

## An adsorption study of Al(III) ions onto chitosan

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### Abstract

The adsorption of Al(III) from aqueous solutions onto chitosan was studied in a batch system. The isotherms and the kinetics of adsorption with respect to the initial Al(III) concentration and temperature were investigated. Langmuir and Freundlich adsorption models were applied to describe the experimental isotherms. Equilibrium data fitted very well to the Langmuir model in the entire concentration range (5–40 mg/L). The negative values of free energy ( $\Delta G^\circ$ ) and enthalpy ( $\Delta H^\circ$ ) for the adsorption of Al(III) onto chitosan indicated that the adsorption process is a spontaneous and exothermic one. Two simplified kinetic models, based on pseudo first-order and pseudo second-order equations, were tested to describe the adsorption mechanism. The pseudo second-order kinetic model resulted in an activation energy of 56.4 kJ/mol. It is suggested that the overall rate of Al(III) ion adsorption is likely to be controlled by the chemical process. The values of the enthalpy ( $\Delta H^\#$ ) and entropy ( $\Delta S^\#$ ) of activation were 53.7 kJ/mol and  $-164.4$  J/mol K, respectively. The free energy of activation ( $\Delta G^\#$ ) at 30 °C was 103.5 kJ/mol.

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### 1. Introduction

As part of a comprehensive study of dyeing silk and cotton with natural dyes [1–3] we have investigated the aqueous stream from the dyeing process.

Alum, potassium aluminium sulphate, is widely used as a mordant-fixative for natural fibres with natural dyes [4]. It is released into ground or river without treatment especially from domestic dyeing. Aluminium exists only as a trivalent cation and is too reactive to be found in its elemental state in nature [5]. In aqueous solutions aluminum solubility is highly pH dependent [6]. Under acidic or alkaline conditions, or in the presence of appropriate ligands, soluble species are formed, but in the range of physiological pH values (between 6 and 8) Al(III) is generally insoluble. At low pH values (pH < 5), the main species is  $\text{Al}[(\text{H}_2\text{O})_6]^{3+}$ . However, as the pH increases,  $\text{Al}(\text{OH})_2^+$  and  $\text{Al}(\text{OH})_3$  are gradually formed and at neutral pH amorphous  $\text{Al}(\text{OH})_3$  precipitates; at basic pH this precipitate dissolves to form  $\text{Al}(\text{OH})_4^-$ .

Since aluminium is a potential concern with respect to Alzheimer's disease in humans [7–9], the removal of aluminium

from process or waste effluents becomes environmentally important, and in this context the use of activated carbon has been investigated [10].

There are various other natural adsorbents such as chitin, chitosan, natural zeolites, perlite, and agricultural wastes for metal ion removal from contaminated water. Chitosan has received considerable attention for metal ion removal due to its excellent metal binding capacities [11] and its ready availability. It is a partially deacetylated polymer of acetylglucosamine (2-acetamido-2-deoxy-D-glucose-(N-acetylglucan)) which is found in the shells of crabs and shrimps. The chemical structure of chitosan is shown in Fig. 1. Various studies of metal ion adsorption by chitosan have been undertaken in recent years, such as the removal of Cu(II) ions from aqueous solution onto chitosan and cross-linked chitosan beads [12]. The equilibrium sorption studies of Cu(II) ions onto chitosan were found to follow the Langmuir model [13]. In addition, chitosan can be used to achieve adsorption of chromium [14], cadmium [15], iron [16], and nickel [17] ions from aqueous solution.

The aim of the present work was to determine the thermodynamic values related to the interaction of Al(III) ions with chitosan in aqueous solution and the results are reported in this paper. The adsorption rates were determined quantitatively with respect to initial Al(III) concentration and temperature. These

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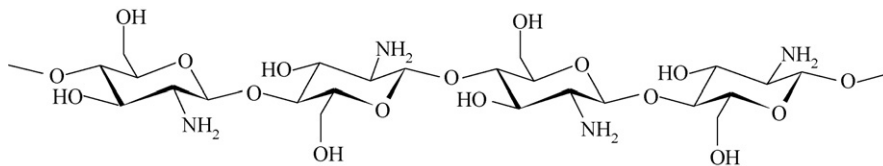


Fig. 1. The chemical structure of chitosan.

results can be useful for understanding the mechanism of interaction and also for further applications in Al(III) removal from wastewater from dyeing processes.

## 2. Materials and methods

### 2.1. Materials

The chitosan (medium molecular weight, viscosity 200,000 cps, CAS 9012-76-4, FW of repeating unit, 161) used in the present investigation was obtained from the Aldrich Chemical Company. The BET surface area of chitosan (1.49 m<sup>2</sup>/g) was measured from N<sub>2</sub> adsorption isotherms with a Micrometrics ASAP 2010. Stock solution (1000 mg/L) of Al(III) ions were prepared by using alum, KAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O (Merck) in deionized water.

### 2.2. Instruments

An atomic absorption spectrophotometer (AAS) (Varian SpectrAA 250 Plus) was used for quantitative determination of the concentration of Al(III) ions. The AAS was equipped with an Al hollow cathode lamp at a wavelength of 396.2 nm and nitrous oxide-acetylene flame. A calibration curve was obtained from a stock solution (1000 mg/L) of KAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O in 0.1 M HNO<sub>3</sub>.

A pH meter (Laboratory pH Meter CG 842, SCHOTT) was used to measure the pH values of the Al(III) solutions.

A thermostatted shaker bath (Type SBD-50, HetoHolten A/S, Denmark), operated at 150 strokes/min, was used to study the adsorption of Al(III) ions onto chitosan.

### 2.3. Batch adsorption experiments

#### 2.3.1. Batch pH studies

Batch pH studies were conducted by shaking 50 mL of an aqueous Al(III) solution with 0.01 g of chitosan for 24 h by using a thermostatted shaker bath operated at 30 °C, over a range of initial pH values from 3.0 to 6.5. The pH of the aqueous solutions was adjusted by using 0.1 M NaOH or 0.1 M HNO<sub>3</sub>. The solution was filtered after pH adjustment. After equilibrium, the aqueous samples were filtered through 0.45 μm filters (RC-membrane, Minisart) and the concentrations of Al(III) in the filtrate were analyzed using an AAS. After adsorption, the suspensions were acidified with HNO<sub>3</sub> to decrease pH below 3 in order to avoid Al precipitation before Al measurement.

The pH values were measured before and after equilibrium. Each experiment was carried out three times under identical conditions. The amount of adsorption at equilibrium  $q_e$  (mg/g

chitosan) was obtained as follows:

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

where  $C_0$  (mg/L) and  $C_e$  (mg/L) are the concentrations in the solution at time  $t=0$  and at equilibrium time  $t$ , respectively,  $V$  is the volume of the solution (L), and  $W$  is the weight of chitosan (g) used.

#### 2.3.2. Batch kinetic studies

The batch kinetics experiments were performed in a similar manner to the batch pH studies. The effect of initial concentration was studied in the range of 5–20 mg/L at pH<sub>a</sub> 4.0 and 30 °C. The effect of temperature was investigated at an initial concentration of 20 mg/L (pH<sub>a</sub> 4.0). At pre-set time intervals the amount of adsorption at time  $t$ ,  $q_t$  (mg/g chitosan) was obtained as follows:

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

where  $C_0$  (mg/L) and  $C_t$  (mg/L) are the concentration in the solution at time  $t=0$  and at time  $t$ , respectively,  $F$  is the volume of the solution (L), and  $W$  is the weight of chitosan (g) used.

#### 2.3.3. Batch isotherm studies

The batch adsorption isotherm studies were conducted in a similar manner to the batch pH studies by varying the Al(III) concentration 5–40 mg/L (pH<sub>a</sub> 4.0) at 30, 45 and 60 °C. The initial and equilibrium Al(III) concentrations were analyzed by using an AAS. The amount adsorbed at equilibrium ( $q_e$ ) was calculated by using Eq. (1).

## 3. Results and discussion

### 3.1. Effect of pH

The pH of a solution strongly affects the adsorption capacity of the chitosan [16]. It was noted that the pH values of the equilibrated solution of Al(III) with chitosan were considerably different from the pH values before chitosan addition. The Al(III) ion is a Lewis acid (electron pair acceptor; electrophile) [5], and the pH values of waste from the dyeing process which contained aluminium varied from 3 to 6 which depending on the amount of alum used. The results of the pH measurements are summarized in Table 1. The adjusted pH of the aqueous Al(III) solution is pH<sub>a</sub>. The measured pH after equilibration with chitosan is pH<sub>e</sub>, and the equilibrium Al(III) concentration is  $C_e$ . The results (Fig. 2) showed that the adsorption of Al(III) increased with increasing pH<sub>a</sub> of the solution from 3.0 to 4.0 and decreased

Table 1

pH values of Al(III) solutions (V, 50 mL; W, 0.01 g; temperature, 30 °C; contact time 24 h); pH<sub>a</sub> was adjusted by using 0.1 M NaOH or 0.1 M HNO<sub>3</sub> and pH<sub>e</sub> is the pH value of the aqueous solution after equilibration at concentration C<sub>e</sub>

C <sub>0</sub> (mg/L)	pH <sub>a</sub>	C <sub>e</sub> (mg/L)	pH <sub>e</sub>
21.03	3.09	19.89	4.24
21.38	3.43	14.94	4.30
21.19	4.00	8.80	4.36
21.22	4.41	5.16	4.44
21.90	4.83	0.00	5.79
21.80	5.50	0.00	5.98
21.90	6.52	0.00	6.58

after pH 4.0. At low pH, more protons will be available to protonate the amine groups in chitosan [16], thus reducing the number of binding sites for the adsorption of Al(III). On the other hand at pH values higher than 4.0, aluminium hydroxide precipitation took place thus decreasing the adsorption with increasing pH<sub>a</sub>. The initial pH of 4.0 was used throughout this study.

### 3.2. Kinetics of adsorption

#### 3.2.1. Effect of initial Al(III) concentration

Fig. 3 shows a plot of the amount of Al(III) adsorbed per gram of chitosan ( $q_t$ ) (mg/g chitosan) at various times versus contact time ( $t$ ) for different initial Al(III) concentrations of 5, 10, and 20 mg/L at pH<sub>a</sub> 4.0 and 30 °C. It was found that the adsorption capacity varied with the initial concentration of Al(III). An increase in the initial concentration led to an increase in the amount of Al(III) adsorbed onto chitosan. This may be a result of an increase in the driving force of the concentration gradient with the increase in the initial concentration [18]. This indicated that the initial concentration plays an important role in the adsorption capacity of Al(III) on chitosan. In all subsequent experiments an initial Al(III) concentration of 20 mg/L was used.

#### 3.2.2. Effect of temperature

The effect of temperature on adsorption of Al(III) onto chitosan at an initial Al(III) concentration of 20 mg/L at pH<sub>a</sub> 4.0 is shown in Fig. 4. Before equilibrium was reached, an increase

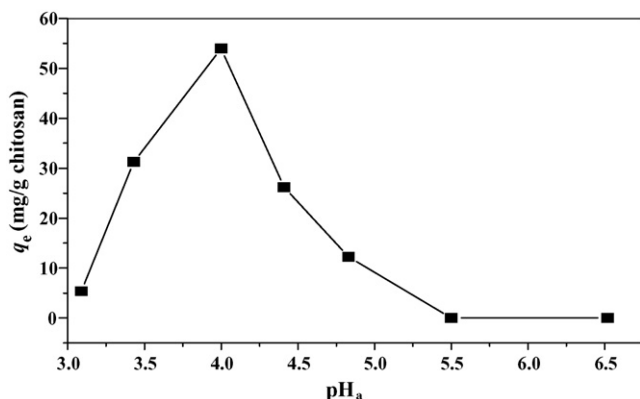


Fig. 2. Effect of initial pH (C<sub>0</sub>, 21 mg/L; W, 0.01 g; V, 50 mL; temperature, 30 °C; contact time 24 h) for Al(III) adsorption on chitosan.

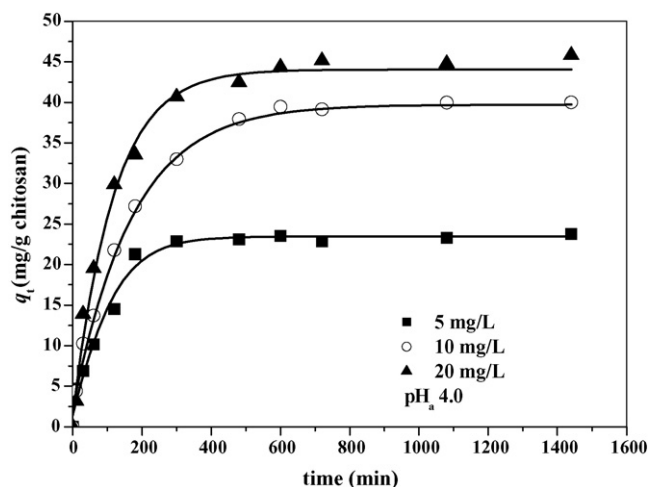


Fig. 3. Adsorption kinetics for Al(III) onto chitosan at different initial Al(III) concentrations (W, 0.01 g; V, 50 mL; temperature 30 °C; pH<sub>a</sub> 4.0).

in the temperature led to an increase in the Al(III) adsorption rate, which indicated a kinetically controlled process. After the equilibrium was attained, the adsorption of Al(III) decreased with increased temperatures consistent with the adsorption being controlled by an exothermic process.

### 3.3. Rate constant studies

In order to investigate the controlling mechanism of the adsorption processes, pseudo first-order and pseudo second-order kinetic analyses were undertaken.

The pseudo first-order equation (Eq. (3)) has been used extensively to describe the adsorption kinetics [2,14,18,19]:

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

where  $k_1$  is the rate constant of pseudo first-order adsorption ( $\text{min}^{-1}$ ),  $q_e$  and  $q_t$  are the amount of Al(III) adsorbed per gram of chitosan (mg/g chitosan) at equilibrium and time  $t$ , respectively. A straight line for the plot of  $\ln(q_e - q_t)$  versus  $t$  would

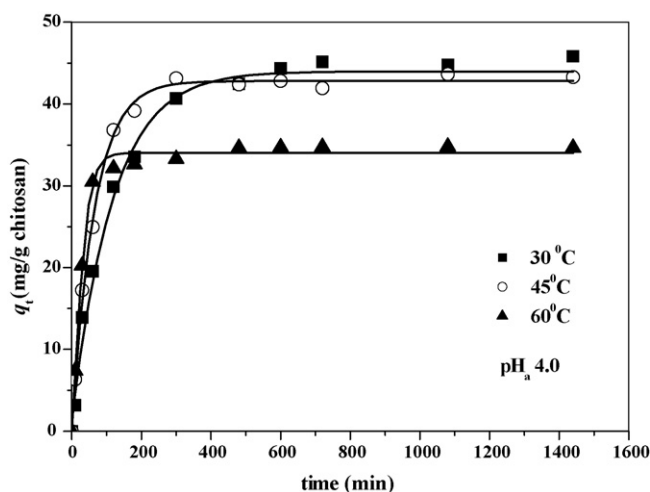


Fig. 4. Adsorption kinetics for Al(III) onto chitosan at different temperatures (C<sub>0</sub>, 20 mg/L; V, 50 mL; M, 0.01 g; pH<sub>a</sub> 4.0).

Table 2  
Comparison of the pseudo first- and second-order adsorption rate constants and the calculated and experimental  $q_e$  values for different initial Al(III) concentrations and temperatures

Parameters	$q_{e,\text{exp}}$ (mg/g chitosan)	Pseudo first-order model			Pseudo second-order model			
		$k_1$ ( $\text{min}^{-1}$ )	$q_{e,\text{cal}}$ (mg/g chitosan)	$R^2$	$k_2$ (g chitosan/mg min)	$q_{e,\text{cal}}$ (mg/g chitosan)	$h_i$ (mg/g chitosan min)	$R^2$
Initial Al(III) concentration; $C_0$ (mg/L): temperature 30 °C; V, 50 mL; pH <sub>a</sub> 4.0; chitosan 0.01 g								
5	23.8	$7.96 \times 10^{-3}$	18.5	0.9524	$7.26 \times 10^{-4}$	24.8	0.45	0.9988
10	40.0	$5.89 \times 10^{-3}$	37.2	0.9986	$2.20 \times 10^{-4}$	43.6	0.44	0.9985
20	45.8	$5.05 \times 10^{-3}$	36.1	0.9776	$2.27 \times 10^{-4}$	49.0	0.58	0.9988
Temperature (°C): initial Al(III) concentration $C_0$ , 20.49 mg/L; V, 50 mL; pH <sub>a</sub> 4.0; chitosan 0.01 g								
30	45.8	$5.05 \times 10^{-3}$	36.1	0.9776	$2.40 \times 10^{-4}$	49.0	0.58	0.9987
45	43.3	$9.85 \times 10^{-3}$	25.4	0.8338	$6.12 \times 10^{-4}$	44.8	1.23	0.9995
60	34.7	$1.44 \times 10^{-2}$	22.3	0.9479	$1.68 \times 10^{-3}$	35.3	2.09	0.9998

then suggest the applicability of this kinetic model to fit the experimental data. The first-order rate constant  $k_1$  and equilibrium adsorption density ( $q_e$ ) can be calculated from the slope and intercept of this line.

The pseudo second-order kinetic model for a sorption process [20] is expressed as:

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

where  $k_2$  (g chitosan/mg min) is the rate constant for a pseudo second-order adsorption. And

$$h_i = k_2 q_e^2 \quad (5)$$

where  $h_i$  is the initial Al(III) adsorption rate (mg/g chitosan min). If pseudo second-order kinetics are applicable, the plot of  $t/q_t$  versus  $t$  would show a linear relationship. The slope and intercept can then be used to calculate the pseudo second-order rate constant  $k_2$  and  $q_e$ .

Table 2 lists the results of rate constant studies for different initial concentrations and temperatures calculated from the pseudo first-order and pseudo second-order models. The correlation coefficient  $R^2$  for the pseudo second-order model had the highest value (>0.99) and its calculated equilibrium adsorption capacities  $q_{e,\text{cal}}$  fit well with the experimental data, suggesting the Al(III) adsorption process is mediated predominantly via the pseudo second-order adsorption mechanism.

The pseudo second-order kinetic model is based on the assumption that the rate-limiting step may be chemisorption involving valency forces through sharing or exchange of electrons between the  $-\text{NH}_2$  groups in chitosan and Al(III) [14,16].

### 3.4. Activation parameters

The values of the rate constant  $k_2$  at different temperatures listed in Table 2 were applied to estimate the activation energy of the adsorption of Al(III) onto chitosan by the Arrhenius equation [21] as follows:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (6)$$

where  $A$  is the pre-exponential factor and  $E_a$  is the activation energy. The pre-exponential factor  $A$  has the same units as the rate constant. A straight line is obtained by plotting of the logarithm of the rate constant against the reciprocal of the absolute temperature and the results are listed in Table 3.

The enthalpy ( $\Delta H^\ddagger$ ), entropy ( $\Delta S^\ddagger$ ) and free energy ( $\Delta G^\ddagger$ ) of activation can be also calculated using the Eyring equation [21] as follows:

$$\ln \left( \frac{k}{T} \right) = \ln \left( \frac{k_b}{h} \right) + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (7)$$

where  $k_b$ , and  $h$  refer to the Boltzmann's constant and the Planck's constant, respectively. The enthalpy ( $\Delta H^\ddagger$ ) and entropy ( $\Delta S^\ddagger$ ) of activation were calculated from the slope and intercept of a plot of  $\ln(k/T)$  versus  $1/T$ . The Gibbs free energy of activation ( $\Delta G^\ddagger$ ) can be written in terms of enthalpy and entropy of activation:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (8)$$

The observed activation energy ( $E_a$ ) and enthalpy of activation ( $\Delta H^\ddagger$ ) for Al(III) onto chitosan shown in Table 3 agreed well with those calculated from the activated complex theory of reaction in solution ( $E_a = \Delta H^\ddagger + RT$ ). The observed activation energy ( $E_a > 42$  kJ/mol) indicated a chemically controlled process [22] for the adsorption of Al(III) onto chitosan.

Table 3  
Activation parameters for the adsorption of Al(III) onto chitosan

Temp (°C)	$k_2$ (g chitosan/mg second)	$E_a$ (kJ/mol)	$R^2$	$\Delta H^\ddagger$ (kJ/mol)	$\Delta S^\ddagger$ (J/mol K)	$\Delta G^\ddagger$ (kJ/mol)	$R^2$
30	$3.72 \times 10^{-6}$					103.5	
45	$1.02 \times 10^{-5}$	56.4	0.9996	53.7	-164.4	106.0	0.9996
60	$2.79 \times 10^{-5}$					108.5	

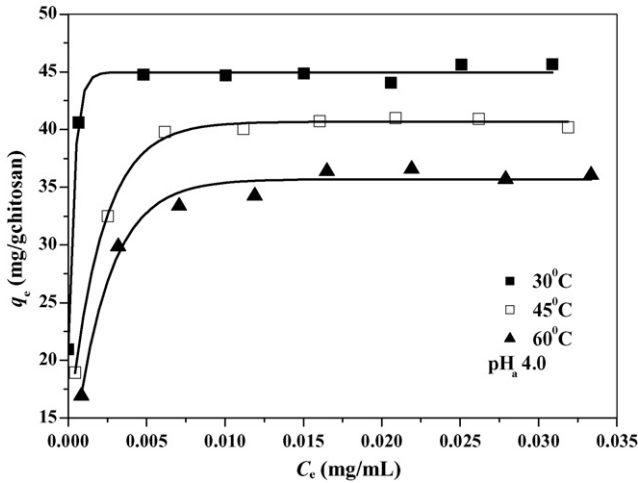


Fig. 5. Langmuir adsorption isotherms for the adsorption of Al(III) onto chitosan ( $W$ , 0.01 g;  $V$ , 50 mL;  $C_0$ , 5–40 mg/L;  $pH_a$  4.0, contact time 24 h).

The value of  $\Delta G^\ddagger$  was calculated at 303, 318 and 333 K for an initial Al(III) concentration of 20 mg/L by using Eq. (8) and these values are listed in Table 3, while the negative  $\Delta S^\ddagger$  reflects the expected structural interaction in the activated state between Al(III) and chitosan. A similar  $\Delta S^\ddagger$  value was obtained from the adsorption kinetics of methyl violet onto perlite [23].

### 3.5. Adsorption isotherm

The Langmuir and Freundlich models are used to describe equilibrium adsorption isotherms. The most widely used Langmuir equation, which is valid for monolayer adsorption onto a surface with a finite number of identical sites, is expressed as [24]:

$$q_e = \frac{QbC_e}{1 + bC_e} \quad (9)$$

where  $Q$  (mg/g chitosan) is the maximum amount of the Al(III) per unit weight of chitosan to form a complete monolayer coverage on the surface bound at high equilibrium Al(III) concentration  $C_e$ ,  $q_e$  is the amount of Al(III) adsorbed per unit weight of chitosan at equilibrium and  $b$  is the Langmuir constant related to the affinity of binding sites. Fig. 5 shows the experimental equilibrium isotherms for adsorption of Al(III) onto chitosan at different temperatures.

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \left(\frac{1}{Q}\right) C_e \quad (10)$$

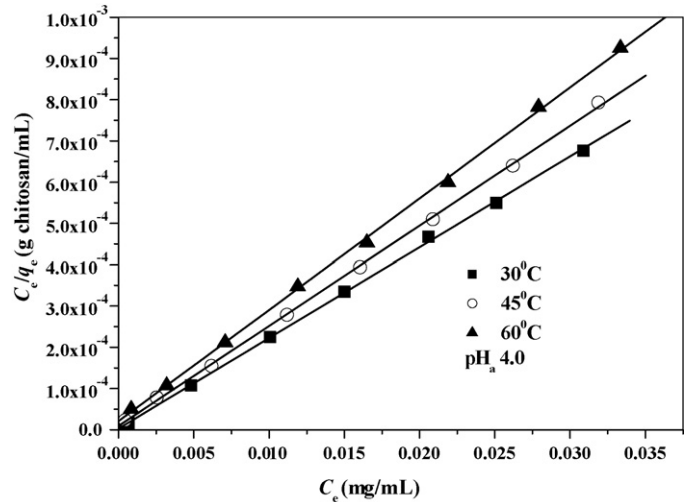


Fig. 6. The linearized Langmuir adsorption isotherms for the adsorption of Al(III) onto chitosan ( $W$ , 0.01 g;  $V$ , 50 mL;  $C_0$ , 5–40 mg/L;  $pH_a$  4.0, contact time 24 h).

From the Eq. (10) a linearized plot of  $(C_e/q_e)$  versus  $C_e$  is obtained as shown in Fig. 6, and  $Q$  and  $b$  are computed from the slopes and intercepts of Eq. (10). Table 4 lists the calculated values of the parameters  $Q$  and  $b$ . It was found that the adsorption capacity ( $Q$ ) values decreased with increasing temperature. The result indicated that the adsorption of Al(III) onto chitosan is an exothermic process.

The Langmuir constant  $b$  is related to the energy of adsorption ( $b \propto \exp(-\Delta H^\circ/RT)$ ). Therefore, the thermodynamic parameters including the free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were also evaluated using the following equations [25]:

$$\Delta G^\circ = -RT \ln b \quad (11)$$

$$\ln(b) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (12)$$

$$\Delta G^\circ = \Delta H^\circ = T\Delta S^\circ \quad (13)$$

The free energy ( $\Delta G^\circ$ ) change was evaluated using Eq. (11), while enthalpy ( $\Delta H^\circ$ ) and entropy changes of adsorption were calculated (Eq. (12)) from the slope of the straight line of a graph of  $\ln(b)$  versus  $1/T$ . The values of  $\Delta H^\circ$  and  $\Delta G^\circ$  were then used together with Eq. (13). The results are listed in Table 5. The negative values of  $\Delta G^\circ$  and  $\Delta H^\circ$  indicate that the adsorption of Al(III) on chitosan is spontaneous and exothermic. The negative value of entropy change ( $\Delta S^\circ$ ) of the process also indicates that the randomness decreases at the solid-solution interface during the adsorption of Al(III) onto chitosan. The obtained thermody-

Table 4  
Langmuir and Freundlich isotherm constants for the adsorption of Al(III) onto chitosan at different temperatures

Temperature (°C)	Langmuir			Freundlich		
	$Q$ (mg/g chitosan)	$b$ (mL/mg)	$R^2$	$Q_f$ (mg/g chitosan)	$n$	$R^2$
30	45.45	7829	0.9995	50.27	36.76	0.8139
45	41.32	2545	0.9995	55.14	12.84	0.6953
60	37.17	1269	0.9994	48.87	12.35	0.8607



Table 5  
Thermodynamic parameters for the adsorption of Al(III) onto chitosan at different temperatures

Temperature (°C)	<i>b</i> (mL/mg)	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol K)	$R^2$
30	7829	−5.52		−150.19	
45	2545	−5.44	−51.03	−150.46	0.9884
60	1269	−5.44		−150.46	

dynamic parameters reconfirmed values reported in our previous study [26].

The essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor for equilibrium parameter,  $R_L$

$$R_L = \frac{1}{1 + bC_0} \quad (14)$$

where  $C_0$  is the initial concentration of Al(III) (in mg/L), and  $b$  is the Langmuir constant (L/mg). The values of  $R_L$  indicate whether the type of isotherm is irreversible ( $R_L = 0$ ), favourable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavourable ( $R_L > 1$ ).

In the present study, the values of  $R_L$  (Table 6) were observed to be in the range of 0–1, indicating that the adsorption of Al(III) onto chitosan was favourable for this study.

The other widely used empirical equation, the Freundlich equation, is based on adsorption on a heterogeneous surface and is given by:

$$q_e = Q_f C_e^{1/n} \quad (15)$$

Table 6  
Langmuir isotherm data for adsorption of Al(III) onto chitosan at different temperatures

Temperature (°C)	<i>b</i> (L/mg)	Initial Al(III) concentration $C_0$ (mg/L)	$R^2$
30	7.829	4.57	0.0272
		9.35	0.0135
		14.29	0.0089
		19.44	0.0065
		24.36	0.0052
		29.58	0.0043
		35.04	0.0036
		40.56	0.0031
45	2.545	4.57	0.0792
		9.35	0.0403
		14.29	0.0268
		19.44	0.0198
		24.36	0.0159
		29.58	0.0131
		35.04	0.0111
		40.56	0.0096
60	1.269	4.57	0.1471
		9.35	0.0777
		14.29	0.0523
		19.44	0.0390
		24.36	0.0313
		29.58	0.0259
		35.04	0.0220
		40.56	0.0191

where  $Q_f$  is roughly an indicator of the adsorption capacity and  $1/n$  of the adsorption intensity. A linear form of the Freundlich expression (Eq. (16)) will yield the constants  $Q_f$  and  $1/n$ .

$$\ln q_e = \ln Q_f + \frac{1}{n} \ln C_e \quad (16)$$

Therefore,  $Q_f$  and  $1/n$  can be determined from the linear plot of  $\ln q_e$  versus  $\ln C_e$ . The magnitude of the exponent  $1/n$  gives an indication of the favourability of adsorption. Values of  $n > 1$  obtained represent favourable adsorption conditions. Table 4 lists the calculated results. The exponent  $n$  is larger than 10 for the adsorption of Al(III) onto chitosan. However, the low correlation coefficients ( $R^2 < 0.86$ ) indicate poor agreement of the Freundlich isotherm data with the experimental data.

#### 4. Conclusions

The adsorption isotherm and kinetics for the adsorption of Al(III) onto chitosan have been investigated. The following results were obtained:

1. The batch pH studies indicated that the Al(III) adsorption capacity was dependent on the pH of the Al(III) solution.
2. Before equilibrium was reached, an increase in temperature lead to an increase in adsorption rate which indicated a kinetically controlled process, while the adsorption of Al(III) on chitosan was controlled by an exothermic process.
3. A pseudo second-order kinetic model agreed well with the behaviour for the adsorption of Al(III) on chitosan, and supported chemical adsorption being the rate-limiting step.
4. The Langmuir equation agrees very well with the experimental data at a high correlation coefficient ( $R^2 > 0.99$ ).
5. The negative values of free energy ( $\Delta G^\circ$ ) and enthalpy ( $\Delta H^\circ$ ) terms for the adsorption of Al(III) onto chitosan indicated that the adsorption process is a spontaneous and exothermic one.

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