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Water Practice & Technology Vol 16 No 2
doi: 10.2166/wpt.2021.007

Adsorption of hexavalent chromium ions from aqueous solutions using nano-chitin: kinetic, isotherms and thermodynamic studies

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Abstract

Treatment of the industrial wastewater before discharging into aquatic ecosystems using a new technology such as nanotechnology seems necessary. There are different methods for the removal of the heavy metals in the wastewater. In this study, nano-chitin was purchased from the Nano-Novin Polymer Company and used as an adsorbent for the removal of chromium (VI) ions from aqueous solution in a batch system. The effects of pH, temperature, contact time, concentration, and adsorbent dose were investigated. According to the results, the optimum conditions of adsorption occurred at pH = 6, temperature = 25 °C, 60 minutes contact time, and 0.6 g·L^{-1} adsorbent dose. Investigation of equilibrium isotherms showed that the isotherm fitted the Freundlich model with a correlation coefficient of $R^2 = 0.9689$. The pseudo second-order model with the larger correlation coefficient had a greater fitness against experimental data in the kinetic studies. Thermodynamic parameters such as Gibbs free energy, enthalpy, and entropy were calculated, which indicated spontaneous, endothermic, and random processes, respectively. Given the good results of this project, nano-chitin can be suggested as a novel adsorbent which is highly capable of adsorbing hexavalent chromium from aqueous solutions.

Key words: adsorption, Cr (VI), isotherm, nano-chitin, nanotechnology

Highlights

- Nano-chitin was purchased from the Nano-Novin Polymer Company.
- Nano-chitin as a novel adsorbent is highly capable of adsorbing chromium from aqueous solutions.
- The results showed that pH = 6, adsorbent dose of 0.1 g/L, 25 °C and 60-minute contact time were the optimum adsorption values in this research.
- The results showed the data better fitted the Freundlich isotherm model and kinetic pseudo-second-order model.

INTRODUCTION

Rapid population growth, industrialization, and urbanization have been associated with extensive use of heavy metals, and have resulted in environmental pollution. Heavy metal contamination is a major concern, especially in aquatic ecosystems, due to the dangerous, toxic, and bio-accumulative effects on the human food chain (Begum *et al.* 2018). The usage of heavy metals in industry is increasing and it will lead to environmental pollution (Maleki *et al.* 2019). Heavy metal ions are found naturally in volcanic activity, weathering of rocks, as well as in many industries with potential impacts on various forms of life (Theydan 2018).

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Due to the high solubility of Cr (VI) in water, its accumulation in aquatic environments is common (Rizzo *et al.* 2019). Hexavalent chromium (VI) is a highly toxic heavy metal that is used by different industries such as leather, manufacturing, catalysts, fungicides, pigment production, ceramics, art, glass, photography, metal plating, and corrosion control (Peng *et al.* 2019). The International Agency for Research on Cancer (IARC) has classified chromium (VI) in the first group (carcinogenic to humans), Exposure to high levels of chromium can cause respiratory problems, lung cancer, gastric ulcer, liver, and kidney damage as well as osteoporosis (Tseng *et al.* 2019).

Removal of heavy metals through application of various adsorbents has been of interest to many researchers because removal of this substance from wastewater before discharge into aquatic systems is necessary. Chitin is one of the most abundant biopolymers following cellulose (Yadav *et al.* 2019). Various technologies have been used in the past including chemical deposition, adsorption, ion exchange, membrane separation, solvent extraction, and biological processes to remove the heavy metals from water and wastewater. Among these technologies, adsorption is the most appropriate method due to its high efficiency, low cost, convenient preparation, and operation (Sun *et al.* 2018). In the current study, the adsorption process was used to remove chromium. Adsorption was favoured over other techniques due to ease of operation, low energy input and removal of pollutant even at trace concentration. The removal of chromium can be achieved by using various adsorbents like corn straw (Ma *et al.* 2019), groundnut shell (Bayuo *et al.* 2019), palm kernel (Razavi Mehr *et al.* 2019), chitosan-based hydrogel (Vilela *et al.* 2019), activated carbon (Rambabu *et al.* 2019).

Chitin is a natural polysaccharide and is prominently found in the hard shell of crustaceans such as crabs and shrimp, insect cuticles, and the cell walls of fungi (Yadav *et al.* 2019). It is the most abundant biopolymer in the world and is considered as an environmentally friendly adsorbent, inexpensive, non-toxic, biodegradable, renewable, and highly accessible in nature (Fooladgar *et al.* 2019). In this study, different methods of purification using chitin adsorbent, as a valuable natural material, have been used to adsorb chromium from aqueous solutions. To the best of our knowledge, no research has been carried out on the adsorption of heavy metals using this adsorbent.

The main objectives of this study were to investigate the effect of pH, initial concentration, contact time, temperature, and adsorbent dose on the adsorption of hexavalent chromium from aqueous solutions using nano-chitin. For determining the mechanism of the adsorption in this study, kinetic, thermodynamic, and adsorption isotherm models were investigated.

BACKGROUND

Chitin

Chitin ($C_8H_{13}O_5N$) n is the second most abundant biopolymer in the world, coming from a renewable organic resource. It is a polysaccharide with a long polymeric chain, and due to this property, it has many advantages for modification during the synthesis of derivatives. From a structural point of view, chitin is a polymer with a high molecular weight, linear sequential units of N-acetyl-d-glucosamine (linked by b-1, 4 units) and it chemically resembles cellulose, in which the hydroxyl group at carbon-2 in cellulose has been substituted by an acetamido group. Chitin can be found in powder form or even in granules (or sheets). Chitin can be purchased at a low cost from organic sources (especially from krill, lobsters, crabs and shrimps) or wastes derived from some industries of seafood processing (Yadav *et al.* 2019). Chitin has a great ability to remove chromium and has good degradation properties in nature and easily returns to the biological cycles (Anastopoulos *et al.* 2017).

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MATERIALS AND METHODS

Materials

This was an applied experimental study conducted on nano-chitin as an adsorbent of heavy metal chromium (VI) ions from aqueous solutions on a laboratory scale in Science and Research Branch of Azad University, Tehran, with two batch replications. In this study, nano-chitin was purchased from Nano-Novin Polymer Company with the physiochemical properties of nano chitin shown in Table 1. The other chemicals were purchased from Merck Company (Germany).

Table 1 | Properties of nano chitin

Name	Chitin nano gel
Formula	$(C_8H_{13}NO_5)n$
Material state	Gel
Color	White
Production method	Chemi-mechanical
Nanofiber diameter	Ave. 30 nm
Purity	99% ≤

Adsorption experiments

The stock solution of 1,000 mg/L was prepared by adding a certain amount of chromium salts and deionized water. The pH of each solution was adjusted using 0.1 M NaOH and 0.1 M HCl. Adsorption experiments were performed in the batch system. The pH of the solutions was measured using Crison pH Meter Basic 20. For agitation of the adsorbent and the heavy metal ions, the Heimolph Unimax 2010 shaker was used. For all treatments, the agitation speed was constant and equal to 120 rpm. After the reaction time, the nano-chitin adsorbent was separated using a Kokusan H-108 centrifuge at 10 min and 4,000 rpm. Chromium ion concentration was measured using the Atomic Absorption Spectrometer (AAS) model (Unicam-919). The effect of pH, adsorbent dose, contact time, initial concentration, and temperature were examined on the efficiency and adsorption capacity of chromium ions by the adsorbents. SPSS and Excel software were used for data analysis.

The adsorption percentage and adsorption capacity of the heavy metal chromium equilibrium were calculated using Equations (1) and (2) (Aslani *et al.* 2018; Liang *et al.* 2018):

$$A(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

In this formula, A is the percentage of adsorption; q_e is the amount of adsorption capacity; C_0 is initial concentration of a metal ion in solution in milligrams per liter; C_e is equilibrium concentration of metal ion in solution in $mg{\cdot}L^{-1}$ and m is adsorbent mass in grams, and V is the volume of solution in liters.

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The Langmuir equation is expressed by Equation (3) (Langmuir 1918):

$$q_e = \frac{q_{max} \times C_e b}{1 + C_e b} \tag{3}$$

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \tag{4}$$

In this equation, C_e ($mg{\cdot}L^{-1}$) is the equilibrium concentration of the metal ion in solution, q_e is the equilibrium adsorption value ($mg{\cdot}g^{-1}$), q_{max} is the maximum adsorption capacity, and b is the equilibrium constant of adsorption.

The Freundlich equation is expressed by Equation (5) (Freundlich 1906):

$$q_e = K_f (C_e)^{1/n} \tag{5}$$

$$Lnq_e = LnK_f + \frac{1}{n} Ln\ C_e \tag{6}$$

In this respect, q_e is the amount absorbed in $mg{\cdot}g^{-1}$, C_e is the equilibrium concentration of the adsorbed ions in $mg{\cdot}L^{-1}$ and K_f is the Freundlich constant.

The study of adsorption through the use of biologically derived nanomaterials at the temperature range produces thermodynamic constants such as the change of free energy of Gibbs ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$).

The free energy of Gibbs is expressed by Equation (7) (Moussout *et al.* 2018):

$$\Delta G = -RT\ Ln\ K_C \tag{7}$$

T: temperature (Kelvin), R is the ideal gas constant equal to 8.314 $J{\cdot}mol^{-1}{\cdot}k^{-1}$ K_C: the thermodynamic equilibrium constant obtained from Equation (8):

$$K_C = \frac{C_a}{C_e} \tag{8}$$

Ca: mg of adsorbent, which absorbs per liter of solution
Ce: soluble equilibrium concentration in milligrams per liter

According to the laws of thermodynamics, the free energy of Gibbs at constant temperature depends on the enthalpy changes and the entropy changes expressed by Van't Hoff's Equation (9) (Kumar *et al.* 2018):

$$LnKc = \frac{-\Delta H°}{R}\frac{1}{T} + \frac{\Delta S°}{R} \tag{9}$$

where $\Delta H°$ and $\Delta S°$ are obtained from the slope and intercept of the origin of the LnK_C graph in terms of $\frac{1}{T}$, respectively.

The kinetic model

Pseudo-first-order kinetic is expressed by Equation (10) (Bao *et al.* 2020):

$$Ln(q_e - q_t) = Lnq_e - k_1 t \tag{10}$$

q_t and q_e ($mg{\cdot}g^{-1}$) are the amount of metal ions absorbed at time t (Min.) and at equilibrium time and k_1 is pseudo first order rate constant, respectively.

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Pseudo-second-order kinetic is expressed by Equation (11) (Naseem *et al.* 2019):

$$t/q_t = 1/(k_2 q_e^2) - t/q_e \tag{11}$$

RESULTS AND DISCUSSION

Fourier transform infrared spectrometry (FTIR)

FTIR analysis was used to determine the nano-chitin surface groups. As seen in Figure 1, in the FTIR spectrum from the left, the broad and wide peak within the 3,000–3,600 cm^{-1} (3,442.39 cm^{-1}) region belongs to the OH- (hydroxyl) and -NH functional groups. The peak at 1,605.67 cm^{-1} belongs to the C = O functional group. The peak corresponding to 1,040.78 cm^{-1} region belongs to the C – O functional group. The weak peak in the 2,919.06 cm^{-1} region is attributable to the CH_3 and CH_2 tensile group SP^3 and the presence of single carbon-carbon bands. The weak peak at 3,096.65 cm^{-1} region was related to the C-H tensile group of SP^2 and the presence of carbon-carbon double bands. The weak peak at 3,262.95 cm^{-1} region was related to the C-H tensile functional group SP and the carbon-carbon triple bands.

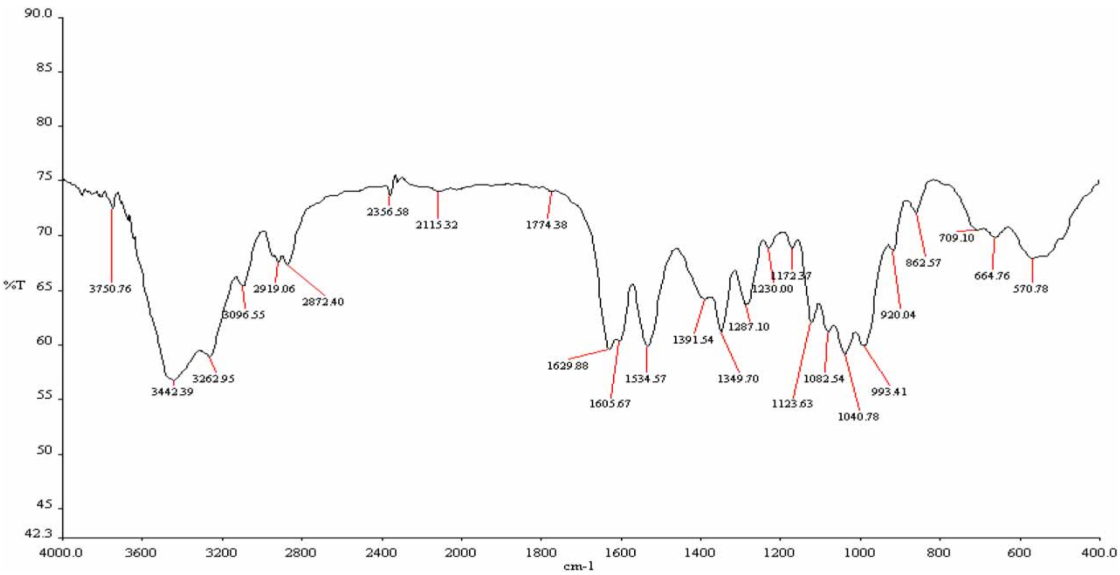

Figure 1 | FTIR analysis of nano chitin.

X-ray diffraction (XRD)

X-ray analysis determines the crystalline structure of the adsorbent. As seen in Figure 2, the XRD curve of nano crystalline peaks at 2θ is observed to be 20, 22.5, 22, 27, 28, and 39, all indicating the crystal structure of nano-chitin.

Scanning electron microscope (SEM)

The image shows the transmission and scanning electron microscope obtained from the nano-chitin. According to Figure 3, the diameter of the used material is less than 100 nm (nanometer range) and has a fibrous and network structure.

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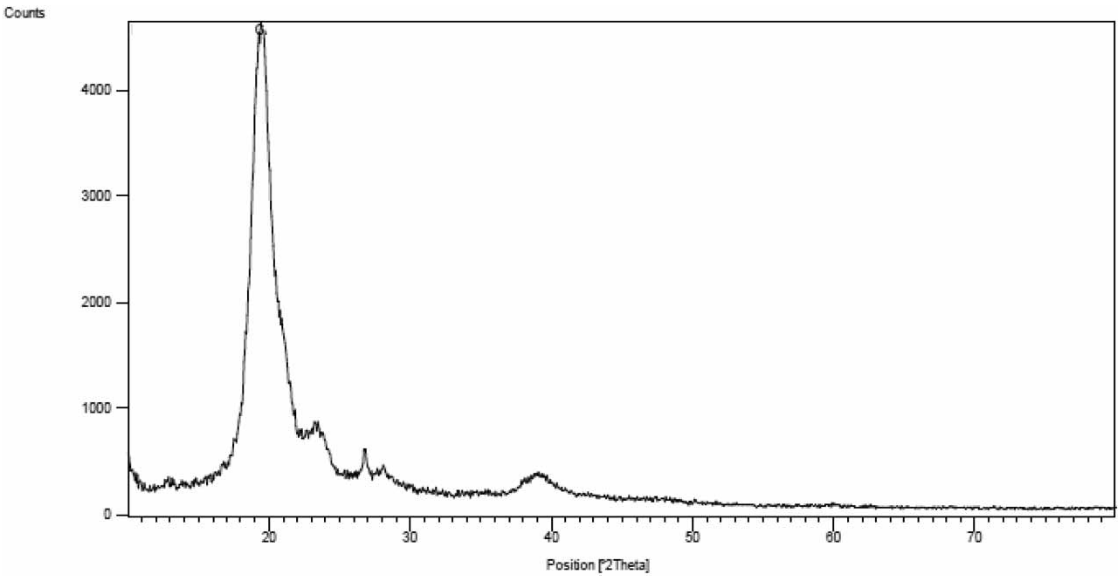

Figure 2 | XRD patterns for the nano chitin.

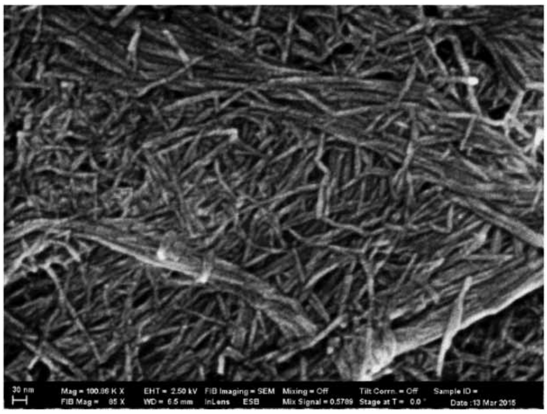

Figure 3 | SEM micrograph of nano chitin.

Effect of pH

pH of a solution is an important parameter in any adsorption process because it affects both aqueous chemistry and surface binding sites of the adsorbents (Srivastava *et al.* 2015). The effect of different pH (2–7) was investigated on the amount of chromium ion uptake, initial concentration of 5 mg·L^{-1} chromium (VI), adsorbent dose of 0.1 g/L, 25 °C and 60-minute contact time. For all treatments, the agitation speed was constant and equal to 120 rpm. pH is an important factor affecting metals and should be studied in the adsorption process (Huang *et al.* 2018; Shaban *et al.* 2018). The soluble pH during the reaction affects the solubility of the adsorbed material, concentration of ions, adsorbent functional groups, the degree of ionization of the adsorbed material (Al-Othman *et al.* 2012). According to Figure 4, the highest adsorption percentage and adsorption capacity of chromium at pH = 6 were 90% and 9 mg·g^{-1}, respectively. Other researchers reported similar results for adsorption of chromium by different adsorbents (Bibi *et al.* 2018; Sethy & Sahoo 2019). Further, statistical analysis of data by one-way analysis of variance (ANOVA) test indicated the directional effect of pH on adsorption rate, which was significant ($p < 0.05$). Duncan's statistical test also showed that the optimum pH was 6. Duncan test results also indicated significant differences in all cases, with the exception of the average pH at (5 and 6) and (5 and 7).

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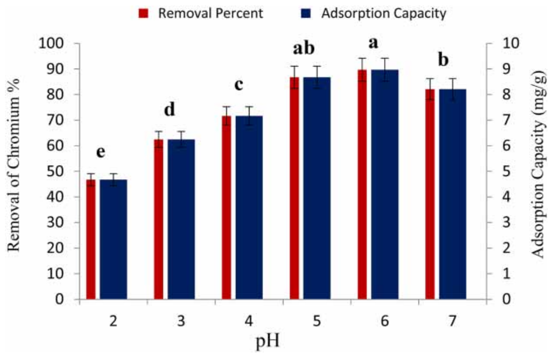

Figure 4 | The effect of pH on the adsorption percent-capacity of chromium (VI) ions by nano chitin (initial concentration = 10 mg/L, adsorbent dose = 0.1 g/L, contact time = 60 min and T = 25 °C).

Effect of initial concentration of hexavalent chromium

Initial concentration is one of important driving forces that affects the sorption process. The initial metal ion concentration of the solution provides the necessary driving force to overcome the mass transfer resistance for adsorption between the solution and solid phases (Yadav *et al.* 2013). The effect of initial concentration of chromium(VI) ions was examined within the range of 5–50 mg /L, pH = 6, adsorbent dose 0.1 g/L, 25 °C and 60 minute contact time. For all treatments, the agitation speed was constant and equal to 120 rpm**.** Figure 5 displays the effect of the initial concentration of chromium on the adsorption capacity of chromium by nano chitin. According to Figure 5, the maximum adsorption percentage at a concentration of 50 mg/L was 90.5%. The initial concentration had a significant effect on the adsorption capacity; as shown in Figure 5, the adsorption capacity increased from 5 to 50 mg·L^{-1} concentration (Liu *et al.* 2019). Upon elevation of the initial concentration, the efficiency of adsorption did not diminish (Islam *et al.* 2019). The adsorption percentage at low concentrations was higher, as at lower concentrations more adsorption sites are available for the adsorption of chromium metal ions and the ions are able to react with more adsorption sites on the adsorbent surface (Jacob *et al.* 2018). Adsorption capacity was found to be increased with increase of metal concentration. This behavior may be due to utilization of all the available binding sites for adsorption at higher metal concentration (Srivastava *et al.* 2015). Other researchers have reported similar results for the adsorption of chromium by different adsorbents (Abbas & Ali 2018; Mahmoud *et al.* 2019). Statistical analysis of data by one-way ANOVA revealed the directional effect of the initial concentration on adsorption, which was significant ($p < 0.05$).

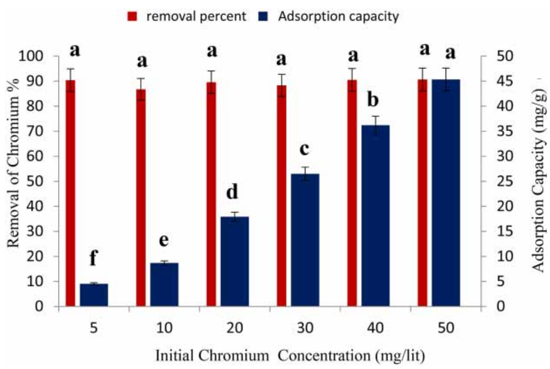

Figure 5 | The effect of concentration on the adsorption percent - capacity of chromium (VI) ions by nano chitin (adsorbent dose = 0.1 g, pH = 5, contact time = 60 min and T = 25 °C).

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Effect of adsorbent dose

Adsorbent dose is another important parameter, which affects the removal of chromium ions. The effect of different amounts of adsorbent was within the range of 0.1–0.6 g at an initial concentration of 5 mg·L^{-1} chromium, pH = 6, 25 °C and 60 minute contact time. For all treatments, the agitation speed was constant and equal to 120 rpm. Figure 6 reveals the effect of different amounts of nano-chitin adsorbent on the chromium uptake. According to Figure 6, the maximum absorption rate at a dose of 0.3 g was 92%. According to Figure 6, the maximum adsorbent dose at the absorption capacity of 0.1 g was 8.8 mg·g^{-1}. With the increasing amount of adsorbent, the adsorption efficiency of chromium was enhanced, since the available adsorption sites increased (Olad *et al.* 2019). The adsorption capacity declines with increasing adsorbent due to the increase in the number of unsaturated adsorption sites in the adsorbent (Fayazi & Ghanbarian 2019). Other researchers reported similar results for the adsorption of chromium by different adsorbents (Samani & Toghraie 2019; Zhang *et al.* 2019). Also, the statistical analysis of data by one-way ANOVA showed that the effect of adsorbent dose on adsorption rate was significant ($p < 0.05$). Duncan's statistical test indicated that the optimum adsorbent dose was 0.3 g. Duncan test results also indicated significant differences in all cases, with the exception of the average adsorbent dose (0.2 g/L and 0.3 g/L) and (0.1 g/L, 0.4 g/L and 0.5 g/L).

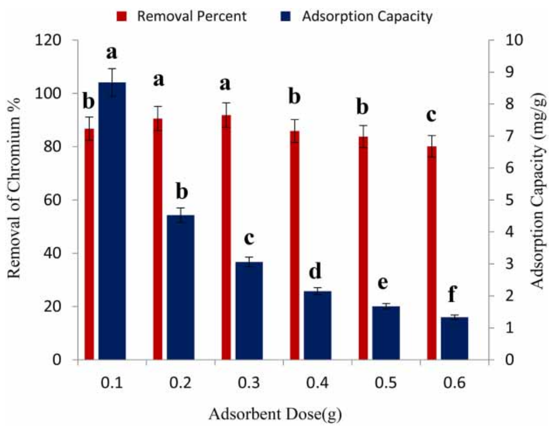

Figure 6 | The effect of adsorbent dosage on the adsorption percent - capacity of chromium (VI) ions by nano chitin (initial concentration = 10 mg/L, pH = 5, contact time = 60 min and T = 25 °C).

Effect of contact time

The effect of contact time was investigated within the range of 15–120 minutes, pH = 5, initial concentration of 5 mg·L^{-1} chromium, adsorbent dose of 0.1 g and temperature of 25 °C. For all treatments, the agitation speed was constant and equal to 120 rpm. Contact time plays an important role in the absorption of heavy metals (Huang *et al.* 2018). Figure 7 reveals the effect of contact time on the adsorption rate and adsorption capacity of chromium by nano chitin. As can be seen in Figure 7, the absorption rate was elevated from 15 to 120 minutes. By prolonging the contact time, the adsorption capacity of the adsorbent would not increase considerably (Altun 2019). From the time of contact, it can be concluded that the absorption rate initially increased and then equilibrated (Wu *et al.* 2019). Due to a larger number of active sites, the structure and area of the adsorbent are faster in the early times and allow heavy metal to penetrate to a large extent (Bhowmik *et al.* 2018; Davarnejad *et al.* 2018). Other researchers reported similar results for adsorption of chromium by different adsorbents (Theydan 2018; Jamshidifard *et al.* 2019; Li *et al.* 2019). Further, the statistical analysis of data by one-way ANOVA test showed that the effect of contact time was significant on

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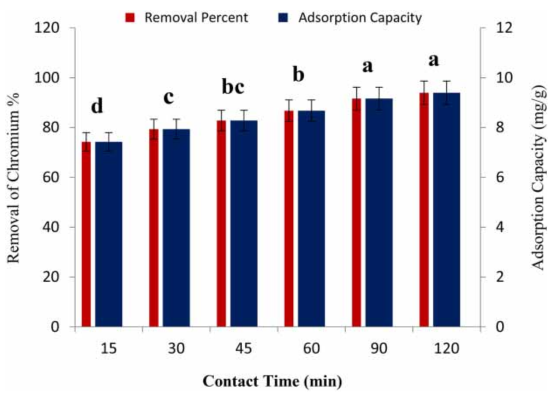

Figure 7 | The effect of contact time on the adsorption percent - capacity of chromium (VI) ions by nano chitin (initial concentration = 10 mg/L, pH = 5, adsorbent dose = 0.1 g and T = 25 °C).

the adsorption rate ($p < 0.05$). Duncan's statistical test also revealed that the optimal contact time was 60 minutes. Duncan test results also indicated significant differences in all cases, with the exception of the average contact time at (90 minutes and 120 minutes), (45 minutes and 60 minutes) and (30 minutes and 45 minutes).

Effect of temperature

The effect of temperature was tested within the temperature range of 15–40 °C, pH = 6, initial concentration of 5 mg·L^{-1} chromium, adsorbent dose 0.1 g and contact time of 60 min. Figure 8 displays the effect of temperature on the adsorption rate and adsorption capacity of chromium by nano chitin. As observed in Figure 8, the trend is ascending up to 25 °C and then descending from 30 to 40 °C. There is no clear reason for a slight increase or decrease in adsorption with increasing temperature. Figure 8 depicts the maximum adsorption capacity at 25 °C and the minimum adsorption capacity at 15 °C. Temperature has a significant effect on the removal capacity (Fakhre & Ibrahim 2018). The proper temperature can enhance the ion exchange and collision of atoms, thereby improving the adsorption process (Shao *et al.* 2019). The maximum absorption occurred at 25 °C, reducing the operating temperature and costs associated with cooling and heating (Almeida *et al.* 2019). Other researchers have found similar results for chromium uptake (Mobarak *et al.* 2018). The statistical analysis of data by one-way ANOVA test revealed that temperature had a significant influence on the adsorption rate ($p < 0.05$). Duncan's statistical test also showed that the optimum temperature is 25 °C. Duncan test results also indicated significant differences in all cases, with the exception of the average temperature at 20 °C, 25 °C and 30 °C.

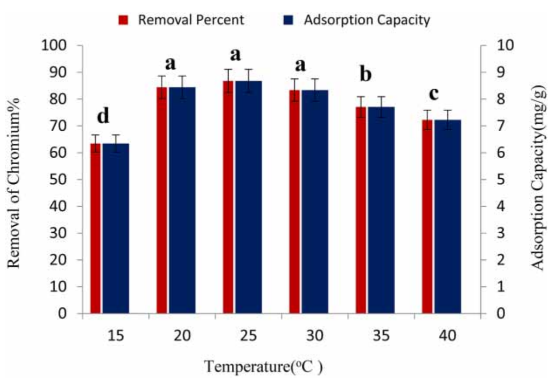

Figure 8 | The effect of temperature on the adsorption percent - capacity of chromium (VI) ions by nano chitin (initial concentration = 10 mg/L, pH = 5, contact time = 60 min and adsorbent dose = 0.1 g).

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Adsorption isotherms

The adsorption isotherm explains how the adsorption molecules are distributed among the liquid and solid phases in the equilibrium phase of the adsorption process. Langmuir and Freundlich models were used to analyze the isotherm data (Abbas & Ali 2018). The Langmuir and Freundlich adsorption isotherm models are shown in Figures 9 and 10. The Langmuir model represents monolayer adsorption while the Freundlich model indicates multilayer adsorption (Bartczak *et al.* 2015; Gopalakannan *et al.* 2018). The Freundlich isotherm model can be used to describe the adsorption on heterogeneous surfaces. It assumes that the uptake of adsorbent ions occurs on a heterogeneous adsorbent surface (Yadav *et al.* 2013). The Langmuir isotherm model assumes that at equilibrium, monolayer adsorption of solute occurs at a fixed number of homogeneously distributed adsorption sites over the adsorption surface and these sites also have equal affinity for the adsorption (Choudhary & Paul 2018). According to Figures 9, 10 and Table 2 data, the Freundlich model with $R^2 = 0.96$ compared to Langmuir with $R^2 = 0.11$ can better describe the adsorption of chromium ions by nano-chitin, indicating that

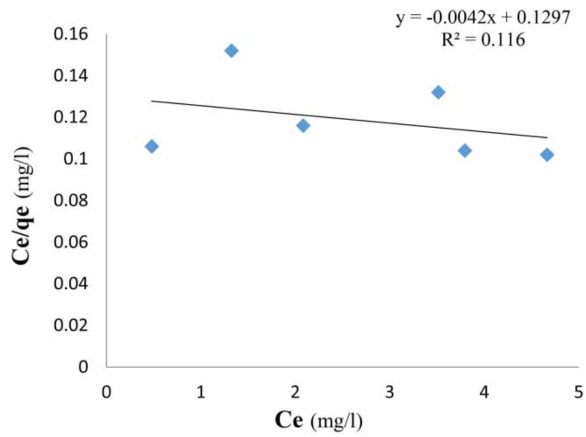

Figure 9 | Langmuir adsorption isotherm curve for chromium (VI) ions absorption using nano chitin.

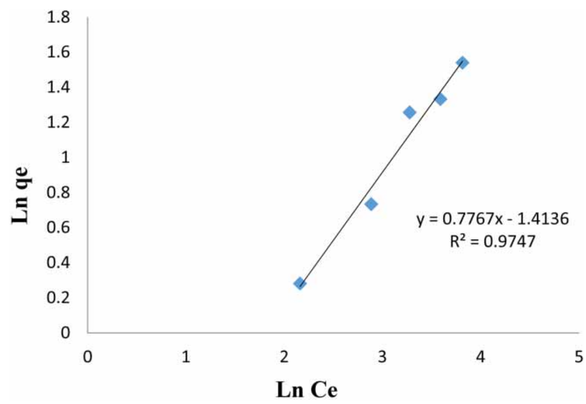

Figure 10 | Freundlich adsorption isotherm curve for chromium (VI) ions absorption using nano chitin.

Table 2 | Langmuir and Freundlich constants and coefficients in the adsorption of chromium (VI) using nano chitin

Freundlich		Langmuir	
4.1107	K_f	0.032	b
1.287	n	238.095	q_{max}
0.9747	R^2	0.116	R^2

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the data are consistent with the Freundlich model (Bhaumik *et al.* 2018; Mortazavian *et al.* 2018; Pang *et al.* 2018; Seraj *et al.* 2018). Maximum adsorption capacity (qmax) was equal to 238.095 $mg \cdot g^{-1}$, which indicates that the adsorbent has a relatively high adsorption capacity. Therefore, it can be said that this adsorbent has the ability to absorb heavy metals in high concentrations. Equilibrium constant of adsorption (b) was equal to 0.032.

According to Table 2, K_f is the Freundlich constant related to the bonding energy (L/g), and n is an empirical constant characterizing the heterogeneity of the process (g/L). According to the Freundlich model assumptions, if $n < 1$, the adsorption process is unfavourable, while if $1 < n > 10$, the adsorption process is favourable (Bhatti *et al.* 2020). Results show that n was equal to 1.287 and that indicated the favourable process for this adsorbent. Table 2 shows the constant coefficients and correlation coefficients of the Langmuir and Freundlich isotherms in chromium adsorption using nano-chitin.

Since R^2 is larger in Freundlich, the adsorption isotherm follows the Freundlich model. The Freundlich isotherm is applicable to adsorption processes that occur on heterogonous surfaces. This isotherm gives an expression which defines the surface heterogeneity and the exponential distribution of active sites and their energies.

Models of adsorption kinetics

Kinetics of the adsorption process is essential for aqueous solutions, since it gives essential information on the rate of adsorption uptake and controls the equilibrium time (Baghani *et al.* 2016). The adsorption process and the possible rate determining steps are crucial to examine for the design for industrial applications. The kinetic models that are widely used are pseudo first order and pseudo second order (Bhatti *et al.* 2020). Kinetic models are crucial for application, design, and performance of the adsorption kinetics process (Alomá *et al.* 2012). Table 3 shows the pseudo first order kinetics and pseudo second order kinetics parameters in the adsorption of chromium (VI) using nano chitin. In order to evaluate the applicability of these kinetic models to fit the experimental data, K_1 and K_2 constants were determined experimentally from the slope and intercept of straight-line plots. As displayed in Figures 11 and 12, the results of the kinetic equation analysis showed that the adsorption data of chromium by nano chitin correspond to the pseudo-second-order model with $R^2 = 0.99$. Thus, the

Table 3 | Pseudo first order kinetics and pseudo second order kinetics parameters in adsorption of chromium (VI) using nano chitin

Pseudo second order kinetics		Pseudo first order kinetics	
0.0984	K_2	0.0151	K_1
0.9988	R^2	0.8525	R^2

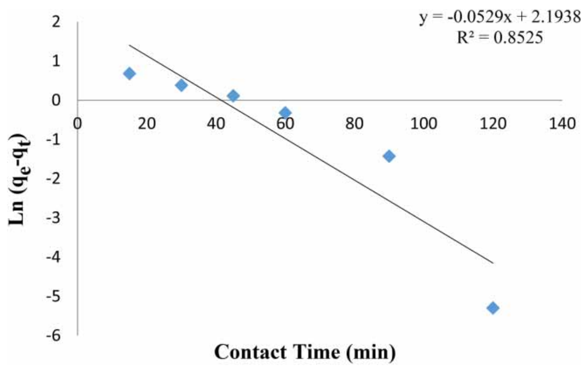

Figure 11 | Pseudo first order adsorption kinetics adsorption in chromium (VI) ions absorption using nano chitin.

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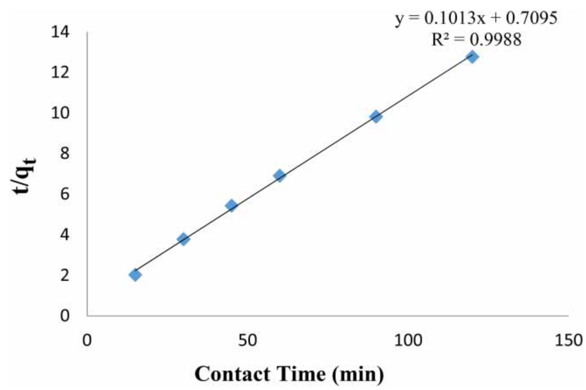

Figure 12 | Pseudo second order adsorption kinetics adsorption in chromium (VI) ions absorption using nano chitin.

adsorption data follow the pseudo-second order kinetic model (Omorogie *et al.* 2016; Samuel *et al.* 2018; Anush & Vishalakshi 2019; Li *et al.* 2019; Samuel *et al.* 2019).

The analysis of the adsorption kinetics data according to the model Equations (10) and (11) resulted in parameters listed in Table 3. The plot of Ln ($q_e - q_t$) vs. t should yield a straight line if the experimental data conform to this pseudo first order kinetic model. The plot of t/q_t vs. t will give a straight line if the experimental data conform to this pseudo second order kinetic model, and the values of q_e and K_2 are obtained, respectively from the slope and intercept of such a plot.

The results showed that both the pseudo-first-order equation kinetic model and the pseudo-second-order kinetic model were followed, but it fitted more with the second order equation. In this model, the rate-limiting step is surface adsorption, which involves chemisorption, where the removal from a solution is due to physicochemical interactions between the two phases. The model is usually represented by its linear form.

Thermodynamics

Effect of temperature was an essential parameter during adsorption studies to select the proper temperature and to evaluate thermodynamic parameters. Thermodynamic parameters were obtained by varying temperature conditions over the range 10–40 °C by keeping other variables constant. The values of the thermodynamic parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$, describing chromium ion uptake by nano-chitin, were calculated using the thermodynamic equations. The thermodynamic parameter indicates whether the adsorption reaction is spontaneous, random, exothermic or endothermic (Sahebjamee *et al.* 2019). The temperature parameter indicates the endothermic or exothermic processes. Thermodynamic studies showed that the adsorption was spontaneous or non-spontaneous ($\Delta G° < 0$, $\Delta G° > 0$, absolute value 0.23–76.54 kJ/mol), endothermic or exothermic ($\Delta H° < 0$, $\Delta H° > 0$, absolute value 2.16–132.59 kJ/mol), with positive or negative entropy values (absolute value 0.01–0.185 kJ/mol_K). The results of thermodynamics parameters are reported in Figure 13 and Table 4, where the values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ of the chromium adsorption process by nano-chitin represent spontaneous, endothermic and random reactions, respectively (Khosravi *et al.* 2018; Kumar *et al.* 2018; Wang *et al.* 2018; Periyasamy *et al.* 2019). The results of chromium ions adsorption onto nano-chitin based adsorbent are reported in the literature.

The thermodynamics of chromium adsorption at various temperatures were studied according to Table 4, where Gibbs free energy (ΔG °), enthalpy (ΔH °) and entropy (ΔS °) are calculated.

Thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ are indicators of the possible nature of adsorption. Conclusively, the adsorption of Cr (VI) ions by adsorbents is spontaneous in most cases ($\Delta G° < 0$). Since the thermodynamic parameters were evaluated from very different adsorbent/adsorbate combinations, it is not possible to note a correlation between the corresponding enthalpy change ($\Delta H°$) and

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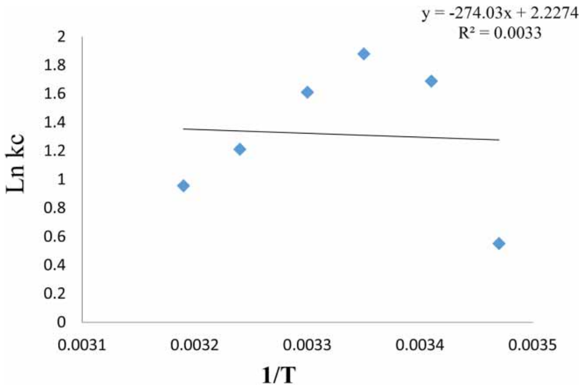

Figure 13 | Thermodynamics in chromium (VI) ions absorption using nano chitin.

Table 4 | Thermodynamic parameters of chromium (VI) adsorption using nano chitin

T (°C)	ΔG (kJ·mol)	ΔH (kJ·mol)	ΔS (J·mol·k)
15	− 1,319.332	2,278.285	18.5186
20	− 4,111.971		
25	− 4,655.357		
30	− 4,055.818		
35	− 3,101.022		
40	− 2,487.781		

entropy change ($\Delta S°$) following adsorption. Thermodynamically, enthalpy of adsorption is the heat released or absorbed during the adsorption process. In the majority of cases, adsorption is an endothermic process and positive entropy, making it thermodynamically favorable.

CONCLUSION

In this study, the application of nano chitin was investigated for the adsorption of hexavalent chromium from aqueous solutions in a batch system. The results showed that pH = 6, adsorbent dose 0.1 g/L, 25 °C, and 60 min contact time offered the optimum percentages of adsorption in this research. The adsorption data better fitted the Freundlich isotherm model. Kinetic studies also showed that the data corresponded to the pseudo-second-order model. The calculation of thermodynamic parameters (Gibbs free energy, enthalpy, entropy) showed a spontaneous, endothermic, and random process. The maximum adsorption capacity was 238.095 $mg{\cdot}g^{-1}$, indicating the high efficiency and cost-effectiveness of the adsorbent. Chitin, as the most abundant amino polysaccharide in nature, has been characterized as to possess high biocompatibility, low toxicity, high biodegradability, and antimicrobial properties. Thus, researchers are interested in such a substance. According to the results of this study, nano chitin has a high potential for adsorption of chromium (VI) ions from aqueous solutions.

ACKNOWLEDGEMENTS

The authors thank The Islamic Azad University Science and Research Branch of Iran for providing laboratory materials and facilities as well as Mr Sharif Jalali for his technical assistance.

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doi: 10.2166/wpt.2021.007

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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First received 1 September 2020; accepted in revised form 27 January 2021. Available online 9 February 2021