by increasing concentration of Cr(VI) in the solution, the existing sites on the adsorbent surface are highly reduced, so the removal percentage is decreased. The results of this study are quite consistent with the study by Karthikeyan et al., which was performed on the adsorption of Cr(VI) by sawdust activated carbon. In this study, it was found that by increasing Cr(VI) concentration, the removal efficiency significantly reduced [26].

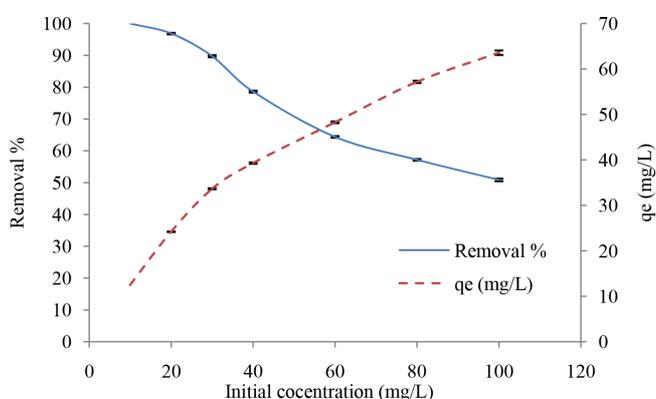


Fig. 7. Effect of initial concentration for the removal of Cr(VI) using almond green hull magnetized by Fe_3O_4 (temperature: ambient temperature 24–25°C, adsorbent dose 0.8 g/L, hexavalent chromium concentration 20 mg/L, pH = 2, velocity 300 rpm, time 60 min).

3.5. Effect of contact time

In Fig. 8 the results of the effect of contact time on the removal of Cr(VI) have been shown by almond green hull magnetized by Fe_3O_4 . As shown, by increasing the contact time, the removal efficiency of Cr(VI) is increased frequently. The maximum removal efficiency reached 98.43% at 60 min. At this time, the adsorption capacity of almond green hull magnetized by Fe_3O_4 was 24.61 mg/g.

In Fig. 8 it is obvious that the adsorption of Cr(VI) was quick within the first few minutes, and a steep slope can be seen in the graph, which is due to the lack of active adsorbent sites. Then, the slope becomes slightly milder, which is due to the resistance to penetration. After the empty sites are occupied by metal ions and saturated, repulsive forces are generated between the adsorbent molecules and hence adsorption of Cr(VI) decreases. Finally, the adsorption is balanced, and from this time onwards, the adsorption rate becomes nearly constant [27–30]. In this regard, the same results of Chen et al., on the removal of Cr(VI) by mesoporous carbon nitride are obtained [31].

3.6. Effect of temperature and thermodynamic parameters

Table 1, Figs. 9 and 10 show the effect of temperature and thermodynamic parameters for the removal of Cr(VI) by almond green hull magnetized by Fe_3O_4 . As shown, with an increase in the temperature, the removal efficiency of

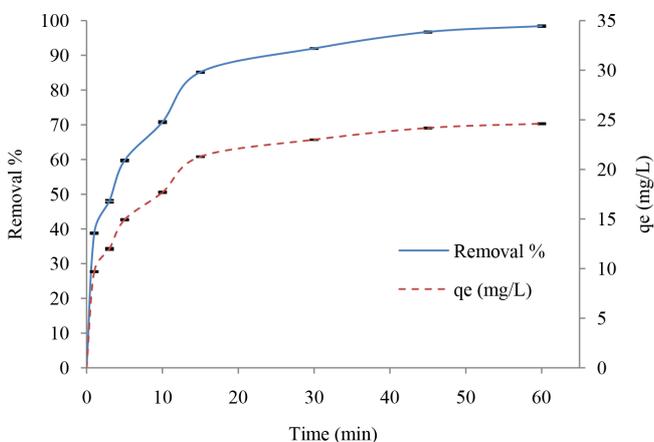


Fig. 8. Effect of contact time for the removal of Cr(VI) using almond green hull magnetized by Fe_3O_4 (temperature: ambient temperature 24–25°C, adsorbent dose 0.8 g/L, pH = 2, velocity 300 rpm, hexavalent chromium concentration 20 mg/L).

Table 1

Thermodynamic parameters for the removal of Cr(VI) using almond green hull magnetized by Fe_3O_4

T (°C)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol·k)
5	-20.57	0.044	82.56
10	-21.94		
20	-23.34		
40	-25.51		
50	-26.62		

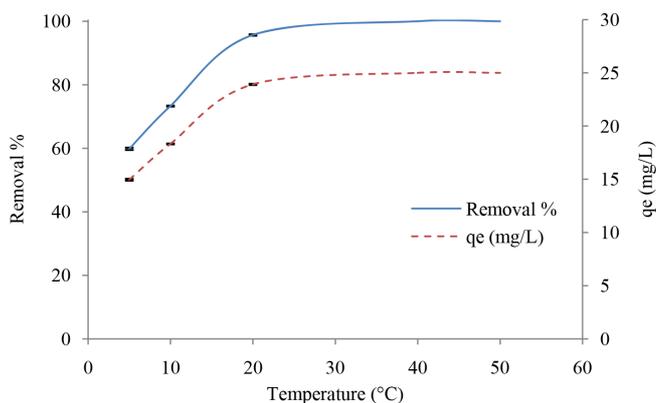


Fig. 9. Effect of temperature for the removal of Cr(VI) using almond green hull magnetized by Fe_3O_4 (time 60 min, adsorbent dose 0.8 g/L, pH = 2, velocity 300 rpm, hexavalent chromium concentration 20 mg/L).

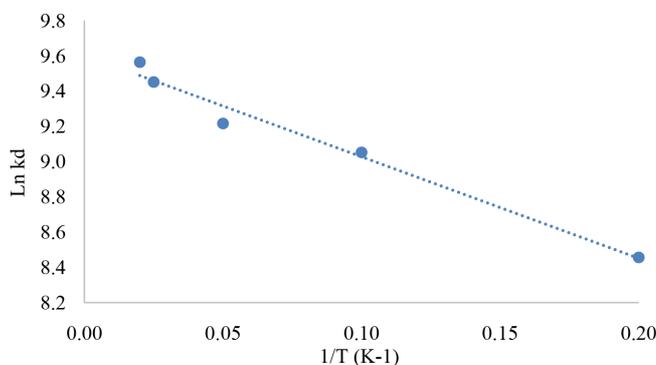


Fig. 10. The thermodynamic behavior for the removal of Cr(VI) using almond green hull magnetized by Fe_3O_4 .

Cr(VI) increases. The removal efficiency at temperatures of 5, 10, 20, 40 and 50°C were 59.84, 73.29, 95.68, 100, and 100%, respectively.

As shown in Fig. 9, the increase in temperature has led to an increase in the adsorption capacity and removal efficiency of Cr(VI). By increasing the temperature, the kinetic energy of $\text{Cr}_2\text{O}_7^{2-}$, which is the main form of hexavalent chromium in acidic conditions, is increased, and as a result, the contact of these ions with adsorbent is increased. The increase in temperature may lead to the development of new sites on the adsorbent [32]. In this regard, Moussavi and Barikbin reported that with the increase in temperature from 5 to 40°C, the chromium adsorption also increases [32]. Dunder et al. performed biosorption of Cr(VI) by the litter of natural trembling poplar forest and defined the temperature of 45°C as optimal temperature [33].

According to Table 1 and the negative total ΔG , the Cr(VI) adsorption process almond green hull magnetized by Fe_3O_4 is spontaneous. In addition, the decrease in ΔG values with increasing temperature indicates that the increase in the rate of spontaneous adsorption. The positivity of the enthalpy (ΔH) of the adsorption process on the almond green hull magnetized by Fe_3O_4 indicates that this process is endothermic. In addition, the positive values of ΔS indicate increased randomness at the solid–solution interface during adsorption [34,35].

3.7. Adsorption isotherm

Table 2 shows the adsorption isotherm of Cr(VI) by almond green hull magnetized by Fe₃O₄. Isotherm adsorption is the most important factor in the design of adsorption systems. This factor determines the relationship between adsorbate concentration and adsorption capacity of an adsorbent. According to the Table below, it was found that Langmuir model (R² = 0.9906) was more suitable for adsorption data compared with Freundlich model (R² = 0.9791).

Langmuir isotherm based on the single layer and uniform and homogeneous adsorption of the adsorbate has the same energy on all levels of an adsorbent. The Freundlich isotherm, in contrast to Langmuir model, is based on the multilayer and heterogeneous adsorption of adsorbate on the adsorbent [36]. In the Langmuir model, the K_L coefficient is a constant that increases with increasing particle size. In addition, the tendency of pollutant to adsorbent is evaluated using a dimensionless parameter (R_L). If R_L = 0 the adsorption is irreversible, if 1 > R_L > 0, the adsorption is desirable, if R_L = 1 the adsorption is linear and if 1 < R_L, the adsorption is undesirable. In this study, based on the calculated results, since R_L is between 0 and 1, the adsorption process is desirable. In this regard, the similar results were reported by Malkoc et al. [37].

3.8. Kinetic adsorption

Table 3 represents the components of containment adsorption kinetics in this research by almond green hull adsorbent magnetized by Fe₃O₄. In this research, the applicability of pseudo-first-order and pseudo-second-order kinetics model was investigated by a kinetic study at initial concentrations different from adsorbate. The results of evaluating kinetic models of Cr(VI) adsorption by almond green hull magnetized by Fe₃O₄ showed that this process follows the pseudo-second-order kinetics.

The results of determining adsorption process kinetics are shown in Table 3. In the pseudo-first-order kinetic

Table 2
Isotherm models constant for the removal of Cr(VI) using almond green hull magnetized by Fe₃O₄

Model	Units	Values
Langmuir equation	–	$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$
Plot	–	$\left(\frac{C_e}{q_e}\right) vs. C_e$
Fitted model	–	$\frac{C_e}{q_e} = 0.001 + 0.0986 C_e$
q _{max}	mg/g	10.142
K _L	L/mg	95.96
R ²	–	0.9906
R _L = 1/1 + K _L C ₀	–	0.0005
Freundlich equation	–	$Ln q_e = Ln K_f + \frac{1}{n} Ln C_e$
Plot	–	$Ln q_e vs. Ln C_e$
Fitted model	–	$Ln q_e = 1.7902 + 0.6379 Ln C_e$
K _f	(mg/g (L/mg) ^{1/n})	5.99
N	–	1.568
R ²	–	0.9791

model, the graph log (q_e – q_t) was depicted against t to determine constant value of K₁ and R² coefficient, and graph t/q_t was depicted against t to obtain velocity parameters in

Table 3
Results of kinetic models for removal of Cr(VI) by almond green hull magnetized by Fe₃O₄

Model	Pseudo-first order equation	Pseudo-second order equation
Equation	$Ln(q_e - q_t) = Ln q_e - k_1 t$	$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \frac{t}{q_e}$
Plot	$Ln(q_e - q_t) vs. t$	$\frac{t}{q_t} vs. t$
Concentration	20	20
Fitted model	$Ln(q_e - q_t) = 2.185 - 0.028 t$	$\frac{t}{q_t} = 0.311 + 0.061 t$
R ²	0.973	0.991
Constant	$k_1 = -0.028 \text{ min}^{-1}$	$k_2 = 0.0435 \text{ mg} / (\text{g min})$
Calculated q _e (q _{e,cal})	(16.132 mg)/g	(16.123 mg)/g
Experimental q _e (q _{e,exp})	(8.890 mg)/g	(16.39 mg)/g

the pseudo-second-order model. The values of q_e and K_2 were determined from calculating gradient and width from origin of this graph. Since experimental q_e [Eq. (2)] is more consistent with calculated q_e in pseudo-second order kinetics, it can be said that the adsorption process follows this kinetic model. Also, the comparison of R^2 coefficients in two kinetic models shows the consistence of adsorption with pseudo-second-order model, which is similar to the results of Hasan et al. [19].

3.9. Comparison of our adsorbent with other adsorbent

The comparison of this adsorbents (almond green hull magnetized by Fe_3O_4) efficiency with the other reported adsorbents in terms of the removal of Cr(VI) are shown in Table 4. As shown, the adsorbent used in this study (almond green hull magnetized by Fe_3O_4) for removal of Cr(VI) has a higher adsorption capacity than some other adsorbent. However, due to the experimental conditions of the variable, direct comparison between different adsorbents cannot be done.

4. Conclusion

In this study, it was found that the removal of Cr(VI) with decreased pH was increased due to the dominant ion type HCrO_4^- at acidic pH (pH = 2). By increasing the initial concentration of this metal, the removal percentage also reduced. The removal of Cr(VI) was increased by increasing the adsorbent dose and the contact time. The adsorption process is endothermic, so, as the temperature increases, the

Table 4

Comparison of this adsorbents (almond green hull magnetized by Fe_3O_4) with the other reported adsorbents in terms of the removal of Cr(VI)

Adsorbent	pH	q_e (mg/g)	References
Almond green hull magnetized by Fe_3O_4	2	25	This study
Almond green hull	6	2.04	[38]
Walnut shell	3.5	8.01	[39]
Hazelnut shell	3.5	8.28	[39]
Almond shell	3.2	3.40	[39]
Pea (<i>Pisum sativum</i>) pod	2	4.33	[40]
Tea (<i>Camellia sinensis</i>) waste	2	4.29	[40]
Banana (<i>Musa lacatan</i>) waste	2	10	[40]
Treated waste newspaper	3	59.88	[41]
Gulmohar's fruit shell	2	12.28	[42]
Activated carbon prepared from mango kernel	2	7.8	[43]
Swietenia mahagoni fruit shell	3	2.309	[44]

reaction rate increases and the adsorption process performs well and more efficiently. The results of this study showed that in optimal conditions, the removal percentage of hexavalent chromium by almond green hull magnetized by Fe_3O_4 was equal to 100% and maximum adsorption capacity was 25 mg/g (optimal conditions: pH = 2, adsorbent dose: 0.8 g/L, Cr(VI) concentration: 20 mg/L, time: 60 min, temperature: 50°C). The results also showed that the adsorption process is more consistent with Langmuir isotherm and pseudo-second-order kinetics. Overall, the results of the experiments in this study showed that the adsorption process could be used on almond green hull magnetized by Fe_3O_4 as a new, effective, and fast method in the removal of hexavalent chromium from aqueous solutions.

Acknowledgment

The authors would like to thank Payame Noor University of Tehran for technically supporting this research.

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