



Removal of chromium (VI) from aqueous solutions using quaternized chitosan microspheres[☆]

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ARTICLE INFO

Article history:

Received 16 July 2016

Received in revised form 16 August 2016

Accepted 30 August 2016

Available online 13 September 2016

Keywords:

Chromium (VI)

Adsorption

Quaternized chitosan microspheres

Isotherms

Thermodynamics

ABSTRACT

In this study, quaternized chitosan microspheres (QCMS) were prepared and its Cr (VI) removal potential was investigated. Batch experiments were conducted to examine kinetics, adsorption isotherm, pH effect, and thermodynamic parameters. Equilibrium was attained within 50 min and maximum removal of 97.34% was achieved under the optimum conditions at pH 5. Adsorption data for Cr (VI) uptake by the QCMS were analyzed according to Langmuir, Freundlich, and Temkin adsorption models. The maximum uptake of Cr (VI) was 39.1 mg·g⁻¹. Thermodynamic parameters for the adsorption system were determined at 293 K, 303 K, 313 K and 323 K. ($\Delta H^\circ = 16.08 \text{ kJ} \cdot \text{mol}^{-1}$; $\Delta G^\circ = -5.84 \text{ to } -8.08 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta S^\circ = 74.81 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$). So the positive values of both ΔH° and ΔS° suggest an endothermic reaction and increase in randomness at the solid–liquid interface during the adsorption. ΔG° values obtained were negative indicating a spontaneous adsorption process. The kinetic process was described by a pseudo-second-order rate equation very well. The results of the present study indicated that the QCMS could be considered as a potential adsorbent for Cr (VI) in aqueous solutions.

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1. Introduction

Process waste streams from electroplating, printing, pigments and other industries often contain metal ions at concentrations above local discharge limits [1]. Unlike the organic pollutants which are often biodegraded, metal ions cannot be degraded or readily detoxified biologically [2]. This has led to increasing concern about the effect of toxic heavy metals. Among all heavy metals, chromium is one of the most toxic pollutants which cause a severe significant environmental problem [3,4]. Chromium exists in the aqueous environment as in trivalent and hexavalent forms. Cr (III), an essential trace element for human beings, may play a role in the metabolism of glucose, but Cr (VI) is toxic, carcinogenic and mutagenic in nature [5].

Cr (VI) is known to have 100 times more toxic than Cr (III) because of its high water solubility and mobility, as well as easy reduction [6]. Its toxicity includes cancer as well as kidney, liver and gastric kidney, liver and gastric damages [7]. Due to environmental concern, discharge limits of Cr (VI) have been investigated by most countries. Considering Cr (VI) toxic and carcinogenic nature, the World Health Organization (WHO)

has set a maximum allowable level of 0.05 mg·L⁻¹ total chromium for drinking water [8]. At present, the permissible concentration of Cr (VI) in drinking water is also 0.05 mg·L⁻¹ in China [9]. A variety of methods have been developed to treat Cr (VI) contaminated wastewaters, which include chemical precipitation, adsorption, ion-exchange, membrane separation, reverse osmosis, coagulation/flocculation and solvent extraction [10–16]. Among these methods, adsorption is one of the popular methods for the removal of chromium from wastewaters. To date, a variety of materials have been tried as adsorbents for Cr (VI) removal. These include zeolites, clay minerals, metal oxides, chitosan, sulfonated lignite [17], organic resins and waste products from industrial operations such as fly ash and coal [18].

Chitosan is an excellent biosorbent for the removal of metal ions from wastewater due to its non-toxicity, polyfunctionality, biocompatibility, and biodegradability. Taking into account these properties, it is one of the most frequently reported biosorbents. In addition, its adsorption capacity can be improved by chemical means such as crosslinking, addition of functional groups. Several chemical changes have been applied to chitosan in order to enhance its interaction with Cr (VI) [19–22]. The quaternary ammonium groups are the effective adsorption function groups for the treatment of Cr (VI) ions from aqueous solutions. In this study, Cr (VI) adsorption behavior on the quaternized chitosan microspheres (QCMS) in the aqueous solution was investigated. The influence of several operating parameters for adsorption of Cr

[☆] Supported by the National Key Basic Research Development Plan (No. 2013CB632602), and the National Natural Science Foundation of China (No. 21306198).

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(VI), such as contact time, temperature, pH and adsorbent dose, was investigated in batch mode. The kinetic data were fitted to different models and the isotherm equilibrium data were fitted to Langmuir, Freundlich and Temkin.

2. Materials and Methods

2.1. Materials and analytical method

Chitosan (85% deacetylated) was purchased from Sinopharm Chemical Reagent Co., Ltd. (China). 3-Chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) aqueous solution (65 wt%) was obtained from Quab Chemical Co. (USA). Other chemicals and reagents used in this work had a pure analytical quality. Deionized water was used for all dilution and reagent preparations. Potassium dichromate ($K_2Cr_2O_7$) was used as a source of Cr (VI). The stock solution ($1000\text{ mg}\cdot\text{L}^{-1}$) was prepared by dissolving 2.829 g of potassium dichromate ($K_2Cr_2O_7$) (AR grade) in 1000 ml of deionized water. All working solutions of possessing varying concentrations were obtained by appropriate dilution. The concentration of Cr (VI) was analyzed by spectrophotometer (UV-1201 model) using 1, 5-diphenylcarbazide as the complexing agent at the wavelength of 540 nm (GB7467-87) [23].

The adsorbed amount of Cr (VI) equilibrium, q_e ($\text{mg}\cdot\text{g}^{-1}$) was calculated by using the mass balance:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where V is the solution volume (L), W is the amount of adsorbent (g), and C_0 and C_e are the initial and equilibrium Cr (VI) concentrations ($\text{mg}\cdot\text{L}^{-1}$), respectively.

2.2. Preparation of adsorbent

Chitosan powder (2.5 g) was dissolved in 60 ml of 2% acetic acid under stirring at room temperature, then PEG2000 (0.015 g) was added, and the mixture was added to liquid paraffin in a three-necked flask. Span80 (1.5 ml) was dropwise added to emulsification for about 0.6 h. Then, 5.8 ml of formaldehyde was added, and the solution was stirred for another 1 h. Then epoxy chloropropane was added to the mixture under controlled stirring for 2 h. Sodium hydroxide solution was slowly added into the mixture and then stirred for 3 h. The products were suction filtered carefully and washed thoroughly with acetone and deionized water. The obtained chitosan microspheres were transferred into a 100 ml three-necked flask with $0.4\text{ mol}\cdot\text{L}^{-1}$ NaOH solution. After 30 min, an aqueous solution of CHPTAC was added to the reaction mixture. The mixture was stirred for 8 h at $60\text{ }^\circ\text{C}$. Subsequently, dilute hydrochloric acid was added to the mixture to stop the reaction. The resulting products were thoroughly washed with deionized water, and then vacuum-dried at $45\text{ }^\circ\text{C}$ to produce quaternized chitosan microspheres. The dried modified chitosan microspheres were used for Cr (VI) adsorption studies.

2.3. Effect of contact time

The contact time of adsorbent with adsorbate is of great importance in adsorption since contact time depends on the nature of the system used. The effect of contact time was studied as follows: to each of 0.05 g the QCMS, 100 ml of solution containing $20\text{ mg}\cdot\text{L}^{-1}$ of Cr (VI) was added. The samples were shaken at room temperature for periods ranging from 5 min to 80 min and then centrifuged and 5 ml portions of liquid phases were measured.

2.4. Effect of pH

It is well known that the initial pH of a system is an important parameter in the adsorption of Cr (VI). At higher pH values, Cr (VI) ions precipitate as hydroxides. In the present work, the effect of pH on the removal of Cr (VI) is investigated by varying the pH values from 2 to 8 at a temperature of $(20 \pm 1)\text{ }^\circ\text{C}$ and for fixed initial Cr (VI) concentration of $20\text{ mg}\cdot\text{L}^{-1}$. The pH is adjusted using $0.1\text{ mol}\cdot\text{L}^{-1}$ HCl and $0.1\text{ mol}\cdot\text{L}^{-1}$ NaOH. The contact time has been fixed at 1 h for all experiments.

2.5. Effect of amount of adsorbent

Under optimum conditions of shaking time and pH, the effect of adsorbent dosage on the removal of Cr (VI) at $C_0 = 20\text{ mg}\cdot\text{L}^{-1}$ was also studied by shaking 50 ml of metal solution with 0.025–0.325 g of adsorbent.

2.6. Characterization of the Sorbents

The morphologies of the QCMS were characterized by scanning electron microscopy (Hitachi S-3500N, Hitachi Company, JPN). The FTIR spectra of chitosan and the QCMS were recorded on a FTIR Spectrometer (Nexus 470, Thermo Nicolet, USA) using KBr pellets over the range $4000\text{--}400\text{ cm}^{-1}$.

2.7. Adsorption kinetics

Adsorption kinetics is important as it provides valuable insights into the reaction pathways and the mechanism of the reactions. Experiments were also performed in order to understand the kinetics of Cr (VI) removal by the QCMS. At various time intervals, samples were taken and the concentration was measured. The amount of Cr (VI) adsorbed q_t at time t was determined by the following equation:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

where q_t is the amount of Cr (VI) adsorbed at time t ($\text{mg}\cdot\text{g}^{-1}$), V is the volume of the solution (L), W (g) is the mass of the adsorbent, C_0 and C_t are the concentrations of the Cr (VI) at initial ($t = 0$) and at time t , respectively.

The kinetic data were analyzed using Lagergren pseudo-first-order and Ho pseudo-second-order equation [24,25].

Lagergren pseudo-first-order:

$$\lg(q_e - q_t) = \lg(q_e) - \frac{k_1}{2.303}t \quad (3)$$

Ho pseudo-second-order:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (4)$$

where q_t and q_e are the amounts of Cr (VI) adsorbed ($\text{mg}\cdot\text{g}^{-1}$) at time t and at equilibrium, respectively; k_1 (min^{-1}) and k_2 ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$) are the pseudo-first-order and pseudo-second-order rate constants.

2.8. The adsorption isotherms

The adsorption isotherms were studied by varying the concentration of Cr (VI) solutions with a fixed dose of adsorbent. To investigate the sorption isotherms, Langmuir, Freundlich, and Temkin model were used to analyze the experimental data [26–28]. The linearised isotherm equations are expressed as the following:

Langmuir:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b} \quad (5)$$

Freundlich:

$$\lg q_e = \lg K + \frac{1}{n} \lg C_e \quad (6)$$

Temkin:

$$q_e = A + B \ln C_e \quad (7)$$

where C_e is the equilibrium liquid phase concentration ($\text{mg} \cdot \text{L}^{-1}$), q_e is the amount of sorbent adsorbed per unit mass ($\text{mg} \cdot \text{g}^{-1}$); and Q_0 and b are the Langmuir constants related to the sorption capacity and the rate of adsorption, respectively. K and $1/n$ are Freundlich constants. The values of K and $1/n$, which roughly correspond to the adsorption capacity and the heterogeneity factor representing the deviation from linearity of adsorption, respectively. A and B are Temkin isotherm constants.

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L [29], also known as the separation factor, given by Eq. (8):

$$R_L = \frac{1}{1 + bC_0} \quad (8)$$

where b ($\text{L} \cdot \text{mg}^{-1}$) is the Langmuir constant and C_0 ($\text{mg} \cdot \text{L}^{-1}$) is the initial highest concentration of metal ion. The value of R_L lies between 0 and 1 for a favorable adsorption, while $R_L > 1$ represents an unfavorable adsorption, and $R_L = 1$ represents the linear adsorption, while the adsorption operation is irreversible if $R_L = 0$.

2.9. Thermodynamic parameters

To study the thermodynamics of the adsorption of Cr (VI) onto the QCMS, the thermodynamic parameters, free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) can be evaluated from the following equations [30,31]:

$$K_c = \frac{C_{Ae}}{C_e} \quad (9)$$

$$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (10)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

where K_c is the equilibrium constant, C_{Ae} is the amount of Cr (VI) ion (mg) adsorbed on the adsorbent per liter of the solution at equilibrium, and C_e is the equilibrium concentration ($\text{mg} \cdot \text{L}^{-1}$) of the Cr (VI) ion in the solution. R is the universal gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) and T is the absolute temperature (in Kelvin).

3. Results and Discussion

3.1. Sorbent characterization

Fig. 1 shows a general SEM micrograph of the QCMS, and it can clearly be seen that the modified chitosan are well shaped spheres. The QCMS have the diameter size range of 10–30 μm . Fig. 2 shows the FT-IR spectra of chitosan, the QCMS and the QCMS loaded with Cr (VI). In chitosan obvious translocations are observed at 3200–3500 cm^{-1} due to O–H and N–H group. The peak at 2928 cm^{-1} and 2878 cm^{-1} was attributed to the stretching vibration of $-\text{CH}_3$ and $-\text{CH}_2$ group. The peak at 1595 cm^{-1} is the N–H₂ deformation vibration of amino groups. Compared to chitosan, the peak at 1595 cm^{-1} disappears in the QCMS. The peak at



Fig. 1. SEM images of the QCMS.

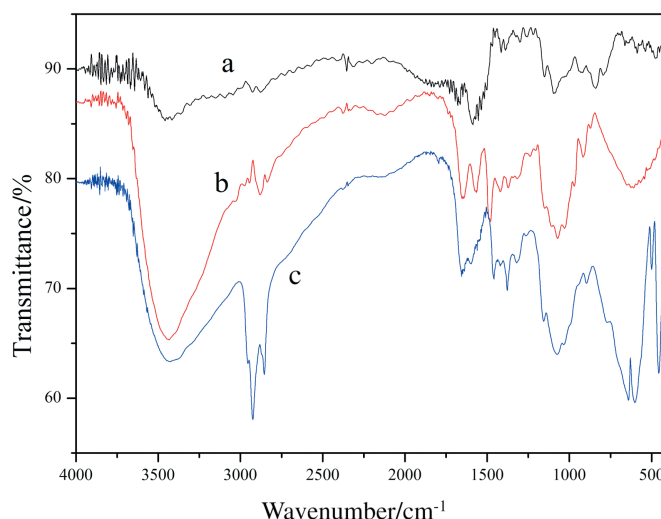


Fig. 2. FTIR spectra of chitosan (a), the QCMS (b) and the QCMS loaded with Cr (VI) (c).

1573 m^{-1} is the N–H₂ deformation vibration of amino groups. The peak at 1474 cm^{-1} is assigned to asymmetric CH stretching vibration of quaternary ammonium salts. The peak at 971 cm^{-1} is assigned to absorption peak of quaternary ammonium salt. The above analyses indicated that the adsorbent (QCMS) had been successfully prepared. In the FT-IR spectra of the QCMS loaded with Cr (VI), the ratio of amino ($\sim 3400 \text{ cm}^{-1}$) and alkyl (2750–2900 cm^{-1}) signal intensity changed significantly. The number of amino and alkyl experienced significant changes, indicating the location of the chromium atoms to chelate on the amino group of the QCMS.

3.2. Effect of contact time

The results of adsorption experiment for different contact times are presented in Fig. 3, where it is clear that adsorption of Cr (VI) into the QCMS is rather quick and the percentage removal of Cr (VI) becomes asymptotic to the time axis, nearly representing an equilibrium pattern. The adsorption of Cr (VI) increased with increasing contact time and the adsorption reached equilibrium in about 50 min. The observed removal efficiency was 99.66% at 50 min. This behavior shows that adsorption of Cr (VI) occurred in a single step and that the adsorption before 50 min can be explained.

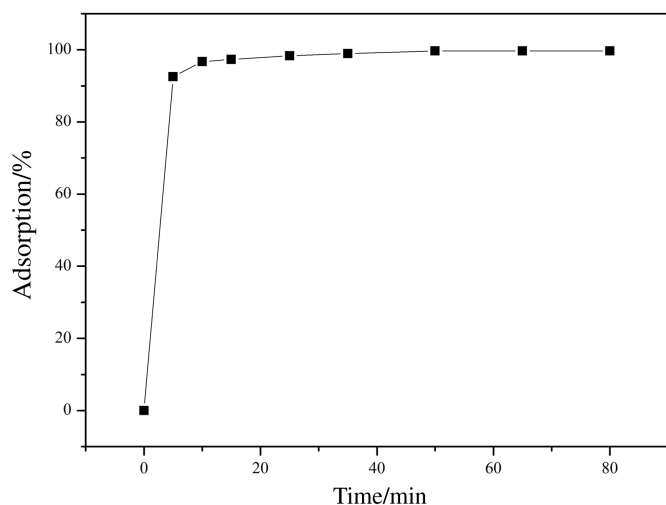


Fig. 3. Adsorption of Cr (VI) on the QCMS as a function of contact time.

3.3. Effect of pH

The pH of the solutions plays an important role in the adsorption process as the adsorbent surface acquires positive or negative charge in response to change in pH. Fig. 4 shows the effect of the initial solution pH (2.0–8.0) on the adsorption of Cr (VI) onto the QCMS. Accordingly, the percentage of Cr (VI) removal increased gradually from 61% to 97% with the increase in pH value of ranging from 2.0 to 5.0. This could be explained by the fact that, at a lower pH, the Cr (VI) mainly existed in the form of HCrO_4^- which could easily bond with positively charged amino groups via electrostatic attraction. Above a pH of 5.0, the adsorption capacity of Cr (VI) began to decrease. $\text{pH} > 5$, the amount of CrO_4^{2-} ions in aqueous solution tended to increase, which consumed two positively charged amino group, making the adsorption capacity of Cr (VI) decreased gradually. The optimal pH of 5.0 found here has been selected for further study in the experiments.

3.4. Effect of amount of adsorbent

The effect of adsorbent dosage on the percentage removal of chromium (VI) has been shown in Fig. 5. It can be seen from the figure that with an increase in adsorbent dosage, the Cr (VI) ion removal

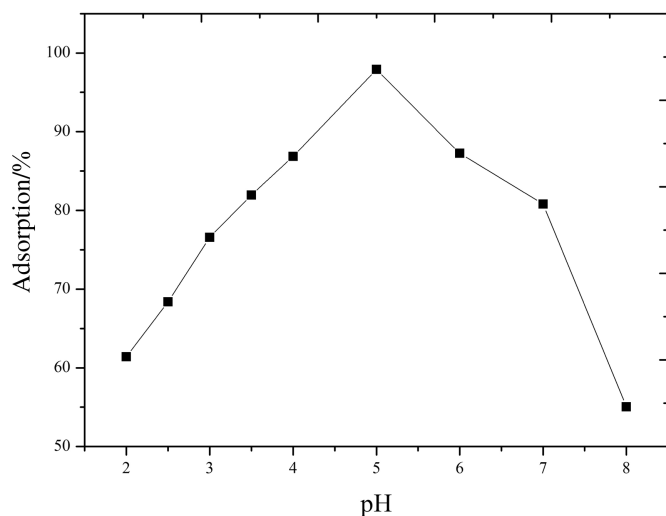


Fig. 4. Influence of initial pH on Cr (VI) adsorption.

increases until a certain value is reached; afterwards, the removal efficiency is maintained constant even if the QCMS is added. A maximum removal of Cr (VI) (99%) is achieved by the QCMS at an optimum adsorbent dose of 0.25 g. So the use of $5 \text{ g} \cdot \text{L}^{-1}$ adsorbent dose is justified for economical purposes.

3.5. Adsorption kinetics

The plots of $\lg(q_e - q_t)$ versus t and t/q_t versus t are shown in Figs. 6 and 7. The kinetic parameters together with correlation coefficients (R^2) have been postulated from the slopes and the intercepts

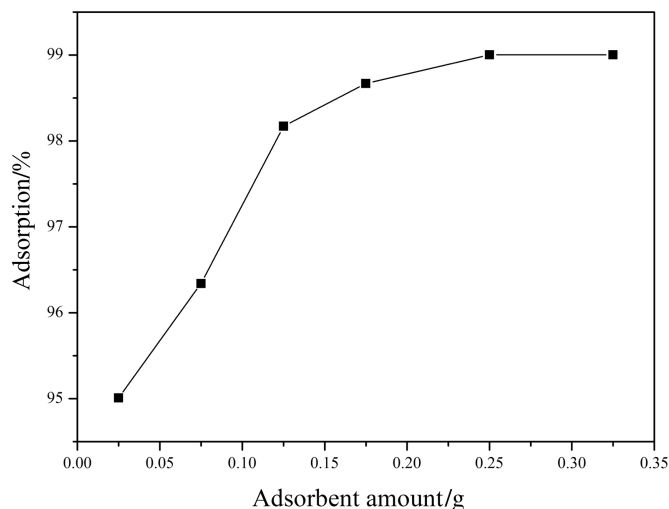


Fig. 5. Dependence of Cr (VI) adsorption on the amount of adsorbent.

of respective plots and are listed in Table 1. The correlation coefficients for the pseudo-first-order equation obtained at all the studied concentrations were low. The results of the regression analysis proved that Cr (VI) adsorption on the QCMS was best described by the pseudo-second-order equation ($R^2 \approx 1.000$) for all the studied concentrations. The calculated q_{e2} values also agree very well with the experimental data. This strongly suggests that the sorption of Cr (VI) onto the QCMS is most appropriately represented by a pseudo-second-order rate process.

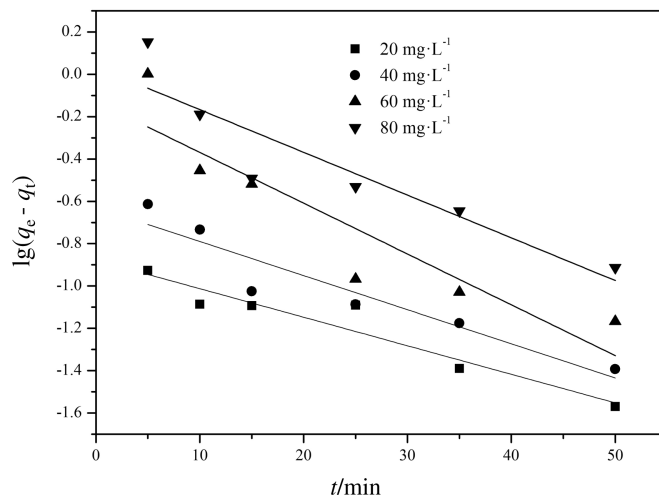


Fig. 6. Lagergren first-order kinetic plot for the sorption of Cr (VI) on the QCMS.

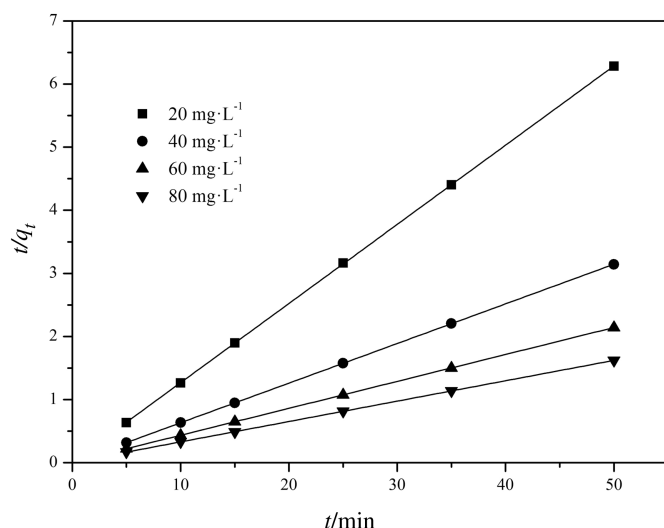


Fig. 7. Ho second-order kinetic plot for the sorption of Cr (VI) on the QCMS.

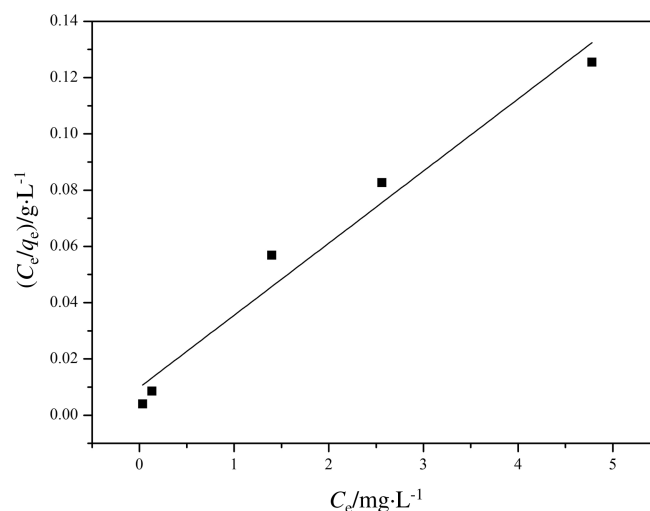


Fig. 8. Langmuir adsorption isotherm for Cr (VI) ions adsorption on the QCMS.

3.6. The adsorption isotherms

Isotherms are represented in Figs. 8–10 the Langmuir, Freundlich and Temkin models, respectively. All the isotherms were fitted to experimental data, and the goodness of fit was compared. Isotherm parameters for the Langmuir, Freundlich and Temkin models for the QCMS are reported in Table 2. The correlation coefficient of Langmuir isotherm (0.977) is higher than that of Freundlich isotherm (0.971) and Temkin isotherm (0.955). This reinforces the fact that Langmuir isotherm is useful to explain the adsorption of Cr (VI) from the solution on the current adsorbent when it follows the monolayer mode, rather than the multilayer mode. The maximum adsorption capacity was obtained with $39.11 \text{ mg} \cdot \text{g}^{-1}$ using the Langmuir model. The value of R_L in the present investigation has been found $0 < R_L < 1$. Hence the sorption process was very favorable and the QCMS employed exhibited a good potential for the removal of Cr (VI) from aqueous solution.

3.7. Thermodynamic parameters

The values of ΔH° and ΔS° were calculated from the slope and intercept of the Van't Hoff plot ($\ln K_c$ vs. $1/T$) shown in Fig. 11. The calculated values are given in Table 3. The positive values of ΔH° ($16.08 \text{ kJ} \cdot \text{mol}^{-1}$) suggest an endothermic nature of adsorption of Cr (VI) ions on the QCMS. The entropy change (ΔS°) was $74.81 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, the positive values of ΔS° show the increasing randomness at the solid/solution interface during the adsorption process. It is also suggested that the positive values of entropy indicate some structural changes in the adsorbate and adsorbent. As the free energy changes are negative and accompanied by positive entropy changes, the adsorption reactions are spontaneous with a high affinity.

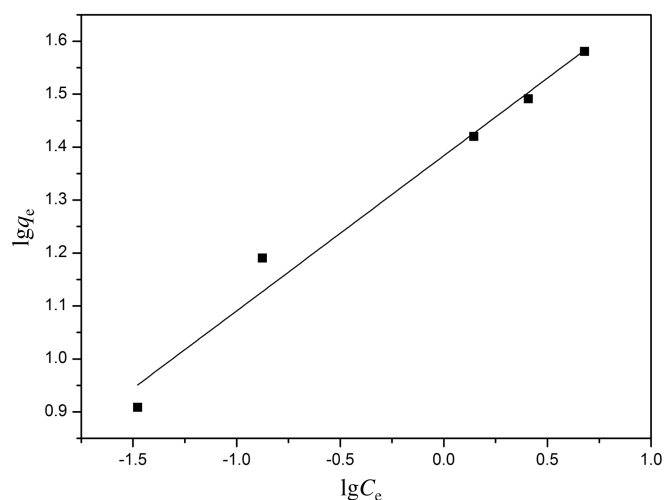


Fig. 9. Freundlich adsorption isotherm for Cr (VI) adsorption on the QCMS.

4. Conclusions

Quaternized chitosan microspheres were prepared and characterized in this work. The Cr (VI) adsorption behavior on the prepared QCMS has been studied under various conditions of different solution pH values and adsorption contact times. Accordingly, equilibrium was attained within 50 min and maximum removal of 97.34% was achieved under the optimum conditions at pH 5. The Cr (VI) adsorption was favored at higher temperatures. Experimental isotherms of Cr (VI)

Table 1

Kinetic parameters for pseudo-first order and pseudo-second order

Pseudo-first order				Pseudo-second order			
$C_0/\text{mg} \cdot \text{L}^{-1}$	k_1/min^{-1}	$q_{e1}/\text{mg} \cdot \text{g}^{-1}$	R^2	$k_2/\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$	$q_{e2}/\text{mg} \cdot \text{g}^{-1}$	R^2	$q_{e, \text{exp}}/\text{mg} \cdot \text{g}^{-1}$
20	0.0313	0.131	0.894	1.182	7.97	0.999	7.93
40	0.0372	0.233	0.871	0.714	15.93	1.000	15.39
60	0.0555	0.742	0.802	0.217	23.44	1.000	23.18
80	0.0468	0.925	0.806	0.150	30.98	0.999	30.01

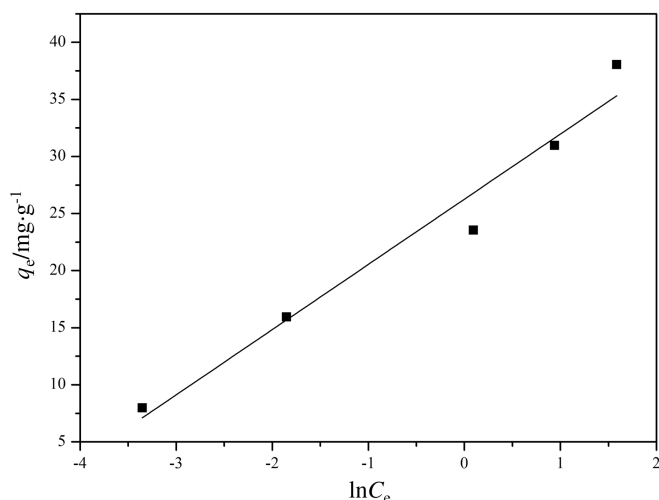


Fig. 10. Temkin isotherm for Cr (VI) adsorption on the QCMS.

Table 2

Parameters of the Langmuir, Freundlich and Temkin isotherm models

T/K	Langmuir			Freundlich			Temkin		
	$Q_0/\text{mg}\cdot\text{g}^{-1}$	$b/\text{L}\cdot\text{mg}^{-1}$	R^2	K	n	R^2	A	B	R^2
299	39.11	2.78	0.977	23.81	3.35	0.971	26.25	5.71	0.955

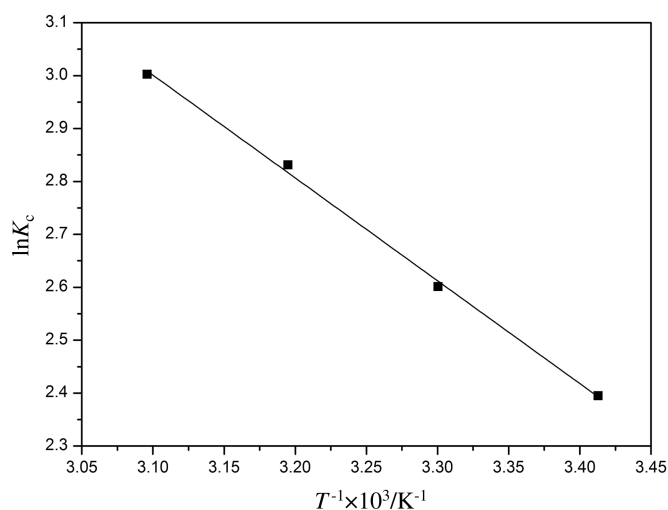


Fig. 11. Plot of $\lg K_c$ vs. $1/T$ for Cr (VI) adsorption on the QCMS.

Table 3

Thermodynamic parameters for sorption of Cr (VI) on the QCMS

Temperature/K	$\Delta G^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta S^\circ/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
293	−5.84	16.08	74.81
303	−6.59		
313	−7.34		
323	−8.08		

were successfully fit to Langmuir isotherms models. The values of ΔH° , ΔS° and ΔG° prove that the adsorption of Cr (VI) on the QCMS is an endothermic and a spontaneous process. The results indicate that the QCMS is an effective adsorbent for the removal of Cr (VI) ions from aqueous solutions, and it could be useful in treatment of Cr (VI) polluted wastewaters.

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