Separation of chromium(VI) by adsorption onto garlic peels: kinetics, thermodynamic and isotherm study

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ABSTRACT

Garlic peel, an agriculture by-product, was modified using nitric acid as a simple method. Therefore, this study aims to remove and/or minimize of Cr(VI) ions from aqueous media using HNO₃ modified garlic peel (HNO₃-GP). Scanning electron microscopy, energy-dispersive X-ray spectroscopy and Fourier-transform infrared spectroscopy analysis of the HNO₃-GP , as a solid phase extractor, were performed. The operational parameters of the adsorption such as solution pH, initial concentration of analyte, adsorbent dose, temperature and shaking time were performed. The equilibrium data of Cr(VI) showed a better fit with Langmuir isotherm model with $R^2 = 0.9956$ and adsorption capacity equals to 31.7 mg/g. Moreover, the kinetic data of analyte retained revealed that the present system fitted well with pseudo-second-order kinetic model ($R^2 = 0.9918$). Thermodynamic studies indicated that the retention step was endothermic and spontaneous in nature depending on the value of $\Delta H^\circ$ (118.292 J/mol) and $\Delta G^\circ$ (–117.41 kJ/mol). The positive value of $\Delta S^\circ$ (394.39 J/mol·K) confirmed that the biosorption process was carried out with high randomness on the surface of HNO₃-GP. The results showed that the proposed adsorbent (HNO₃-GP) provides an effective and economical approach in highly minimization or almost removal of Cr(VI) ions from the aqueous solution.

Keywords: Chromium(VI); Garlic; Pseudo-second-order; Thermodynamic; Isotherm; Water samples

1. Introduction

Chromium is one of the heavy metals that have an oxidation states from +2 until +6 [1]. Due to its toxicity, Cr(VI) has received a great attention [2]. The use of chromium has increased right now due to the increase of industries which consequently rises its existence in the aqueous medium [3]. Cr(VI) has been used in several industries such as leather tanning, steel fabrication, metal finishing, electroplating [2] pigments, paints [3] plastic and textile industries [2,3]. Cr(VI) is considered to be more toxic than Cr(III) because its high-water solubility and mobility [4]. For this reason, it was classified as causing cancer to humanity [5]. People are exposed to chromium by ingestion through a food pipe or other paths such as inhalation and skin contact and then pile up in human tissues causing harmful diseases [3]. The maximum allowable limit of Cr(VI) is 0.1 mg/L for the drainage into inland surface water and 0.05 mg/L into drinkable water [3].

There are several instruments used to estimate Cr(VI) such as flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), UV-visible spectrophotometer, inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission (ICP-OES) [6–10].

Several methods have been advanced to purify water from Cr(VI) including preconcentration and separation
methods such as dispersive liquid–liquid microextraction (DLLME), single-drop microextraction (SDME), nanofiltration, electro membrane extraction (EME), liquid ion-exchange with cloud point extraction [7,9,11–13]. Each technique has many advantages and disadvantages [14,15]. For example, chemical precipitation method has the advantage of simple operation and low-cost, while one of its disadvantages is that great amounts of chemical products are created and thus lead to problems in landfill. Besides, high separation efficiency is one of the advantages of membrane separation method, but high maintenance cost and low economic feasibility are its disadvantages [16].

Among these methods, solid–phase extraction (SPE) plays an important role in sample pretreatment as it is characterized by its low consumption of solvents, high reproducibility, high preconcentration efficiencies, reduction of processing times, and low cost [17,18]. Moreover, it does not require devices of phase separation as in liquid–liquid extraction (LLE), DLLME and liquid-phase microextraction (LPME) methods [7,19–21]. There are different adsorbents as solid phase such as chitosan as adsorbent for removal of some organic dyes [22] and coal fly ash and modified montmorillonite clay with [23] zinc oxide (ZnO) nanoparticles have been investigated [24–28].

Agricultural by-products are an effective and economical alternative of adsorbents materials because of their chemical composition with abundant reactive groups since the hydroxyl groups are present in hemicellulose, cellulose and lignin which found in agricultural by-products have an affinity and reactivity towards heavy metals such as truffle peels that used for separation of Cr(VI) from aqueous solutions and organic pollutants such as natural pomegranate peels which used for separation of Rhodamine B dye from aqueous media [29–32].

Garlic peel (GP) is one of the agricultural wastes that can be obtained in most parts of the world. It has been used as biomass to remove organic and inorganic pollutants from the environment [33]. GP is a natural bio-fiber consisting of cellulose, hemicellulose and pectic components [34]. There are many functional groups present in these components such as hydroxyl, carboxyl and amino groups that assist in bond formation with many metals’ ions [35].

Therefore, the objective of this study is exploring the ability and efficiency of modified garlic peels by nitric acid in order to remove Cr(VI) from aqueous media. Characterization of HNO₃ modified garlic peel (HNO₃-GP) as sorbent, studying the effect of optimum conditions such as pH of the medium, the dose of sorbent, initial Cr(VI) concentration, temperature and contact time on sorption process were studied. Furthermore, different kinetic models, various adsorption isotherms, thermodynamic parameters of the uptake Cr(VI) using the developed solid extractor were also studied. Finally, the validation of this methodology was supported by its application in real environmental water samples for the extraction of Cr(VI).

2. Experimental set-up

2.1. Reagents and materials

All chemicals used in this study were purchased from BDH Chemicals (Poole, England). Throughout the experiments, all glassware was cleaned using deionized water, followed by drying. Natural garlic peels were bought from a local market of Jeddah City which is located in the west region of Kingdom of Saudi Arabia. A standard stock solution (1,000 ppm) of K₂Cr₂O₇ was prepared by dissolving an accurate weight of the compound in 1,000 mL deionized distilled water. Solutions at different concentrations (5–30 ppm) were prepared by adding the appropriate amount of stock solution of Cr(VI). 1 M of HCl and 1 M of NaOH were used to adjust pH of the solution. Also, 1 M of HNO₃ was used to treated garlic peels.

2.2. Apparatus

In order to record the spectra and the absorbance measurements of Cr(VI) were made by UV–Vis Double Beam Spectrophotometer (GENESYS 10S Model, Thermo Scientific, New York) (200–700 nm) using a couple of quartz cuvette with 1 cm optical path length. A digital pH meter (Thermo Fisher Scientific Orine Model 720 pH meter) (Milford, MA, USA) was used for pH measurements of solutions. A shaker incubator (SI-100 model, HUMAN Lab, Korea) with a rate in the range of 10–300 rpm was used to shake and mix the solutions of Cr(VI) with HNO₃-GP in the conical flasks.

2.3. Recommended procedures

2.3.1. Preparation of HNO₃ modified garlic peel

Garlic was collected from a local market of Jeddah City, Kingdom of Saudi Arabia. Firstly, it was peeled and then washed with tap water for several times followed by washing with deionized distilled water to remove dust and other impurities. After that, GP was soaked in 500 mL of 1 M HNO₃ and kept for 4 h at laboratory temperature. Then, GP was washed with deionized distilled water for several times. Finally, HNO₃ modified garlic peel (HNO₃-GP) has been dried under sunlight for 5 d. Also, it was dried again in an oven at 70°C for 3 h. HNO₃-GP was turned into a fine powder by using an electric grinder (ELEKTA EFBG 1586 model) and it was sieved by a sieve with 0.85 mm. Then, it was stored in an airtight bottle.

2.3.2. Static experiments

The experiments were conducted to investigate the effects of some parameters including solution pH, initial concentration, adsorbent dose, contact time and temperature on the adsorption Cr(VI) by HNO₃-GP. In a series of conical flasks (50 mL), an accurate weight (0.5 ± 0.001 g) of HNO₃-GP was mixed with an aqueous solution (50 mL) containing Cr(VI) (5 ppm) at different pH (1–7). The mixture was shaken for 60 min on a mechanical shaker (SI-100 model, HUMAN Lab, Korea) with a rate in the range of 200 rpm was used for the equilibration experiments at 25°C. After adsorption, the mixture was filtered through filter paper and the adsorption efficiency was measured using UV-Vis Double Beam Spectrophotometer (GENESYS 10S Model, Thermo Scientific, New York) (200–700 nm). The concentration of Cr(VI) retained onto HNO₃-GP was then calculated from the difference between absorbance of Cr(VI) in the aqueous phase before and after extraction (A₀ − Aₜ) using HNO₃-GP, respectively. The extraction of percentage (%)E, the amount
of Cr(VI) retained at equilibrium (\( q_e \)) and the distribution ratio (\( D \)) of Cr(VI) uptake by HNO\(_3\)-GP sorbent were determined by the following equations [36]:

\[
\%E = \left( \frac{A_0 - A_e}{A_0} \right) \times 100 \tag{1}
\]

\[
q_e = \frac{(A_0 - A_e)V}{m} \tag{2}
\]

\[
D = \frac{\%E}{100 - \%E} \times \frac{V(ml)}{W(g)} \tag{3}
\]

where \( V \) and \( W \) represent the volume of the solutions (ml) and \( m \) is the amount of HNO\(_3\)-GP (g), respectively.

### 2.4. Sampling of real water

To examine the applicability of the suggested method for Cr(VI) removal, it was implemented on different environmental samples of water which were collected from Jeddah City, Kingdom of Saudi Arabia including bottle, tap and seawater. The tap water samples were attained from the chemistry laboratory at King Fahd Medical Research Centre and seawater samples were collected from the northern coastal area in Jeddah. All water samples (50 mL) were filtered through 0.45 \( \mu \)m cellulose membrane filter paper to remove any impurities before uses. Different concentrations (5–15 ppm) of Cr(VI) were then introduced to each type of water sample at pH = 1 in presence of 0.5 g of HNO\(_3\)-GP and then was shaken separately for 20 min. All real water samples were analyzed using standard addition method under the batch conditions.

### 3. Results and discussion

Adsorbent materials used in solid phase extraction method play a major role in obtaining high extraction rates. Therefore, it is considered as one of the most important factors that has effect on the separation efficiency [17]. Therefore, the development of adsorbent materials to become more effective, economic and environmentally friendly has enticed specific attention in this field. In addition, they are biodegradable and does not contain any unpleasant odor [30,37–39].

Lately, numerous studies have confirmed that chemical modification can promote selectivity or adsorption capacity of the biosorbents and decrease some organic materials released into solutions when functional groups are introduced or changed on the surface of agricultural by-products. Among of these biosorbents, GP has been used as a low-cost and an ideal biomass for pre concentration and removal of Cr(VI) in this study. GP is a natural bio-fiber consisting of cellulose, hemicellulose and pectic components [34]. There are many functional groups present in these components such as hydroxyl, carboxyl and amino groups that assist in bond formation with many metals’ ions [35]. Ability of GP for sorption can be improved by optimizing several experimental factors. Thus, a detailed study on the characterization of natural and modified GP with HNO\(_3\) in addition to its analytical application.

#### 3.1. Characterization of GP adsorbent

Some techniques were utilized to make a complete characterization for GP before and after modification with HNO\(_3\) such as scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and Fourier-transform infrared spectroscopy (FTIR).

The surface morphology of unmodified garlic peel and after modification with HNO\(_3\) is depicted by SEM in Fig. 1. Fig. 1a and b show that unmodified GP with irregular and rough surface while Fig. 1d and e show that HNO\(_3\)-GP with a corroded net structure and large pore irregularly dispersed on the surface. Modification of garlic peel with HNO\(_3\) could erode the surface of GP to generate more pores and increase the total pore volume thus increasing the surface area of GP, which assure that HNO\(_3\)-GP has a suitable surface morphology for binding heavy metals [33].

EDX Analysis was performed for natural garlic peel before and after modification with HNO\(_3\) (Fig. 2a and b) which showed the proportions of main components for unmodified GP and modified GP with HNO\(_3\) respectively. The results showed that the percentage of C decreased, while the percentage of O increased after modification by HNO\(_3\). As the modification increases the number of acidic groups of oxygen which increases the surface area of GP. All these differences indicate a change in the chemical structure of the GP after modification by HNO\(_3\) [33,42]. The existence of Ca element is due to the calcium component such as calcium pectate in the cell wall of GP. Ion-exchange between heavy metal ions in the solution and Ca\(^{2+}\) of GP was intended to be the adsorption process [40].

The difference in functional groups of unmodified garlic peel and after modification with HNO\(_3\) is observed by spectra of FTIR in Fig. 3a and b. In both spectra, the broad and intense peaks from 3,500 to 3,000 cm\(^{-1}\) were observed, which indicate the presence of O-H or N-H stretching vibrations of amine due to inter- and intra-molecular hydrogen bonding of polymeric compounds (macromolecular associations), such as alcohols, phenols, and carboxylic acids, as in pectin, cellulose and lignin, thus, showing the presence of “free” hydroxyl groups on HNO\(_3\)-GP surface [40–42].

The peak observed at 2,920 cm\(^{-1}\) was attributed to C-H stretching vibrations of aliphatic acids. The peak from 1,700 to 1,850 cm\(^{-1}\) was characterized by C=O stretching vibrations of carboxylic acids. Besides the peak at 1,610 cm\(^{-1}\) was attributed to C=C or C=N while the peak at 1,055 cm\(^{-1}\) in both spectra attributed to C-O bending variation in –COOH. Aliphatic acid group vibration at 1,237 cm\(^{-1}\) may be assigned to deformation vibration of C=O and stretching formation of –OH of carboxylic acids and phenols [40]. The adsorptions in the range of 1,530 to 1,201 cm\(^{-1}\) in the spectra of HNO\(_3\)-GP were assigned to stretching of C=C bond in aromatic rings, which was not obviously observed in the spectra of GP. This might be related to the presence of aromatic rings [33].

In FTIR spectra of HNO\(_3\)-GP, the peak around 1,745 cm\(^{-1}\) (–COOH) was relatively stronger and the peak around 1,610 cm\(^{-1}\) (–COO\(^-\)) became relatively weaker compared with
the spectra of GP, which indicate that the modification by HNO₃ could cause oxidization of some unreactive groups into –COOH. This result confirmed the results of EDX where the percentage of oxygen increased in garlic peel after modification with HNO₃. Since the modification increases the surface acidic groups of oxygen which increases the surface area of GP.

Analysis of FTIR spectra indicated that the chemical modification led to different chemical properties, which causes an increase in the adsorption capacities [33,42].
aqueous solutions at pH ≈ 1 by HNO
study, the effect of shaking time for 5 ppm of Cr(VI) from
equilibrium for Cr(VI) adsorption onto HNO
3-GP . In this
mine the probable order as well as time required to reach
the percentage achieved the maximum value (100%) after
10 min, while the extraction
amount reached to 68% after 10 min, and the extraction

The pH of the solution is one of the most important fac-
tors that controls the degree of ionization of the metal and
the surface charge of the adsorbent [43]. The influence of
pH (1–7) on the adsorption of Cr(VI) by HNO
3-GP in terms of the percentage of extraction is shown in
Fig. 4.

The percentage of Cr(VI) extraction decreases by increas-
ing the pH of solution from 1.0 to 7.0. It is important to pay
attention that Cr(VI) extraction percentage achieved the
maximum value (99.2%) at pH 1 thus, which was adopted
in next experiments. Moreover, the existence of the func-
tional groups such as phenolic –OH and carboxylic –COOH
on HNO
3-GP surface bind electrostatically with nega-
tively charged metal complex [(CrO
3Cl)–]. Therefore, the
decrease in the adsorption with increase in pH may be due
to the decrease in electrostatic force of attraction between
HNO
3-GP and Cr(VI) ions and the increased concentration of
OH– ions that complicates the adsorption process [3,33,44].

Extraction percentage (%E) of Cr(VI) was calculated by
finding the difference between Cr(VI) absorbance before
(A0) and after (Af) adsorption by HNO
3-GP, as mentioned
before in Eq. (1):

\[
%E = \left( \frac{A_0 - A_f}{A_0} \right) \times 100
\]  (1)

Contact time is considered an effective factor to deter-
mine the probable order as well as time required to reach
equilibrium for Cr(VI) adsorption onto HNO
3-GP. In this
study, the effect of shaking time for 5 ppm of Cr(VI) from
aqueous solutions at pH = 1 by HNO
3-GP was investigated
at a period of time ranging from 0.0 to 60.0 min.

The increasing of extraction percentage of Cr(VI) with
increasing of shaking time resulted from the fast adsorp-
tion kinetics of HNO
3-GP toward Cr(VI) as shown in Fig. 5.
Also, it is observed clearly in Fig. 5 that adsorbed Cr(VI)
amount reached to 68% after 10 min, while the extraction
percentage achieved the maximum value (100%) after
20 min. Thus, a shaking time of 20 min was adopted in next
experiments.

The rate of adsorption of heavy metal ions was ini-
tially higher due to a ready availability of active sites on the
adsorbent’s surface. Further increase in contact time makes
the adsorption rate less effective due to saturation of bind-
ingsites and accumulation of the heavy metal ions around
the active site inhibited further adsorption [45].

The sorption percentage of a constant quantity of Cr(VI)
(5 ppm) in aqueous medium (50 mL) was studied by vary-
ing HNO
3-GP dose (0.5–1.5 g) at pH ≈ 1 after 20 min shak-
ing. The results are demonstrated in Fig. 6. Cr(VI) retention
decreased on increasing HNO
3-GP dose from 0.5 to 1.5 g and
reached maximum at a dose of 0.5 g where the percentage
of removal was 99.2%. Thus, it no longer can increase with
increasing dose of adsorbent. Due to potential aggregation
and intraparticle interactions between HNO
3-GP molecules
at the solid phase extractor, which resulted in a reduction in
the total surface area of the HNO
3-GP and an increase in dif-
 fusional path length, this behavior is most likely explained
by the decrease in the available adsorption site [41,46].
Therefore, 0.5 g was chosen for later removal studies.

3.3. Sorption isotherm of Cr(VI) retention by HNO
3-GP

Sorption isotherms were used to describe mechanism of
the interaction of Cr(VI) ions on the sorbent surface. Depen-
ding on the nature of the sorption system, the equi-
librium studies are useful to calculate the maximum sorp-
tion capacity of HNO
3-GP toward Cr(VI) ions and determine
some important surface properties of the tested sorbent.
The sorption characteristics of Cr(VI) ions wide range of
equilibrium concentrations (5–30 ppm) from aqueous solu-
tion at pH = 1 onto HNO
3-GP were studied at the optimized
parameters.

Fig. 7 shows the plot of the amount of Cr(VI) retained
(q) onto HNO
3-GP vs. the equilibrium concentration (C)

Fig. 3. Fourier-transform infrared spectra of garlic peel (a) and
HNO
3-GP (b).

Fig. 4. Influence of pH on the adsorption of Cr(VI) onto
HNO
3-GP at 25°C.

Fig. 5. Shaking time effect on the adsorption of Cr(VI) from
aqueous solution onto HNO
3-GP after 1 h shaking time at 25°C.
in the bulk aqueous solution. The plot shows a clear rise in Cr(VI) retained at low concentration followed by a convergent or slight rise at a concentration higher than 5 ppm. It is important to pay attention that Cr(VI) extraction percentage achieved the maximum value (86.96%) at 5 ppm of Cr(VI). This is indicating that at low equilibrium concentration of Cr(VI), the surface coverage of the adsorbent could be low and the available active sites of HNO3-GP are not fully occupied by Cr(VI). The slight increase of the plot on increasing the analyte concentration due to an increase in the surface coverage and the restriction of the available active sites of HNO3-GP [47,48].

The equilibrium data of this work were subjected to different adsorption isotherm models for example Langmuir, Freundlich and Dubinin–Radushkevich over a wide range of equilibrium concentration through linear regression in a condition of best fit.

3.3.1. Langmuir isotherm

The retention behavior of Cr(VI) from the aqueous solution onto HNO3-GP was subjected to Langmuir model. This model assumes that the adsorption is a monolayer and a single layer of molecules on the adsorbent surface is absorbed. The solid surface of adsorbent is homogeneous and adsorption energy is uniform for all sites and the adsorption on the surface is localized which means that the atoms or molecules are adsorbed at specific and localized sites [48–50]. The linear form of Langmuir model is expressed by the following equation [51]:

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e
\]

where \( C_e \) represents the equilibrium concentration of adsorbate (mg/L), \( q_e \) is the amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium (mg/g), \( q_m \) donates the maximum adsorption capacity (mg/g) and \( K_L \) is the Langmuir constant (L/mg). The plot of \( C_e/q_e \) vs. \( C_e \) over the entire Cr(VI) concentration range as seen in Fig. 8.

Langmuir maximum adsorption capacity (\( q_m \)) and Langmuir constant (\( K_L \)) were calculated from the slope and intercept values and were found equal to 31.7 mg/g and 0.0552 L/mg, respectively. Moreover, the determination of correlation coefficient (\( R^2 \)) for Langmuir model was 0.9956 that indicates the adsorption process is favorable and it is monolayer adsorption of Cr(VI) on the outer surface of HNO3-GP [48].

The value of dimensionless constant (\( R_L \)) which is an equilibrium parameter referred to as separation factor is expressed as follows [51]:

\[
R_L = \frac{1}{1 + K_L C_i}
\]

where \( C_i \) is the initial concentration of adsorbate (mg/L). The dimensionless constant equilibrium parameter is mainly depending on the initial concentration at a given temperature. Table 1 clarifies \( R_L \) values at different initial concentration (\( C_i \)) of Cr(VI) at room temperature.

From the data obtained from Table 1, it was found that, at all initial concentrations, \( 0 < R_L < 1 \) which confirms the favorable adsorption of Cr(VI) on the proposed sorbent.

3.3.2. Freundlich isotherm

Freundlich adsorption isotherm is a physical and empirical isotherm and another form of Langmuir that can be applied to multilayer adsorption. The stronger binding sites are occupied firstly, until adsorption energy is exponentially decreased upon the completion of adsorption process [48]. The linear form of the Freundlich model is expressed by the following equation [48]:
where $K_F$ and $n$ are Freundlich constants. $K_F$ denotes the adsorption capacity (mg$^{1-(1/n)}/$L$^{1/n}$·g) and $n$ indicates the adsorption intensity. The plot of log$q_e$ against log$C_e$ as shown in Fig. 9. Freundlich constants $(1/n)$ and $(K_F)$ were calculated from the slope and intercept values and were found equal 0.28 and 1.13 mg$^{1-(1/n)}/$L$^{1/n}$·g, respectively.

The value of $(1/n)$ gets closer to 0, indicates that the surface of HNO$_3$-GP was more heterogeneous and the obtained value of the correlation coefficient ($R^2 = 0.9889$) which is close to value of ($R^2 = 0.9956$) in Langmuir model, indicating that the Freundlich model is applicable to describe the adsorption of Cr(VI) ions onto HNO$_3$-GP.

### 3.3.3. Dubinin–Radushkevich isotherm

The Dubinin–Radushkevich adsorption isotherm model is applied to identify the characteristics of porosity, the mechanism of adsorption, and the free energy distribution onto a heterogeneous surface. This would precisely assign the nature of chemical or physical adsorption process of the retention step of Cr(VI) by the established solid adsorbent [48,52]. The linear form of this model is expressed as the following [48]:

$$\ln q_e = \ln q_{m} - K_{DR} \varepsilon^2$$

(7)

where $K_{DR}$ is Dubinin–Radushkevich model constant indicates the adsorption energy (mol$^{-1}$/kJ$^2$) and $\varepsilon$ represents the Polanyi potential. The plot of $\ln q_e$ against $\varepsilon^2$ was linear ($R^2 = 0.9274$) as shown in Fig. 10. From Eq. (7) the slope equals to $-K_{DR}$ and the intercept equals to $\ln q_{m}$. According to the plot in Fig. 10, the slope was found to be $-0.147$ so the value of Dubinin–Radushkevich constant $(K_{DR})$ was found to be 0.147 mol$^2$/kJ$^2$. The intercept value was found to be 3.2573, so the maximum adsorption capacity $(q_m)$ equals to 25.9793 mg/g. Moreover, the value of mean free energy ($E$) for the biosorption process of Cr(VI) on the surface of HNO$_3$-GP can be calculated via the following equation [48]:

$$E = \frac{1}{\sqrt{2K_{DR}}}$$

(8)

The value of $(E = 1.84$ kJ/mol) achieved this condition $E < 8$ kJ/mol which confirms the adsorption process is physical process [48].

### 3.4. Kinetics of Cr(VI) sorption on HNO$_3$-GP surface

Investigation of adsorption kinetics is important to explain the reaction mechanism. Therefore, Cr(VI) adsorption process onto HNO$_3$-GP was studied by various kinetic models for example Weber–Morris, pseudo-first-order, pseudo-second-order, Bhattacharya and Venkobachar, Elovich and finally Reichenberg model.

#### 3.4.1. Intraparticle diffusion model

It is important to include diffusion-based kinetic modeling to clarify the role of diffusion processes, like film and intraparticle diffusion [53]. The data of this study were subjected to intraparticle diffusion rate model expressed by the Weber–Morris equation as the following [53]:

$$q_i = k_i t^{1/2} + C$$

(9)

where $q_i$ is the amount of adsorbate adsorbed (mg/g), $k_i$ is the rate of intraparticle diffusion (mg/g·min$^{1/2}$), $t$ denotes the contact time (min) and $C$ is a constant linked to the thickness of the boundary layer (mg/g).
The plot of $q_t$ vs. time is displayed in Fig. 11. As shown, the plot was divided into two parts with two distinct slopes; the first one was linear with a high correlation value ($R^2 = 0.9777$) and the second stage was linear with a lower value ($R^2 = 0.8151$).

The adsorption sorption process of Cr(VI) by HNO$_3$-GP was very fast in the early stage and deviated by increasing the shaking time. The linear plot does not pass through the origin indicating that intraparticle diffusion is not the only rate-controlling step. The diffusion rate was high firstly and then decreased by increase shaking period revealing that the rate of the retention step is film diffusion at the early stage of extraction. In the second stage, the diffusion remains fairly constant where the pores volume of HNO$_3$-GP were consumed.

Fig. 11 shows the values of $k_i$ computed from the two distinct slopes in the initial and second stages of Weber–Morris plots for HNO$_3$-GP were found 4.0448 mg/g·min$^{-1/2}$ and the second value was 0.3119 mg/g·min$^{-1/2}$. This change in the slope is most likely due to the existence of different pore size.

The values of $k_i$ indicated that intraparticle diffusion step can be considered as the rate controlling step, thus, the uptake of tested Cr(VI) onto the employed sorbent is most likely involved following three steps:

- Bulk transport of Cr(VI) in solution.
- Film transfer involving diffusion of Cr(VI) within the pore volume of the HNO$_3$-GP and/ or along the wall surface to the active sorption sites of the adsorbent.
- Finally, formation of the complex ion associate [48,53,54].

### 3.4.2. Pseudo-first-order model

The experimental data were also subjected to pseudo-first-order model. The linear form is given as [55]:

$$\log(q_t - q_e) = \log q_e - k_1 \frac{t}{2.303}$$

(10)

where $k_1$ is the rate constant of pseudo-first-order (min$^{-1}$). The plot of $\log(q_t - q_e)$ against time ($t$) as shown in Fig. 12.

The value of correlation coefficient ($R^2 = 0.9505$). The slope is $(-k_1/2.303)$ and the intercept is $\log(q_e)$. In addition, the calculated value $k_1$ and $q_e$ were found to be 0.153 min$^{-1}$ and 26.26 mg/g, respectively.

### 3.4.3. Pseudo-second-order model

Pseudo-second-order model assumed that two active adsorption sites were adsorbing one Cr(VI) ion on the adsorbent [54]. The linear form is given as the following [56]:

$$t = \frac{1}{q_e k_2} + \frac{t}{q_e}$$

(11)

where $h = k_2 q_e^2$ that can be regarded as the initial rate of adsorption (mg/g·min) where $k_2$ is the rate constant of pseudo-second-order (g/mg·min). The plot of $t/q_e$ vs. time ($t$) as shown in Fig. 13. The value of correlation coefficient ($R^2 = 0.9918$).
In addition, the calculated value of $k_2$ and $b$ were found equal 0.0132 g/mg·min and 178.57 mg/g·min, respectively. The straight line with excellent $R^2$ value obtained from the plot (Fig. 13) confirmed the fitness of pseudo-second-order model for the description of Cr(VI) removal using HNO$_3$-GP from aqueous solutions.

Good agreement between the values of the experimental value $q_e$ (116.25 mg/g) and that is calculated value (117.6 mg/g) for pseudo-second-order kinetic model; these findings confirm the suitability of the pseudo-second-order equation for the description of Cr(VI) biosorption by the developed sorbent from aqueous solutions.

3.4.4. Bhattacharya and Venkobachar model

This model based on concentration of solution to study the mechanism of adsorption and characteristic constants of adsorption [57]. The linear form of this model is expressed as the following equation [57]:

$$\log\left[1 - U(T)\right] = -\left(\frac{k_4}{2.303}\right) t$$

where $U(T)$ is the fractional attainment of equilibrium and $k_4$ is constant of Bhattacharya and Venkobachar (min$^{-1}$). The value of $k_4$ can be obtained from the slope of the linear plot of log(1−$U(t)$) against $t$ which was 0.090 min$^{-1}$. Moreover, the correlation coefficient ($R^2$) was found to be 0.9768 as shown in Fig. 14.

3.4.5. Elovich model

This model has been used for the chemisorption process [58]. The linear form is given as the following [48]:

$$q_t = \frac{1}{\beta} \ln(a\beta) + \frac{1}{\beta} \ln(t)$$

where $a$ is the initial adsorption rate constant which give information about the high affinity (mg/g·min) and $\beta$ is an adsorption constant linked to the extent of surface coverage (mg/g). The plot of $q_t$ vs. Int will be linear ($R^2 = 0.9703$) and Elovich coefficients $a$ and $\beta$ can be determined from the slope and intercept of the plot, respectively. The slope value = 1/\beta while the intercept value = 1/\beta ln(a\beta). As clarified in Fig. 15, the slope value equal 6.6159 so $\beta$ = 0.1512 mg/g while the intercept value = 5.1195 so $a$ = 14.34 mg/g·min.

The high $a$ value gives strong indication about higher removal of Cr(VI) because of the higher surface area of HNO$_3$-GP that possessed strong adsorption active sites resulting in strong chemical binding with Cr(VI) ions. Also, the high correlation coefficient ($R^2 = 0.9703$) assures the applicability of Elovich model [59].

3.4.6. Reichenberg model

This model fully used broadly to describe the diffused films inside pores and represented as the following equations [60]:

$$F(t) = \left(1 - \frac{6}{\pi^2}\right)e^{-\beta t}$$

$$B_t = -0.4977 - \ln\left(1 - F(t)\right)$$

where $B_t$ is the Reichenberg constant and $F$ is a mathematical function, $F(t) = q_t/q_e$ is the ratio of amount of adsorbate adsorbed after time $t$ to that at equilibrium time.

If the plot of $B_t$ and $t$ gave linear relation with higher correlation coefficient, this confirms the biosorption was due to film diffusion inside the internal pores of HNO$_3$-GP. As clarified in Fig. 16, a direct relation between $B_t$ and time with higher $R^2$ therefore, that intraparticle diffusion is the rate controlling step with a small fraction of the sorption that occurs through film diffusion because the straight line does not pass through the origin [61].

A comparison between the values of $R^2$ for the data subjected to Weber–Morris, pseudo-first-order, pseudo-second-order, Bhattacharya and Venkobachar, Elovich and Reichenberg models revealed that pseudo-second-order model is reliable and more accurate than other models. Thus,
it can be concluded that the uptake of Cr(VI) by HNO3-GP is most likely proceeds according to the second-order rate equation. The values of the adsorption of Cr(VI) onto HNO3-GP for kinetic processes are summarized in Table 3.

3.5. Thermodynamic behavior of Cr(VI) retention onto HNO3-GP

The sorption behavior of Cr(VI) by HNO3-GP was critically studied over wide range of temperature (298–328 K) to determine the nature of Cr(VI) retention onto HNO3-GP at the settled conditions. The thermodynamic parameters (ΔH°, ΔS° and ΔG°) can be expressed as the following equations [62]:

\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ
\]

(16)

\[
\ln K_c = \frac{-\Delta H^\circ}{R} \frac{\Delta S^\circ}{T}
\]

(17)

where \(\Delta G^\circ\), \(\Delta H^\circ\), \(\Delta S^\circ\) and \(T\) are the change of free energy (kJ/mol), the enthalpy change (kJ/mol), the entropy change (J/mol·K), the gas constant (8.314 J/mol·K) and temperature in Kelvin (K). \(K_c\) is the equilibrium constant for adsorption process of Cr(VI) from aqueous solution and its value can be calculated for adsorption of Cr(VI) employing the equation [62]:

\[
K_c = \frac{\%E}{100 - \%E}
\]

(18)

The plot of \(\ln K_c\) vs. \(1,000/T\) (K⁻¹) was linear over the entire temperature range from 298 to 328 K with good correlation coefficient (\(R^2 = 0.9993\)) as seen in Fig. 17.

From the displayed plot in Fig. 17, the enthalpy changes \(\Delta H^\circ\) was found to be 118.292 J/mol since the slope was equal to –14.228. Also, the entropy change \(\Delta S^\circ\) was found to be 394.39 J/mol·K since the intercept was equal to 47.437. Hence according to Gibb’s equation (16), the change of free energy \(\Delta G^\circ\) was found to be –117.41 kJ/mol.

The negative value of \(\Delta G^\circ\) indicates that the adsorption of Cr(VI) onto HNO3-GP is spontaneous while the positive value of \(\Delta H^\circ\) reflects the endothermic sorption process. In addition, the positive value of \(\Delta S^\circ\) reflects the affinity of HNO3-GP for Cr(VI) and increases the randomness at the solid–solution interface with some structural changes in both adsorbate and adsorbent [55].

The enthalpy change \(\Delta H^\circ\) can be also calculated in terms of distribution ratio (\(D\)) from the slope of Van’t Hoff plot according to the following equation [62]:

\[
\log D = \frac{-\Delta H^\circ}{2.303RT} + C
\]

(19)

The plot of \(\log D\) vs. \(1,000/T\) shown in Fig. 18 was linear with good correlation coefficient (\(R^2 = 0.9993\)). \(\Delta H^\circ\) value for the sorption of Cr(VI) is equal to 118.32 J/mol. Thus, \(\Delta H^\circ\) agrees with the experimental value (118.292 J/mol) that was achieved from Eq. (17) and that confirms adsorption of Cr(VI) on surface of HNO3-GP was endothermic sorption process. Also, the entropy change \(\Delta S^\circ\) was found to be 432.76 J/mol·K since the intercept was equal to 22.602. Hence according to Gibb’s equation (16), the change of free energy \(\Delta G^\circ\) was found to be –128.88 kJ/mol.

The analytical aspects of the created approach were also successfully compared with a number of the reported methods [46,63–67]. The results are shown in Table 4. Moreover, features of heavy metals adsorption onto garlic peel as adsorbent were also effectively compared with several of the published papers as indicated in Table 5. The findings demonstrated that the suggested adsorbent (HNO3-GP)
offers a very efficient and affordable adsorbent in virtually completely removing heavy metals from the aqueous solution.

3.6. Applications of real samples

The applicability of the proposed adsorbent for Cr(VI) removal was examined by applying it, under batch conditions, on different environmental water samples that were collected from Jeddah City, Kingdom of Saudi Arabia including bottle, tap and seawater. Table 6. summarizes the results and shows good extraction percentages of Cr(VI) by using HNO₃-GP .

As shown in Table 6, the recovery percentage of Cr(VI) ranged from 83.94% to 99.62%. Therefore, the suggested method validated the suitability of HNO₃-GP to detect and remove Cr(VI) from real water samples.

4. Conclusion and future perspectives

The removal of Cr(VI) by HNO₃-GP was very fast. The results were confirmed that the best applicable isotherm model was Langmuir ($R^2 = 0.9956$) with excellent adsorption capacity of Cr(VI) (31.7 mg/g) that was achieved at optimum conditions. The results also indicated that the best appropriate kinetic model was pseudo-second-order. The adsorption of Cr(VI) from the aqueous solution on the proposed surface is an endothermic process depending on the positive value of enthalpy and spontaneous process based on the negative value of ΔG°. On the other hand, the sign of entropy change was a positive value confirming that adsorption process was performed with high randomness on the surface of HNO₃-GP . Overall, the results were reliable, achievable and appropriate. Therefore, the proposed adsorbent can be successfully used for a selective separation of other heavy metals from the real water samples.

Conflict of interest

Authors disclose any potential conflict of interest including financial, personal or other relationships with other people or organizations within the time of beginning the submitted work that could inappropriately influence, or be perceived to influence their work.

References


