

Adsorption of Cr(III) from an Aqueous Solution by Chitosan Beads Modified with Sodium Dodecyl Sulfate (SDS)

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Abstract

This study is to prepare chitosan beads modified with sodium dodecyl sulfate (SDS) to effectively remove Cr(III) from an aqueous solution. The characterizations of SDS-chitosan by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), Fourier transform-infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) proved the successful synthesis of the adsorbent. The adsorption of Cr(III) on the SDS material was investigated by varying experimental conditions such as pH, contact time and adsorbent dosage. The maximum adsorption capacity of SDS-chitosan for Cr(III) was estimated to be 3.42 mg·g⁻¹. The results of adsorption kinetics and isothermal models show that the adsorption process conforms to the pseudo-second-order and Langmuir isotherm models, indicating that the adsorption is single-layer chemical adsorption. Thermodynamic analyses indicate that the adsorption of Cr(III) is an endothermic reaction. These results show that the new adsorbent has obvious application prospect to eliminate Cr(III).

Keywords

Chitosan Beads, Sodium Dodecyl Sulfate (SDS), Trivalent Chromium Ions (Cr(III)), Adsorption, Adsorption Isotherms, Adsorption Kinetics

1. Introduction

Due to the emergence of industrialization and urbanization worldwide, heavy metals are excessively produced and discharged into the environment. The pres-

ence of heavy metals in aqueous environments is currently one of the most recent risks due to their toxicity, non-degradability, and accumulation into the food chain [1] [2] [3]. Heavy metals have functional roles that are essential for humans, animals, and plants in low doses but heavy metals in high doses cause serious and chronic toxicity, which can lead to cancer and even death [4].

Chromium is one of the most common pollutants as it is widely used in many industries such as electroplating, leather tanning, textiles, steelworks, wood preservation, artificial fertilizers and nuclear power stations [5] [6] [7]. Chromium mainly exists in two stable oxidation states in nature, namely Cr(VI) and Cr(III) [8]. The typical mobile forms of Cr(VI) in natural environment are CrO_4^{2-} or HCrO_4^- and the relative distribution of each species depends on the solution pH, redox potential and on chromium concentration [9]. Adverse health effects associated with Cr(VI) exposure include bronchitis, liver damage, kidney damage, brain damage, and even lung cancer, whereas trivalent state is the most stable form in reducing conditions and is present as a cationic species $\text{Cr}(\text{OH})^{2+}$ and $\text{Cr}(\text{OH})_2^+$, with the first or second hydrolysis products dominating at pH values from 4 to 8. The low solubility of $\text{Cr}(\text{OH})_3$, considerably limits the concentration of Cr(III) for pH values above about 5 [10] [11]. Cr(III) is considered to be an essential microelement for the maintenance of effective glucose, lipid, and protein metabolism in mammals [12]. Given its high danger to biological systems, many studies have focused on the removal of Cr(VI), while very few articles deal with the adsorption of Cr(III).

Chromium elements, therefore, it is vital to eliminate heavy metals from wastewaters before discharging them into the environment. Various treatment methods have been developed to remove heavy metal ions from different aqueous solutions. These include chemical precipitation [13], adsorption, evaporation, reverse osmosis, ion exchange, membrane filtration, and biosorption [14] [15] [16] [17]. Among these, adsorption is considered to be an alternative process to remove heavy metal ions from wastewater [18] [19] [20]; especially, biological adsorption (biosorption) has emerged as one of the most promising method. It is generally preferred for the removal of lead due to its high efficiency, cost-effectiveness, easy handling, and the availability of different adsorbents [21] [22].

Among the many biosorbents, chitosan is a type of natural polyaminosaccharide, synthesized from the deacetylation of chitin and mainly composed of poly- β -(1,4)-2-deoxy-2-amino-d-glucose. Chitin is the second most abundant polymer in nature after cellulose, and can be extracted from crustacean shells such as prawns, insects, fungi, crabs and other crustaceans [23] [24] [25]. Owing to its many attractive properties such as its hydrophilicity, biocompatibility, biodegradability, and non-toxicity, as well as, the presence of reactive amino ($-\text{NH}_2$) and hydroxyl ($-\text{OH}$) groups in its backbone, chitosan has been used as an effective material for the removal of heavy metals from wastewaters [26] [27] [28].

Chitosan has a few defects such as notable swelling in aqueous media and a nonporous structure resulting in a low surface area [29]. Therefore, many types of physical or chemical modifications can be made to chitosan to improve its chemical stability in an acidic medium, its mechanical strength, and its adsorption capacity. The most common chemical modifications are cross-linking the grafting of a new functional group and acetylation. Cross-linking agents (such as TPP) are commonly used to prepare chitosan beads because they form a non-toxic agent [30] [31]. Recently, the synthesis of biocomposites has presented a novel approach for the modification of several properties of polysaccharides and various types of materials have been used to form composites with chitosan such as a zeolitic imidazolate framework (ZIF) [32], polyvinyl alcohol [33], polyvinyl chloride [34], and silicon dioxide [35] [36].

In this work, chitosan with sodium dodecyl sulfate (SDS) was synthesized to enhance the adsorption potential of heavy metal ions. In our previous paper [37], the adsorption of Cr(VI) by SDS-modified chitosan was investigated. The objective of this work was to explore the efficiency of SDS-modified chitosan bead composites and to use them for removing Cr(III) from an aqueous solution.

2. Result and Discussion

2.1. Adsorption Experiment

2.1.1. Effect of the Initial SDS Concentration

To estimate the optimal initial concentration of SDS loading on chitosan beads for Cr(III) removal, the chitosan beads were modified with SDS solutions by varying the initial SDS concentrations from 10 to 9000 mg/L. The adsorption experiments were performed under the following conditions: an initial concentration of Cr(III) of 1 mg/L, a contact time of 2 days, an adsorbent dosage of 0.05 g, a pH of 4, and a temperature of 25°C. The results are shown in **Figure 1**. With

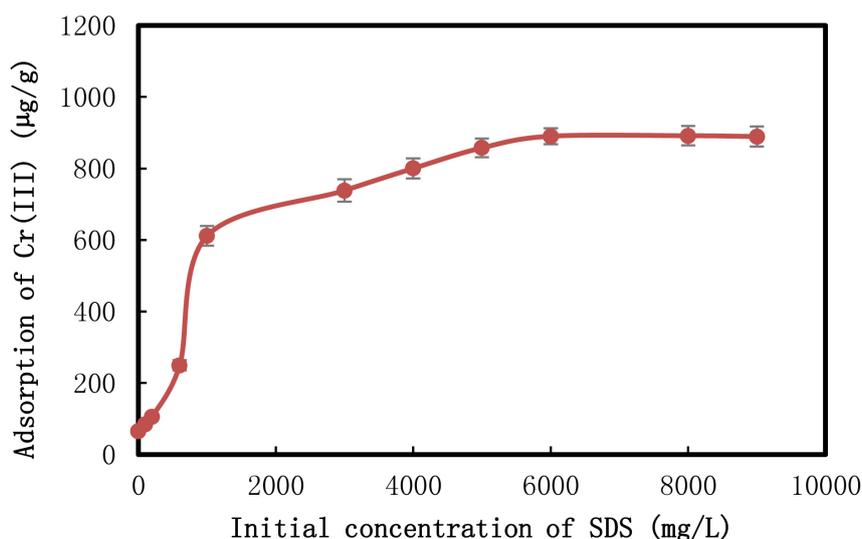


Figure 1. Effect of the initial SDS concentrations on the adsorption of Cr(III).

the increase in SDS concentration, the adsorption capacity continuously increased within 6000 mg/L but the adsorption amount was almost constant at further higher concentrations. Therefore, 6000 mg/L was considered to be the optimum initial SDS concentration for Cr(III).

2.1.2. Effect of pH

Solution pH is most important parameter affecting adsorption characteristics. In this experiment, the effect of pH on Cr(III) adsorption by SDS-chitosan was studied in the pH range of 4 - 7; the contact time was 24 h, the temperature was 25°C, the adsorbent dosage was 0.4 mg/L, and the initial Cr(III) concentration was 1 mg/L. The results are shown in **Figure 2**.

The distribution of Cr(III) in environmental waters is predominantly as Cr^{3+} at a pH of 1 - 3 whereas it exists predominantly as CrOH^{2+} at a pH of 4-6. Cr(III) precipitates as $\text{Cr}(\text{OH})_3$ at a pH of 5.5 or above [38]. For the confirmation of precipitation, the change of the initial Cr(III) concentration on the effect of the pH was measured in the pH range of 4 - 7, as seen in **Figure 3**.

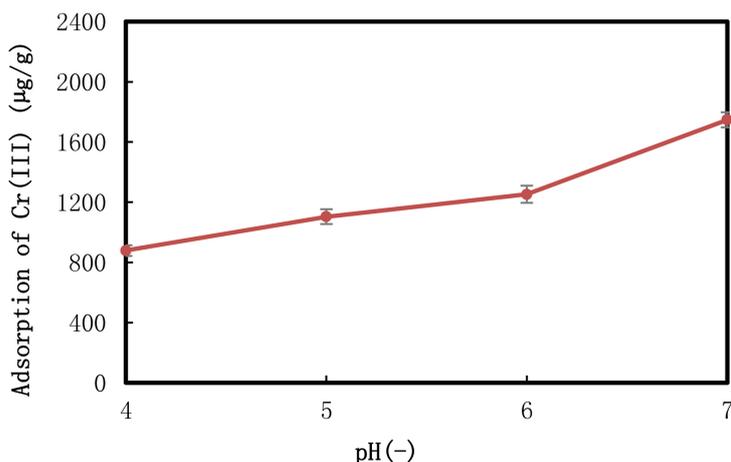


Figure 2. Effect of pH on the adsorption of Cr(III) by SDS-chitosan.

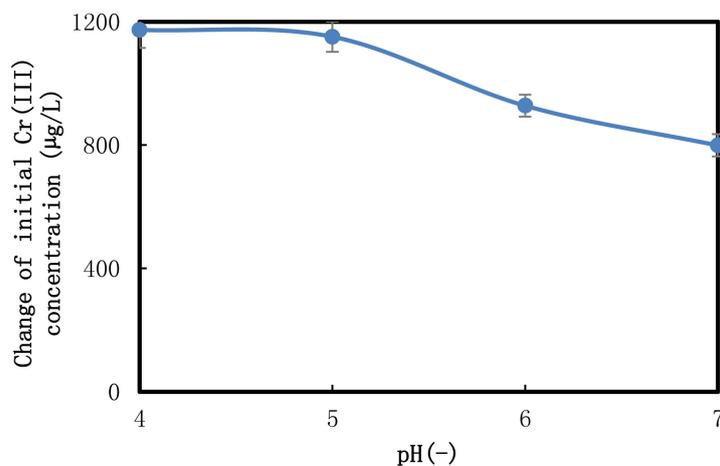


Figure 3. Change of the initial concentration of the Cr(III) solution on the effect of the pH.

As can be seen in **Figure 2**, the adsorption capacity of Cr(III) increased with the increase in the pH value from 4 to 7. The initial Cr(III) concentration in the aqueous solution decreased with the increase in the pH value from 4 to 7 (**Figure 3**). It was observed that Cr(III) precipitated as Cr(OH)₃ at a pH of 6 and 7 due to the decrease in the initial Cr(III) concentration. Therefore, a pH of 6 and 7 were not suitable for the adsorption experiments and a pH of 4 was chosen.

2.1.3. Effect of Contact Time

The influence of contact time on the adsorption of Cr(III) by SDS-chitosan was explored. The experiment was conducted under the following conditions: a pH of 4, a temperature of 25°C, an adsorbent dosage of 0.05 g, and an initial concentration of Cr(III) of 1 mg/L. The effect of contact time on the adsorption of Cr(III) using SDS-chitosan is shown in **Figure 4**. Based on the results of this experiment, the adsorption capacity of SDS-chitosan for Cr(III) increased sharply within the first 24 h, and continued until the contact time reached 48 h. Therefore, 48 h was selected as the optimized contact time.

2.1.4. Effect of the Adsorbent Dosage

The adsorbent dosage is an important factor that affects the adsorption capacity. Adsorption experiments were performed to determine the adsorbent dosage under the conditions of a pH of 4, a temperature of 25°C, a contact time of 24 h, and an initial concentration of Cr(III) of 1 mg/L. **Figure 5** shows the effect of the adsorbent dosage on Cr(III) adsorption by SDS-chitosan. The adsorption rate increased with an increase in the adsorbent dosage and reached approximately 70% at 0.8 mg/L; after that, there was no appreciable increase. Therefore, 1 mg/L was selected as the optimized adsorbent dosage.

2.1.5. Effect of Competitive Ions

In this study, adsorption experiments of Cr(III) were performed in the presence of various competitive ions with different concentrations (0, 50, 100, and 200 mg/L) of Na⁺, Ca²⁺, Ba²⁺, K⁺, Mg²⁺, and Sr²⁺. The initial concentration of Cr(III)

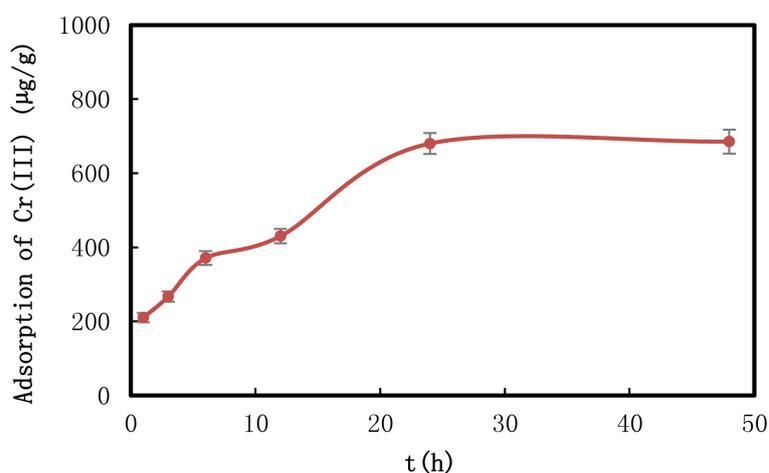


Figure 4. Effect of contact time on the adsorption of Cr(III) by SDS-chitosan.

was set as 1.0 mg/L, the pH was 4, the temperature was 25°C, the contact time was 24 h, and the adsorbent dosage was 1.0 mg/L. The effect of competitive ions on the adsorption of Cr(III) is shown in **Figure 6**. It was confirmed that the adsorption capacity of Cr(III) did not decrease at all even in the presence of other metal ions.

2.2. Characterization of Materials

2.2.1. SEM-EDS Micrographs

The SEM-EDS images of the chitosan beads and SDS-chitosan are shown in **Figure 7**. These images showed an unevenness on the surface. This was probably due to the release of water contained in the adsorbent during the drying process of chitosan. In addition to the aforementioned irregularities, SDS-chitosan showed a mesh-like pattern. This was thought to be due to the effect of SDS

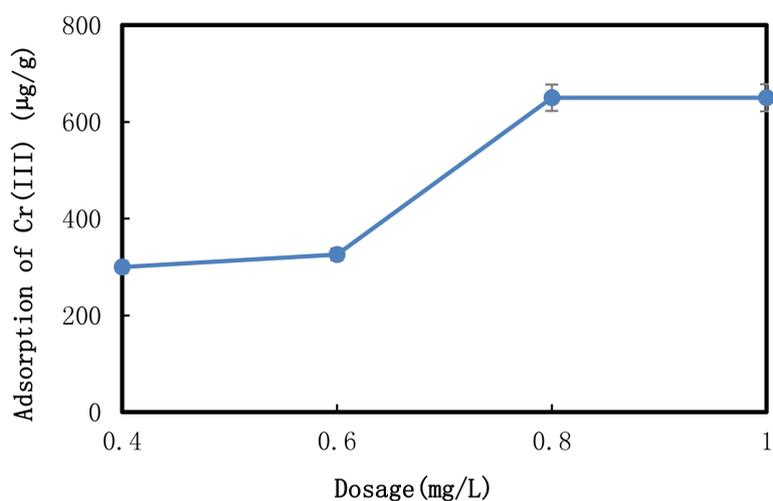


Figure 5. Effect of the adsorbent dosage on the adsorption of Cr(III) by SDS-chitosan.

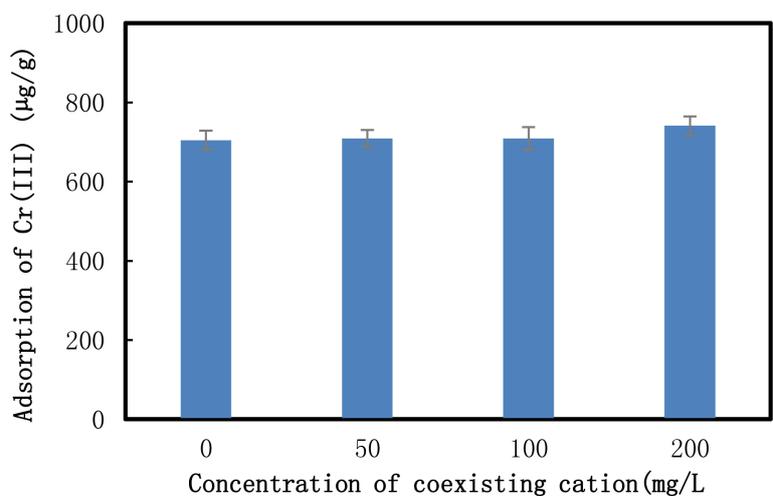


Figure 6. Effect of the coexisting cations on the adsorption of Cr(III) by SDS-chitosan.

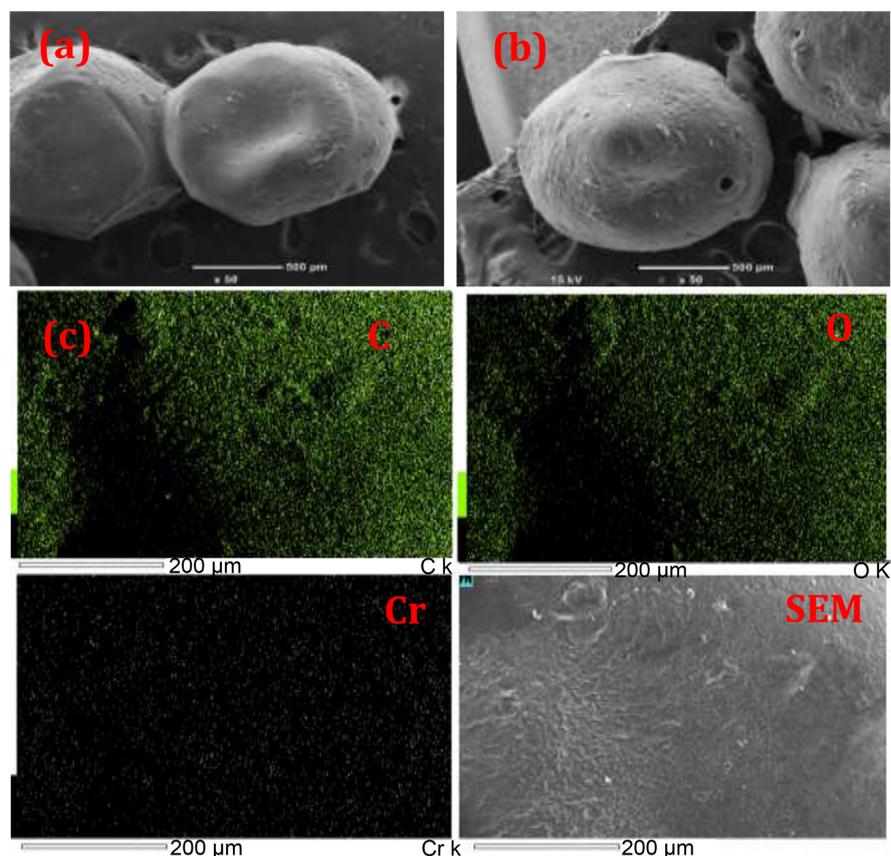


Figure 7. Scanning electron microscopy (SEM) images of chitosan beads (a) and SDS-chitosan (b), and mapping images of SDS-chitosan after the adsorption of Cr(III).

modified on the chitosan surface. In particular, the modified chitosan beads with a high SDS concentration showed a difference compared with the other beads. As the irregularities on the surface of the adsorbent were considered, the adsorption proceeded in two ways: physical and chemical adsorption. From the mapping images, it was confirmed that Cr ions were actually adsorbed onto the adsorbent surface.

2.2.2. FT-IR and XPS Spectra

The surface functional groups and the chemical compositions on the modified SDS-chitosan beads were identified by FTIR and XPS analysis, respectively. The results are fundamentally shown in our previous work [37], and more detailed features are denoted as follows. The FT-IR results are shown in **Figure 8**, where the peaks of SDS-chitosan and the chitosan beads can clearly be seen. It is apparent from this figure that the main peaks common to each adsorbent were due to the -OH group at $3400 - 3500 \text{ cm}^{-1}$ and the aliphatic methylene group at 2871 cm^{-1} . The wide peaks at $1560 - 1640 \text{ cm}^{-1}$ and 1110 cm^{-1} show the amine group and ether group, respectively. For SDS-chitosan, the peak at 1248 cm^{-1} was characteristic of the asymmetrical vibration of the C-O-S group, which confirmed that the prepared adsorbent was a composite of SDS and chitosan.

The XPS results are shown in **Figure 9**, where the chitosan beads with initial

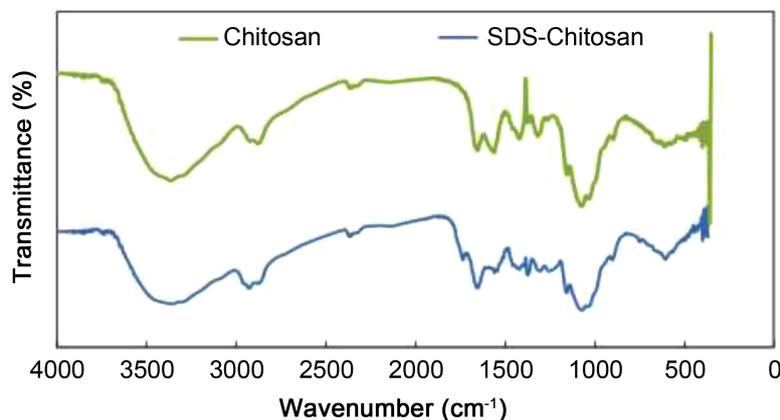


Figure 8. Fourier transform-infrared spectroscopy (FT-IR) spectra of chitosan and SDS-chitosan.

different concentrations of SDS loading were analyzed. The C1s spectra of these samples displayed peaks at 284.5, 286.5, and 288.5 eV, corresponding with C-C, C-O, and C=O bonds, respectively. The S2p spectra of SDS600 and 6000-chitosan displayed peaks at 169 eV. The S that seemed to be derived from SDS was also not detected at SDS concentrations of 0 and 100 mg/L but was detected at concentrations of 600 and 6000 mg/L.

2.3. Adsorption Isotherms

Adsorption isotherms explain the interactive process between the adsorbents and adsorbates in aqueous medium at the attained saturation point. Adsorption isotherms of Cr(III) on SDS-chitosan were identified with different initial concentrations from 0.01 to 2 mg/L under optimized conditions in terms of the pH (4), contact time (48 h), and dosage of the adsorbent (1 mg/L). Typical adsorption isotherms, the Langmuir and Freundlich models were used to evaluate the adsorption of Cr by SDS-chitosan (Figure 10).

The adsorption data obtained for Cr(III) using SDS-chitosan were analyzed by Langmuir (Figure 11) and Freundlich equations (Figure 12).

Langmuir equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{K_L q_{\max}} \quad (1)$$

Freundlich equation:

$$\lg q_e = \lg K_F + (1/n) \lg C_e \quad (2)$$

where C_e and q_e are the concentration of Cr at the equilibrium ($\text{mg}\cdot\text{L}^{-1}$) and the amount of adsorption of Cr(III) at the equilibrium ($\text{mg}\cdot\text{g}^{-1}$), respectively, q_{\max} is the maximum adsorption capacity on the surface of the chitosan bead ($\text{mg}\cdot\text{g}^{-1}$), K_L is the Langmuir constant related to the adsorption strength or intensity ($\text{L}\cdot\text{mg}^{-1}$), K_F is the Freundlich constant and $1/n$ indicates the adsorption intensity of the system [39] [40].

The Langmuir isotherm model assumes that a monolayer adsorption, which

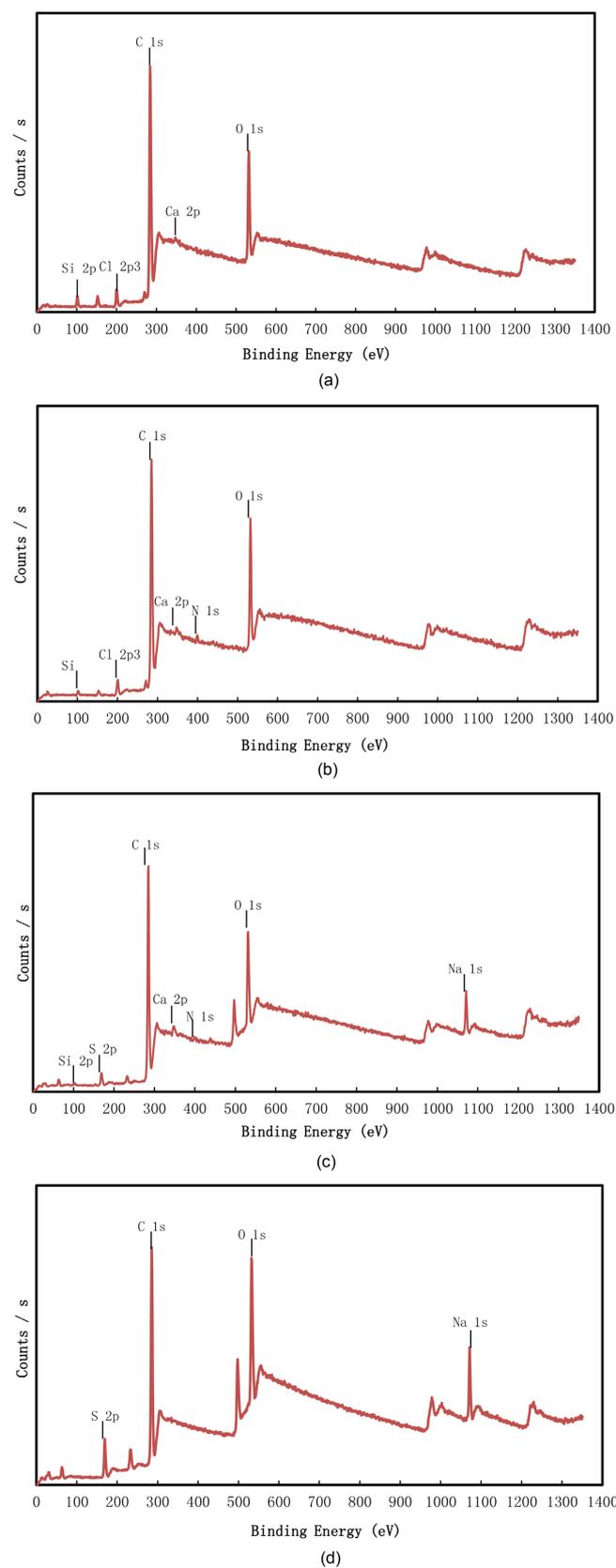


Figure 9. X-ray photoelectron spectroscopy (XPS) spectra of chitosan (a), SDS100-chitosan (b), SDS600-chitosan (c), and SDS6000-chitosan (d) beads.

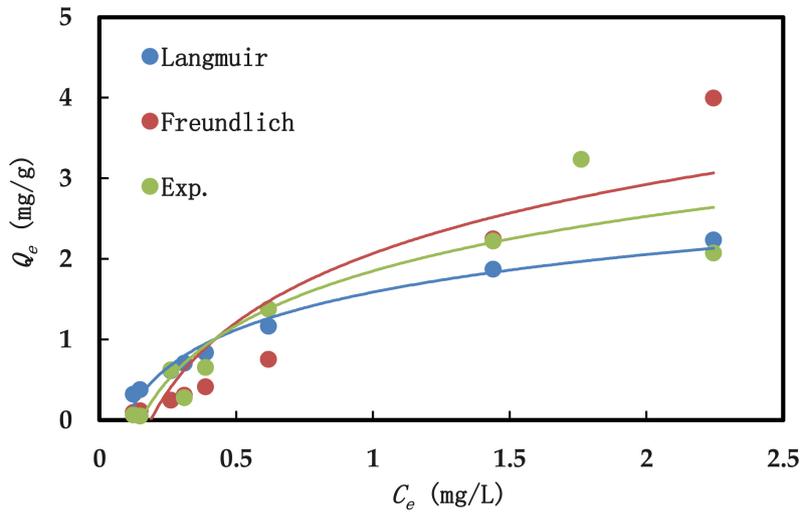


Figure 10. Adsorption isotherms of Cr(III) using SDS-chitosan.

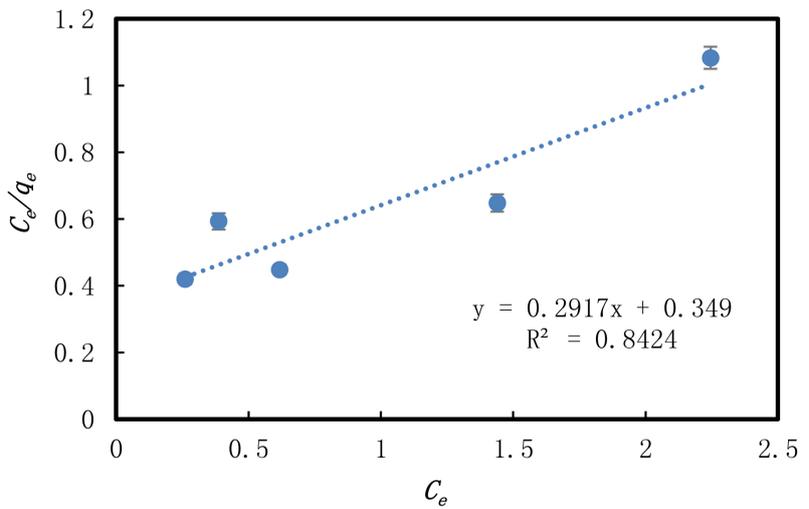


Figure 11. Langmuir isotherm of Cr(III) adsorption onto SDS-chitosan.

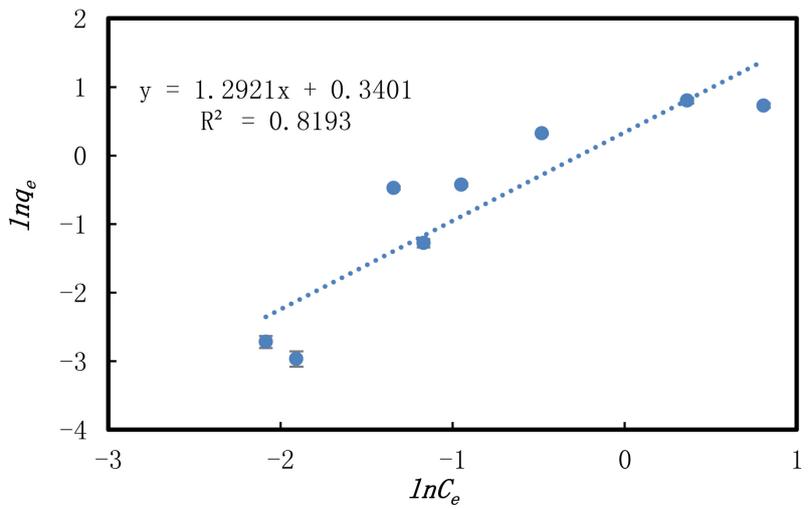


Figure 12. Freundlich isotherm of Cr(III) adsorption onto SDS-chitosan.

occurs on the surface of the adsorbent, is uniform. The slope of the linearized Langmuir isotherm can be used to interpret the type of sorption using the Hall separation factor (R_L), which is favorable ($0 < R_L < 1$), unfavorable ($R_L < 0$), linear ($R_L = 1$) or irreversible ($R_L = 0$) [41]. The Freundlich isotherm model assumes a multilayer adsorption process without considering the adsorption saturation, which occurs on the multilayer heterogeneous surface. The value of the adsorption intensity of the system ($1/n$) can be used to judge the difficulty of the adsorption process: irreversible ($1/n = 0$), favorable ($0 < 1/n < 1$), or unfavorable ($1/n > 1$) [32]. The correlation coefficient (R^2) of these isotherms for Cr(III) on SDS-chitosan is shown in Table 1 along with other relevant parameters.

As shown in Figure 11 and Figure 12, and Table 1, it was found that the R^2 values for Cr(III) were relatively large and a favorable adsorption of Cr(III) on SDS-chitosan was presented. The R^2 value in the Langmuir isotherm was larger than that in the Freundlich isotherm. The maximum adsorption capacity (q_{\max}) calculated from the Langmuir model was 3.42 mg/g, which suggested that the adsorption of Cr(III) on SDS-chitosan mainly occurred by a monolayer reaction.

2.4. Kinetic Studies

The rate-controlling steps of the adsorption system are essential to examine the mechanism of Cr(III). Kinetic studies were performed to explain the adsorption mechanism of Cr(III) ions onto the SDS-chitosan beads. The effects of contact time on the kinetics of Cr(III) adsorption by SDS-chitosan adsorbent are displayed in Figure 13. As can be seen in Figure 13, the removal of Cr(III) from

Table 1. Isotherm parameters for Cr(III) adsorption onto SDS-chitosan.

Metal	$T(K)$	Langmuir Isotherm			Freundlich Isotherm		
		Q_{\max} (mg/g)	R_L	R^2	K_F (mg/g)	$1/n$	R^2
Cr (III)	298	3.42	1.15×10^{-3}	0.84	1.41	1.21	0.82

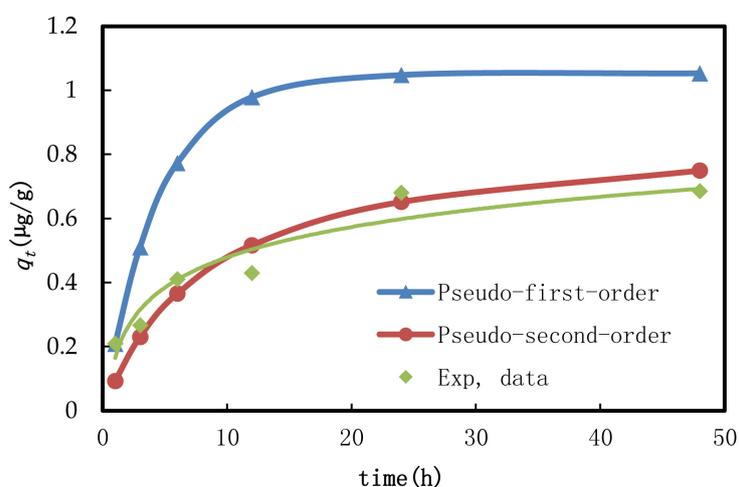


Figure 13. Pseudo-first-order and pseudo-second-order Cr(III) adsorption on SDS-chitosan.

SDS-chitosan increased sharply in the initial 6 h, which indicated that the uptake of Cr(III) was chiefly caused by chemical sorption. It continued at a slower rate and finally reached equilibrium at 48 h.

To investigate the mechanism of adsorption of Cr(III) on SDS-chitosan, fitting was determined according to the pseudo-first-order (Figure 14), pseudo-second-order (Figure 15) and intraparticle diffusion kinetic models (Figure 16).

The equations of these models are given by:

Pseudo-first-order model:

$$\ln(q_t) = \ln(q_e) - k_1 t \quad (3)$$

Pseudo-second-order model:

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

Intraparticle diffusion model:

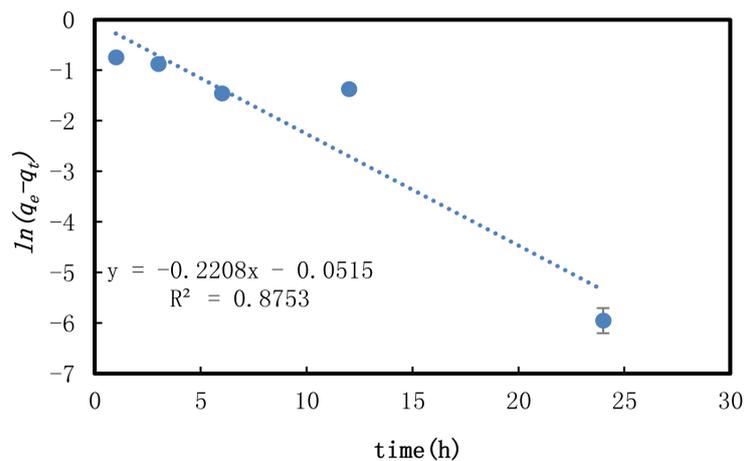


Figure 14. Pseudo-first-order linear kinetic model of Cr(III) adsorption by SDS-chitosan.

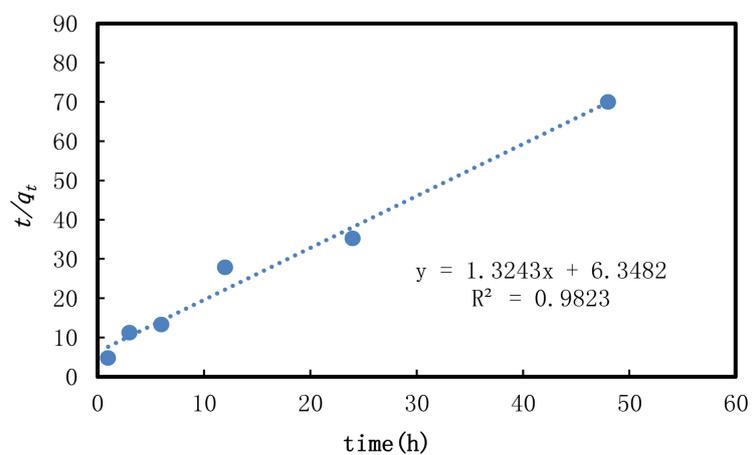


Figure 15. Pseudo-second-order linear kinetic model of Cr(III) adsorption by SDS-chitosan.

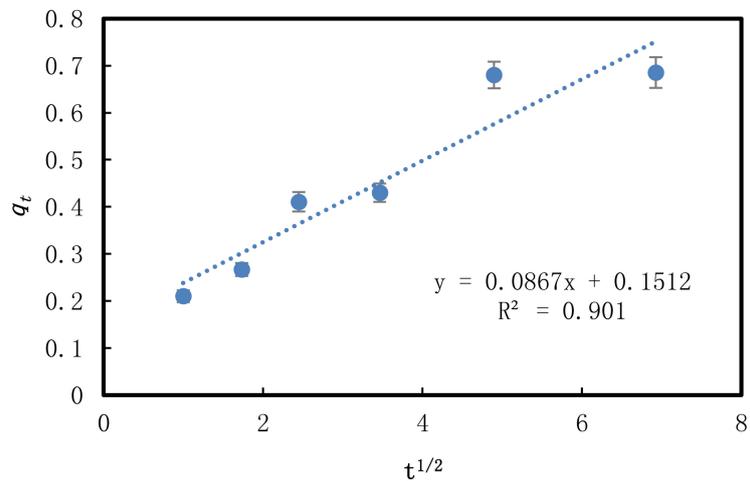


Figure 16. Intraparticle diffusion kinetic model of Cr(III) adsorption by SDS-chitosan.

$$q_t = K_{id}t^{1/2} \quad (5)$$

where q_e and q_t are the adsorption capacities of Cr using the SDS-chitosan beads at the equilibrium and time, t , respectively ($\text{mg}\cdot\text{g}^{-1}$), k_1 is the rate constant of the pseudo-first-order adsorption (h^{-1}), k_2 is the rate constant of the pseudo-second-order adsorption ($\text{g}\cdot\text{mg}^{-1}\cdot\text{h}^{-1}$) and K_{id} is the rate constant of intraparticle diffusion ($\text{mg}\cdot\text{g}^{-1}\cdot\text{h}^{-1/2}$) [42] [43] [44].

The sorption kinetic parameters including k_1, k_2, K_{id}, q_e and the correlation coefficients R^2 are listed in **Table 2**. As can be seen, the correlation coefficient R^2 for the pseudo-second-order model was higher than the pseudo-first-order and intraparticle diffusion models. These results suggest that the sorption kinetics of the Cr(III) ion on SDS-chitosan could be described by the pseudo-second-order model, that the chemical adsorption could be the rate-limiting step of the process of the adsorption system. Based on above, assuming adsorbent particle to be sphere of radius “a” and the diffusion follows Fick’s law that was applied to confirm it. In the law, the relationship between adsorption capacity and time was given by the following Equations [45].

$$\frac{q_t}{q_e} = 6 \left(\frac{D_t}{a^2} \right)^{1/2} \left\{ \pi^{-1/2} + 2 \sum_{n=1}^{\infty} \text{ierfc} \frac{na}{\sqrt{Dt}} \right\} - 3 \frac{Dt}{a^2} \quad (6)$$

After D is replaced with D_1 , at a short time, Equation (6) becomes as:

$$\frac{q_t}{q_e} = 6 \left(\frac{D_1}{\pi a^2} \right)^{1/2} t^{1/2} \quad (7)$$

The film diffusion coefficient D_1 is calculated from the slope of the plot of q_t/q_e versus $t^{1/2}$. For moderate and large times, the diffusion equation given by

$$\frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(\frac{-Dn^2 \pi^2 t}{a^2} \right) \quad (8)$$

If D is replaced with D_2 , at the large time the Equation (8) becomes as:

Table 2. Kinetic parameters of Cr(III) adsorption onto SDS-chitosan.

Adsorbent	q_e (mg/g)	Pseudo-first-order model			Pseudo-second-order model		Intraparticle Diffusion		
		q_e (mg/g)	k_1 (h ⁻¹)	R^2	q_e (mg/g)	k_2 (g·mg ⁻¹ ·h ⁻¹)	R^2	K_{id}	R^2
SDS-chitosan	0.69	1.05	0.22	0.88	0.88	0.13	0.98	0.09	0.90

$$\ln\left(1 - \frac{q_t}{q_e}\right) = \ln\frac{6}{\pi^2} - \left(\frac{D_2\pi^2}{a^2}t\right) \quad (9)$$

The pore diffusion coefficient D_2 is obtained from the slope of the plot of $\ln(1 - q_t/q_e)$ versus t . The values of D_1 and D_2 are presented in **Table 3**.

It is also known that if the adsorption is controlled by the film diffusion, the values of the film diffusion coefficient may be in the range of 10^{-6} - 10^{-8} cm²/s. While if the adsorption mechanism is controlled by the pore diffusion mechanism, the value of the pore diffusion coefficient belongs to the range of 10^{-11} - 10^{-13} cm²/s [46]. As can be seen in **Table 3**, The D_1 and D_2 values in the model based on the Fick's law was larger than that above mentioned ranges. It is confirmed that the sorption kinetics of the Cr(III) ion on SDS-chitosan could be described by the pseudo-second-order model.

2.5. Thermodynamic Study

To investigate the effect of temperature on Cr(III) adsorption by SDS-chitosan, adsorption experiments were conducted from 298 to 318 K. The results are shown in **Figure 17**. In these temperature ranges, the adsorption amount of Cr(III) on SDS-chitosan increased with the increase in temperature.

In addition, based on the experimental results, the thermodynamic parameters of the adsorption, *i.e.* standard Gibb's free energy change (ΔG^0), a change in standard enthalpy (ΔH^0) and standard entropy (ΔS^0), were calculated from the Van 't Hoff equation [47] [48] [49].

$$\Delta G^0 = -RT \ln K_c \quad (10)$$

$$\ln K_c = \frac{\Delta H^0}{-RT} + \frac{\Delta S^0}{R} \quad (11)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (12)$$

where R is the universal gas constant (8.314 J/mol⁻¹·K⁻¹) and T is the temperature (K). The slope and intercept of the plot of $\ln K_c$ versus $1/T$ were used to determine the ΔH^0 and ΔS^0 .

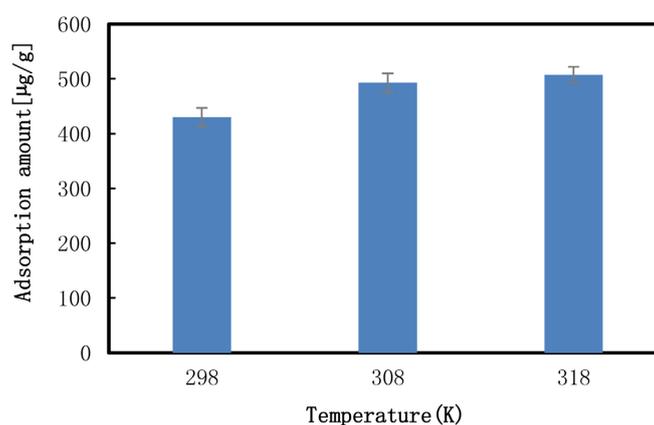
The thermodynamic parameters are shown in **Table 4**. Values of $\Delta G > 0$ were obtained in the temperature range of 298 - 318 K. The values of ΔG at the different temperatures indicated the feasibility of the process and the values decreased with an increase in temperature. This suggested that the adsorption process was more spontaneous at higher temperatures. Positive values of ΔH and ΔS also suggested that the sorption process was endothermic and determined the

Table 3. The film and pore diffusion coefficients of the adsorption.

C_0 (mg/L)	$D_1 \cdot 10^{-8}$ (cm ² /s)	$D_2 \cdot 10^{-12}$ (cm ² /s)
1.00	7.04	1.51

Table 4. Thermodynamic parameters for the adsorption of Cr(III) on SDS-chitosan.

T (K)	ΔH (kJ/mol)	ΔS (J/mol)	ΔG (kJ/mol)
298			0.855
308	12.0	37.4	0.481
318			0.107

**Figure 17.** Effect of temperature on the adsorption of Cr(III) onto SDS-chitosan.

disorderliness of the sorption at the solid-liquid interface. It was then suggested that the adsorption of Cr(III) on SDS-chitosan could be mainly dominated by chemisorption.

2.6. Desorption Study

Repeated use of adsorbent and recovery of the adsorbed metal ions are important parameters indicating economic efficiency. In this study, regeneration experiments were carried out using the SDS-chitosan beads after adsorption of Cr(III). In desorption experiment, the spent adsorbent after adsorption was treated with 50 ml of 0.1 mol/L NaOH solution and ultrapure water as desorption agent, and then filtered. Cr(III) content in the filtrate was determined by ICP-MS [37].

The results of this experiment are shown in **Figure 18**. As can be seen in **Figure 18**, the desorption efficiency of Cr(III) was found to be 57% using 0.1 mol/L NaOH. The desorption of NaOH was larger than ultrapure water. This suggested that NaOH could be a desorption agent for Cr(III).

2.7. Comparison with Other Adsorbents

The comparison of the maximum adsorption capacity of Cr(III) by SDS-chitosan

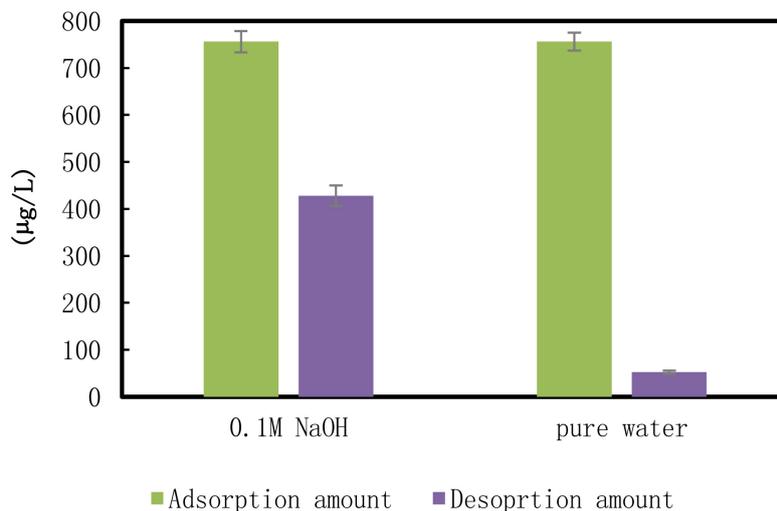


Figure 18. Desorption efficiency of Cr(III) using NaOH and pure water.

in the present study with those of other adsorbents in the literature is presented in **Table 5**. As can be seen in **Table 5**, the adsorption capacity of SDS-chitosan for Cr(III) in this work was not necessarily high compared with other adsorbents. However, it could be regarded as a potential adsorbent for treating Cr(III) from wastewater for practical use as, the synthesis method of the adsorbent is relatively simple and that it can be also available for the removal of Cr(VI) [37].

3. Materials and Methods

Chemical reagents, namely, chitosan and sodium dodecyl sulfate (SDS) were purchased from the Tokyo Chemical Industry Co., Inc. (Tokyo, Japan). CH_3COOH , NaOH, NaSO_4 , HNO_3 , C_7H_8 , and $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ were purchased from the Kanto Chemical Co., Inc. (Tokyo, Japan). All used reagents were of an analytical grade. Ultrapure water ($>18.2 \text{ M}\Omega$), which was treated by an ultrapure water system (Suite a Dublin, California, USA, Advantec aquarius: RFU 424TA), was employed throughout the work. To prepare the Cr standard solution for the calibration curve, a standard solution (Kanto Chemical Co., Inc.,) of $1000 \text{ mg}\cdot\text{dm}^{-3}$ was used.

3.1. Synthesis of the Adsorbent

First, 1.5 g of chitosan was dissolved in an acetic acid solution (2.0%) and stirred for 1 day. The obtained chitosan solution was dropped into the 200 mL of a 0.20 mol/L sodium hydroxide solution to prepare a chitosan beads. After stirring for 1 day, it was washed with ultrapure water until the pH reached 7. The chitosan beads were then placed in 100 mL SDS solution (including the fixed concentration of SDS) and allowed to stand for several days in room temperature. After several days, the chitosan beads were washed with the required quantity of ultrapure water for the resolution of eliminating free SDS, dried at 60°C for 24 h and then stored in a vacuum desiccator for further studies.

Table 5. Comparison of adsorption capacity for Cr(III) by different adsorbents.

Adsorbent	Adsorption Capacity (mg·g ⁻¹)	References
Vesicular basalt	0.98	[50]
Chitosan	1.67	[51]
Attapulгите	11.0	[51]
Chitosan/attapulгите	27.0	[51]
Crystalline hydrous titanium(IV) oxide	14.0	[52]
Natural sepiolite	0.53	[53]
Borax sludge	4.00	[54]
SDS-chitosan-	3.42	This study-

3.2. Characterization of the Adsorbent

The surface morphology of the chitosan beads was observed by scanning electron microscopy (SEM) (JSM-6000, JEOL, Japan) and the elemental analyze of the chitosan samples before and after the adsorption of Cr(III) was performed by EDS (JED-2300, JEOL, Japan). Fourier transform-infrared spectroscopy (FT-IR-4200, Jasco, Japan) was used to identify the functional groups. The KBr was ground and mixed with the dried sample, and the mixture was pressed into thin plates for infrared testing. The surface chemistry properties of the SDS-modified chitosan beads were also identified by X-ray photoelectron spectroscopy (XPS; K-Alpha, Thermo Scientific Center, Waltham, MA, USA).

3.3. Adsorption Experiments

The beads were put into contact with 50 mL of an aqueous solution containing Cr(III) ion with a known initial concentration. The pH of each solution was adjusted using 0.1 mol/L⁻¹ NaOH and 0.1 mol/L⁻¹ HNO₃. The flask was then placed in an automatic shaker. The adsorption experiments were conducted in the pH range of 1 - 7, with a contact time of 1 - 72 h, an SDS initial concentration of 10 - 9000 mg·L⁻¹, an adsorbent dosage of 0.01 - 0.06 g·L⁻³, a temperature of 288 - 318 K, and an initial Cr(III) concentration of 0.1 - 3.0 mg·L⁻¹. The concentrations of Cr in the filtrate were measured by ICP-MS (Thermo Scientific Center: X-series II). The adsorption capacities of the chitosan beads modified with SDS were calculated by the following equation [9]:

$$q_e = (C_i - C_e) \times V / m \quad (13)$$

where q_e represents the adsorption capacity at the equilibrium (mg·g⁻¹), C_i and C_e are the initial and equilibrium concentrations of Cr in the batch system, respectively (mg·L⁻¹), V is the volume of the solution (L), and m is the weight of the adsorbents (g).

4. Conclusions

The efficiency of the SDS-chitosan beads synthesized as an adsorbent for Cr(III)

was investigated by batch techniques. The following conclusions can be drawn considering the results of this work:

1) The optimal conditions of the adsorption of Cr(III) using the SDS-modified chitosan beads were determined. The optimal initial SDS concentration was 6000 mg/L, the optimal contact time was 48 h, the optimal dosage was 1 mg/L, and 4 was considered to be the optimum pH.

2) The adsorption isotherm of Cr(III) by SDS-chitosan was more suitably described by the Langmuir model and the correlation coefficient was 0.84. It suggests that the monolayer chemical adsorption of Cr(III) on SDS-chitosan was more dominant. The maximum adsorption capacity was estimated to be 3.42 mg·g⁻¹ for Cr(III) under the optimum conditions. The best fit was obtained with a pseudo-second-order model when investigating the adsorption kinetics of Cr(III) adsorption on SDS-chitosan and the correlation coefficient was 0.98. The thermodynamic studies indicated that the adsorption process was favorable under the higher temperature condition.

From this work, the SDS-chitosan beads synthesized in this work can be effectively used for removing Cr(III) ions.

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Conflicts of Interest

The authors declare no conflicts of interest.

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