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RESEARCH ARTICLE

Investigation of removal efficiency of Cr (VI) from industrial wastewater using chitosan and synthesized chitosan nanoparticles

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ABSTRACT

Chromium (VI) is present in the effluents from different industries which may cause serious environmental problems. The aim of this study was to synthesis of chitosan nanoparticles and their comparison with chitosan for removal of Cr (VI) ions from industrial waste water. The Synthesizing of the nanoparticle adsorbents was successfully done by the crosslinking method. The nanoparticles sizes were determined between the ranges of 50-100 nm. The effect of the pH solution, adsorbents dosage, initial concentration of chromium ion and contact time for the absorption of Cr (VI) were investigated by means of atomic absorption spectroscopy. Maximum adsorption of chitosan nanoparticles and chitosan were 44 & 16 mg/g, respectively ($P<0.001$). The optimum conditions for removal of Cr (VI) were determined to be pH=5 for nanochitosan solution, 1gr/L of the initial concentration of metal ion, adsorbents dosage of 0.125 g/L and the 3-hour contact time. The results showed that nanochitosan possesses a higher absorption capacity for Cr (VI) compared to the chitosan, which related to the increase in the nanochitosan effective surface.

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INTRODUCTION

Nowadays, industrial heavy metal pollution has become a serious environmental and health problem all around the world. Not only do these heavy metals have toxic and harmful effects on the microorganisms living in the water, but they also have a negative effect on the living organisms in the accumulated food chain. Therefore, these pollutants should be reduced to an acceptable level before their entry into the environment.

Various methods were employed so far to achieve this goal that led to a reduction in the pollution rate of the production wastewater and an improvement in the output water flow quality [1, 2]. A variety of methods such as filtration, reverse osmosis, chemical oxidation or reduction, activated carbon, precipitation, coagulation, ion exchange, membrane processing, electrolyte, and electrochemical treatment are known as the most important processes which used in the past as proposed methods. It is notable that the treatment of the produced chemical sludge in these methods is expensive and is not effective in low concentrations [3-6].

Research suggests that none of the aforementioned methods can provide the two main factors contributing to the separation process,

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i.e. high efficiency and low cost, simultaneously. Therefore, scientists are looking for different ways today to provide the highest efficiency in the refinement of heavy metals. The adsorption technology using biological absorbents such as algae, fungi, bacteria, silica gel, activated charcoal, ash, charcoal ashes, zeolites, etc. is known as one of the important methods in this field [7-9], which was extensively used in water and wastewater purification, due to easy maintenance and application, low power consumption, high absorption capacity, high efficiency, low cost, selective removal of metals, the sorbent revival and metal recycling, and lack of sludge [10-12].

In this regard, biological polymers are highly regarded in the industry due to their capacity to bond with metals, availability, and environmental safety. Chitosan is one of these biopolymers which regarded as an ideal adsorbent due to the presence of –NH2 and –OH groups that can act as chelating and reaction sites [13]. Indeed, high-density amine groups in the structure of this biopolymer not only lead to chitosan being considered as a high-capacity sorbent for the removal of inorganic pollutants (e.g., heavy metal ions, nitrate, phosphate, borate, and fluoride) but also create a high absorption potential for the removal of organic pollutants (e.g., dyes, PPCPs, PFOS, proteins, and humus), and various pollutants from water and wastewater. However, there are some drawbacks that hindering its practical use, such as low solubility in acidic mediums, low mechanical strength, low adsorption capacity, and lack of selectivity. Hence, there are a variety of physical and chemical modification methods to improve the physicochemical properties of chitosan [14-20].

In this field, crosslinking can be mentioned as a common method that leads to an increase in the stability of this biopolymer [14, 20], although crosslinking reduces the adsorption capacity via reducing the number of free amino on chitosan [21]. However, it seems that chitosan nanoparticle (nanochitosan) compared to the chitosan and its derivatives has been more successful and provides higher removal efficiency for metal ions [14, 22, 23]. It can be due to the nanosize of particles, larger adsorption surfaces, and more functional groups.

Among heavy metals, hexavalent chromium is regarded as a toxic and carcinogenic heavy metal that comes in contact with water when it is discharged by several industries, such as chrome plating, textile dye industries, and leather tanning [24, 25]. The hexavalent chromium is more hazardous to public health and environment compared to trivalent chromium [26]. Discharge of industrial wastes containing Cr (VI) surface water creates serious health problems in the nervous system, liver, and brain. The adsorption process has been most economically preferred for Cr (VI) ions into the river and ions uptake from aqueous solutions [27, 28, 29].

The chitosan nanoparticles were synthesized to evaluate the adsorption performance of nanochitosan-based adsorbents. Afterward, the removal of Cr (VI) ions from wastewater in the batch system was performed by means of the synthesized nano-adsorbent, and the mechanisms of adsorption, the effect of pH, and isotherm models are described. Finally, the metal ions sorption capacity via nanochitosan was compared to chitosan.

EXPERIMENTAL SECTION

Reagents

Chitosan was purchased from Sigma Co. (USA) with a deacetylated rate of over 85%. Potassium dichromate ($K_2Cr_2O_7$), hydrochloric acid (HCl), acetic acid (CH3COOH), EDTA, glutaraldehyde and deionized water were all purchased from Merck (Germany).

Synthesis of Chitosan Nanoparticles

To synthesize chitosan nanoparticles, 0.25 gr chitosan with a medium molecular weight and over 85% deacetylated was dissolved in 1000 ml of 1% acetic acid. Later, the solution was stirred using magnet for 30 mins until it became transparent in color. The resulting solution was sonicated at 60% amplitude with a 0.5 cycle for 15 min. Next, the pH of the solution was adjusted to 5. At this pH, the solution begins to colloid which indicates the start of chitosan nanoparticles formation. At this pH, the solution begins to colloid which indicates the start of chitosan nanoparticles formation. Next, the solution was sonicated for 20 min and then passed through a 0.2 µ filter using a special syringe so that the bigger particles separated from the solution and particles with smaller dimensions in nanometer passed through the filter and the chitosan nanoparticles was formed.

After that, 10 µl of glutaraldehyde was added to the chitosan nanoparticles solution. The pH was adjusted to a range of 6 to 7. The resulting solution was stirred on a magnetic stirrer for 24 h until it

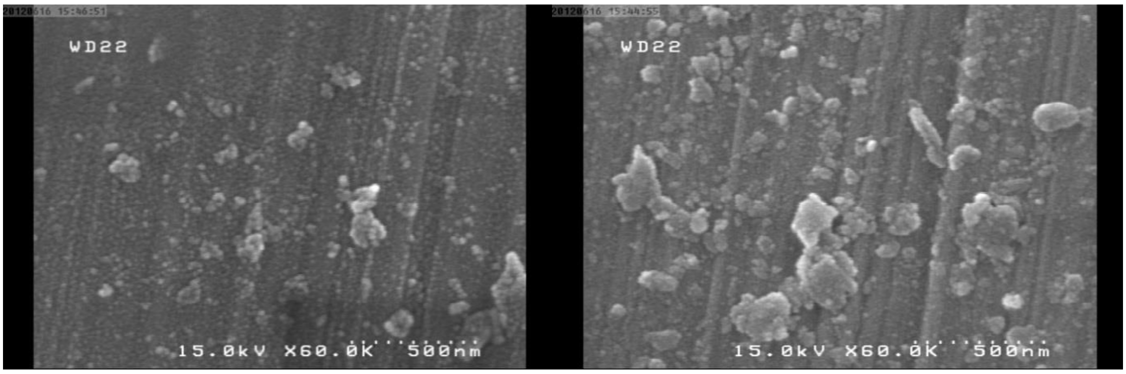

Fig. 1. Field Emission Scanning Electron Microscopy (FE-SEM) images of nanochitosan

became stable. Then, the solution was sonicated. Finally, EDTA was added to the solution. The pH was adjusted to a range of 4.5 to 6.5 and the solution was stirred for 2 hrs. Thus, crosslinked nanoparticle was produced with EDTA. All of the steps were performed at room temperature to produce nanochitosan.

Instruments

To study the resulting chemical changes in the synthesized nano-adsorbent and also the changes in the condition and intensity of the functional groups peak, the structure of the synthesized compounds were brought under scrutiny using a WQF-510 Rayleigh infrared spectrometer. In this study, the FESEM scanning electron microscopy (model XL30 from Philips, Netherlands) was employed to survey chitosan nanoparticles sizes and forms.

The Absorption of Chromium Ions by Nanoparticles

Different concentrations of chromium ion solutions were prepared in 10 ml containers using $K_2Cr_2O_7$ salt. Then, different volumes of synthesized nanochitosan were added to them according to the test conditions. Next, the reaction samples were passed through the membrane filter after centrifugation at different times of 0, 5, 10, 20, 40, 60, 120 and 180 mins. Eventually the remaining metal concentration was measured.

Data analysis

Specifying the absorption capacity (q_t) of the chromium metal ions using chitosan and nano-chitosan was performed via Eq. (1).

$$q_t = (C_0 - C_t)\ v/m \qquad (1)$$

Where, q_t (metal ion absorption capacity, mg/g) is the rate of absorbed ions by the adsorbent at time t, v (ml) is the solution volume, C_0 (mg/l) is the initial concentration of metal ions in the solution, C_t (mg/l) is the metal ions concentration in the solution at each time and m (g) is the adsorbent weight. To calculate the percentage removal of metal ions from solution (R), Eq. (2) was used.

$$\mathbf{100\times\%\ R = [(C_0 - C_t)/\ C_0]} \qquad (2)$$

RESULTS AND DISCUSSION

To study and confirm the synthesized nanoparticles, Field Emission Scanning Electron Microscopy (FE-SEM) images were taken from the nanochitosan. As can be seen in Fig 1, nanoparticle size is in the range of 50 to 100 nanometers.

Spectroscopy

To study the chemical structure of the produced nano-adsorbent, the Fourier Transform Infrared (FTIR) spectrum was taken from the sample. The presence of the peak area up to 1700 is related to the tension of C=O bond and peaks at 3000 to 3500 and is expanding due to the tension –OH confirms the presence of acetic acid in chitosan nanoparticles.

Study of the Adsorption Process

The Effect of pH on the Removal Percentage of Cr (VI) Ions by Nanochitosan

According to some studies, the most important parameter in the heavy metal adsorption by the adsorbent, is the initial pH of the solution that has a great effect on the metal ion adsorption sites on the absorbent surface and also the chemical structure of the metal in water [30-34].

The adsorption of metal ions occurs by one or

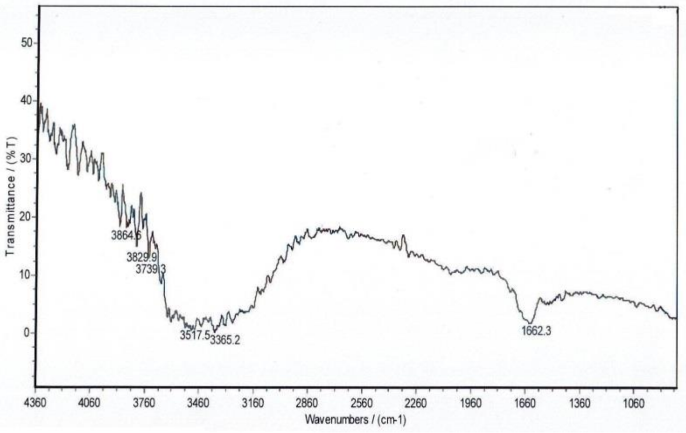

Fig. 2. The Fourier Transform Infrared (FTIR) spectrum of nanochitosan

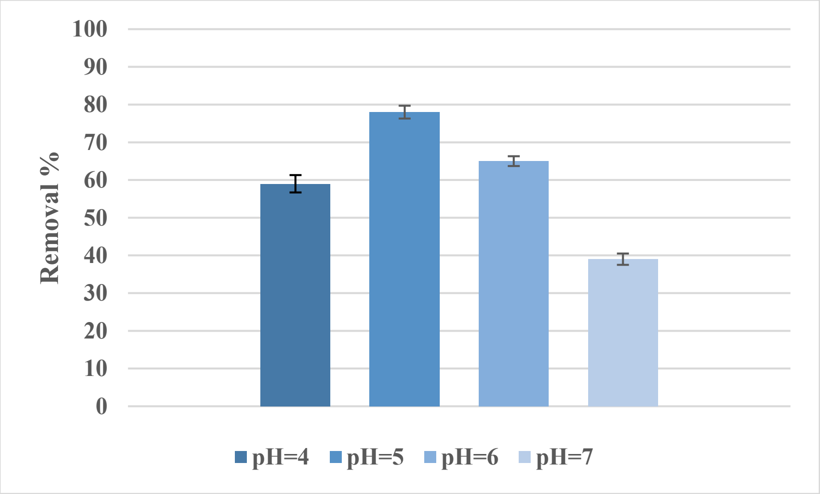

Fig. 3. Effect of pH on the percent removal of Cr (VI) ions by chitosan nanoparticles in the initial concentration of 1 mg/l and the adsorbent amount of 0.125 gr/l

combination of ion exchange mechanisms, chelating and electrostatic absorption [35]. Chitosan dissolves in a pH lower than 3 and metal ions precipitate as hydroxide in a pH greater than 7. Thus, in the present research, to study the effect of the initial pH of the solution on the adsorption rate, experiments were performed in the pH range of 4 to 7.

In Fig 3, the effect of pH on the percent removal of chromium metal ions by nanochitosan is shown. The highest percent removal of Cr (VI) occurred in pH 5. Dominant form of Cr (VI) at acidic pH is HCrO4-. Increase in pH can convert the HCrO4- to CrO4- and Cr2O7- forms. It can be concluded that the active form of Cr (VI) that can be adsorbed by the synthesized nanochitosan was HCrO4-.

The Effect of the adsorbent dosage on the Percent Removal of Cr (VI) Ions by Nanochitosan

To specify the optimum dosage of the adsorbent for the adsorption process, different concentrations of the nano-adsorbent were examined so that the optimum absorption capacity could be achieved for the adsorbent.

Based on the results from Fig. 4, increase in the adsorbent dosage from 0.01 to 0.125 gr/l leads to an increase in the percent removal of chromium metal ions from 33 to 78%. Other study that investigated the removal of chromium from industrial waste

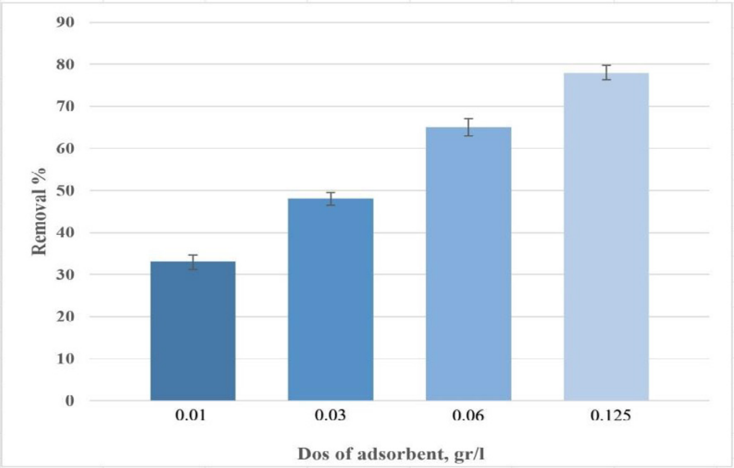

Fig. 4. Effect of the adsorbent dosage on the percent removal of Cr (VI) ions by chitosan nanoparticles in the initial concentration of 1 mg/l and a pH 5

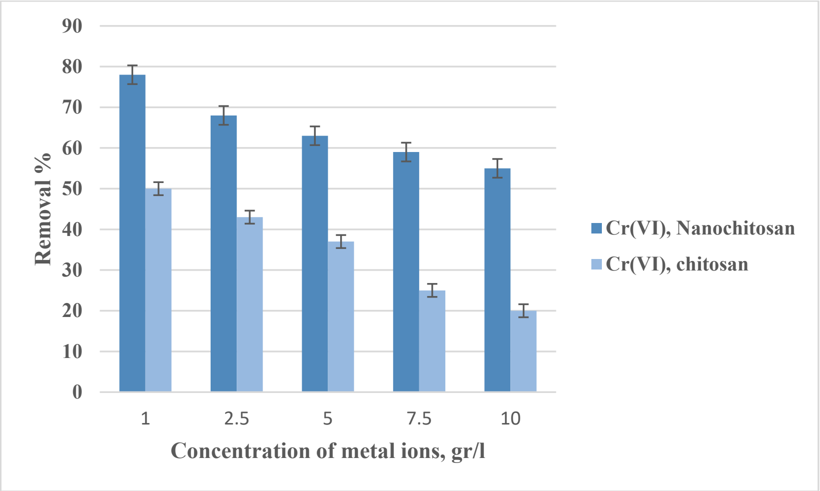

Fig. 5. Effect of the initial concentration of chromium ions on percent removal of Cr (VI) ions by chitosan and nanochitosan with a pH 5 and an adsorbent amount of 0.125 gr/l

by using eucalyptus bark shown that adsorption capacity was found to be 45 mg/g of adsorbent. The maximum (87.4%) removal of chromium was achieved with eucalyptus bark. The percent chromium removal with other three sorbents such as charred rice husk, bagasse and activated carbon were 36%, 35% and 9% respectively [36].

The effect of the Initial Concentration on the Removal Percentage of Cr (VI) Ions by Chitosan and Nanochitosan

One of the major factors contributing to the absorption of metal ions is the initial concentration of metal ions in solution. In the present research, the effect of the initial concentration of the metal ions was studied in the range of 1 to 10 mg/l, a pH=5 and an adsorbent amount of 0.125 gr/l.

In Fig 5, we can observe the effect of the initial concentration on percent absorption of the chromium metal ions. As can be seen in Fig. 5, the removal percentage decreases with every increase in the initial concentration of metal ions. The highest percent absorption of chromium obtained by chitosan with a 1 mg/l concentration, an adsorbent amount of 0.125 mg/l and a pH 5 was 78%.

The maximum capacity of absorption Cr (VI) was achieved 44 mg/g using nanochitosan and

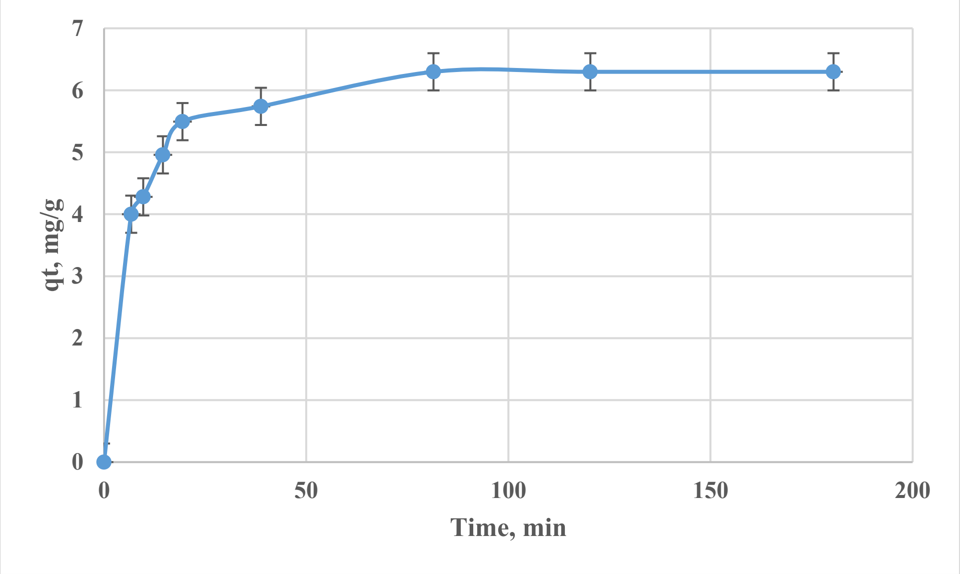

Fig. 6. Effect of contact time on the percent removal of Cr (VI) ions by the chitosan nanoparticles with a 1 mg/l initial concentration and an absorption rate of 0.125 gr/l with pH 5

16 mg/g using chitosan, respectively. The higher capacity of nanochitosan is due to increase in the active and effective surface of the nanochitosan compared to chitosan. The increase rate is significant with regard to the nanoparticle size. Furthermore, functionalization of nanoparticles and their activation by EDTA also increase the ability of nanoparticle capacity to absorb heavy metals. Based on the results obtained from different tests, capacity increases with every increase in the initial concentration of metal ions. This increase in the initial concentration of metal ions leading to an increase in the driving force of the concentrated gradient and an increase in the absorption capacity.

In lower concentrations, due to the high number of active absorption sites, some sites remain empty and no absorption occurs in them while as the initial concentration increases, all of the absorption sites are used and further saturated and start the absorption process with maximum capacity. In higher concentrations, the absorption capacities remain constant due to the saturation of absorption sites [37].

The Effect of Contact Time on the Percent Removal of Cr (VI) Ions by Nanochitosan

Another key parameter in the practical application of a sorbent is the contact time that is indicative of the absorption rate [35]. The effect of contact time on the percent absorption of chromium ions with 1 mg/l initial concentration, pH 6 and an adsorbent amount of 1 mg/l is shown in Fig 6.

The time period studied in this research is 3 hours. As can be seen in Fig 6, in the first 5 minutes, the absorption rate is very fast. And most of the ions are absorbed from solution in the first 40 minutes. After 40 mins, the absorption process proceeds slowly and has a rather constant progress in 80 mins.

The obtained results showed that chromium is better absorbed at pH 5. The results of the subsequent tests suggest that the absorption capacity decreases with the decrease of the metal ions initial concentration from 10 to 1 mg/l while the percent absorption increases.

The optimum conditions for the tests were specified as follows: a pH 5, a metal ion initial concentration of 1 gr/l, an absorption amount of 0.125 gr/l and a 3 hours contact time. Under such conditions, the maximum effective removal was achieved for a 78% Cr (VI) with a 1 mg/l concentration.

Absorption Equilibrium Studies

To optimize the design of the adsorption system to remove contaminants, equilibrium analysis to compare different adsorbents under different

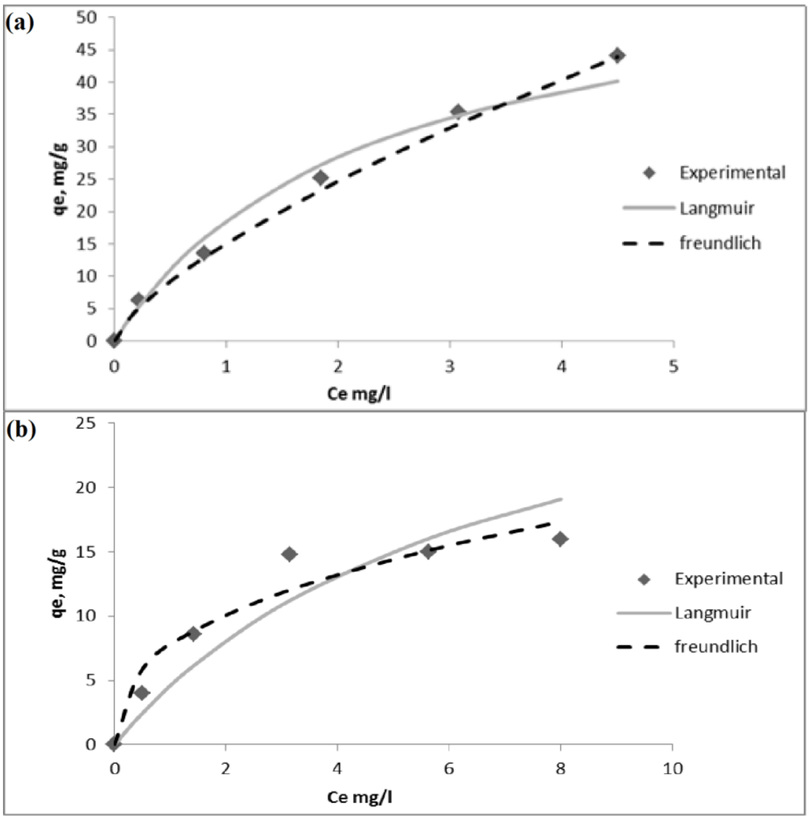

Fig. 7. Compare the models of Langmuir and Freundlich equilibrium temperature for the adsorption of Cr (VI) ions (a) nanochitosan (b) chitosan

operating conditions was used.

For this purpose, two isotherms of Freundlich and Langmuir were used for data analysis. The data obtained from the experiments were drawn using the equations for each isotherm and the amount of fixed isothermal and R2 of each of these models were examined. These constants represent the relationship between adsorption and equilibrium concentration solution. Compare the models of Langmuir and Freundlich equilibrium temperature to absorb metal ions (a) chromium, chitosan nanoparticles (b) chromium, chitosan is shown in Fig. 7.

Langmuir model represents monolayer adsorption and Freundlich isoterm represents multilayer adsorption.

The Langmuir model includes two parameters: qm and kL, where qm parameter represents the maximum absorption capacity in absorbent complete saturation and kL coefficient represents the relationship between absorption and self-absorption material.

Freundlich model is more searchable for heterogeneous surfaces. Constant of this equation contains kf and n, where kf parameters represents the relative measurement of biological absorption capacity and n indicates the intensity of surface adsorption. Effective parameter values of Langmuir and Freundlich models to absorb Cr (VI) are shown in Table 1. In the Langmuir model performance adsorption used, were measured by qm parameter. The high value of KL parameter also indicates high-affinity adsorbent for binding the metal ions.

As a result, the high value of qm and KL parameter in the nanochitosan compared to chitosan represents the higher adsorption performance of the nanosorbent.

Also, the high value of kf parameter in the absorbent of nanochitosan compared with chitosan shows a higher adsorption capacity of absorbent nanoparticles of chitosan. According to the correlation coefficient of each above model, Freundlich equilibrium model shows a better performance in prediction of chromium metal ions absorption.

Table 1. Freundlich and Langmuir isoterms parameters for absorption at 25 °C

Adsorbent	**Freundlich model**			**Langmuir model**		
	R^2	n	K_F (mg/g)	R^2	K_l (1/mg)	q_m (mg/g)
Chitosan nanoparticles	0.99	1.41	15.2	0.97	0.65	60
Chitosan	0.88	2.56	7.7	0.87	0.15	35

CONCLUSIONS

The synthesized nanochitosan showed a higher absorption capacity for Cr (VI) compared to the chitosan that is related to the increase in the active and effective surface of nanochitosan than that of the chitosan. Additionally, the functionalization of nanoparticles and their activation with EDTA were also the contributing factors in nanoparticles capacity to absorb the chromium ions. Based on the obtained results, the increase in the initial concentration of the Cr (VI) led to the driving force of the concentrated gradient and an increase in the absorption capacity. According to our findings, the Freundlich isotherm model gives a better value of adsorption capacity when compared to Langmuir isotherm model.

CONFLICT OF INTEREST STATEMENT

All authors declare that no conflicts of interest exist for the publication of this manuscript.

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