

Studies on the capability and behavior of adsorption of thallium on nano- Al_2O_3

Lei Zhang*, Ting Huang, Min Zhang, Xingjia Guo, Zhu Yuan

College of Chemistry, Liaoning University, Shenyang 110036, People's Republic of China

Received 11 May 2007; received in revised form 29 December 2007; accepted 3 January 2008

Available online 11 January 2008

Abstract

A novel sorbent, nano- Al_2O_3 was employed for the removal of thallium from aqueous solution in batch equilibrium experiments, in order to investigate its adsorption properties. The removal percentage of thallium by the sorbent increased with increasing pH from 1 to 5. The adsorption capacities and removal percentage of Tl(III) onto nano- Al_2O_3 were evaluated as a function of the solution concentration and temperature. Results have been analyzed by the Langmuir, Freundlich adsorption isotherms. Adsorption isothermal data could be well interpreted by the Langmuir model. The mean energy of adsorption 9.32 kJ mol^{-1} was calculated from the Dubinin–Radushkevich (D–R) adsorption isotherm. The kinetic experimental data properly correlated with the second-order kinetic model. The thermodynamic parameters for the process of adsorption have been estimated. The ΔH^0 and ΔG^0 values of thallium(III) adsorption on nano- Al_2O_3 showed endothermic adsorption.

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Keywords: Tl(III); Nano- Al_2O_3 ; Adsorption; Kinetics; Thermodynamics

1. Introduction

Thallium has been identified to be an environmentally significant element because of its toxic effects and is commonly found with lead, zinc, iron, tellurium and the alkalis. And thallium is a heavy metallic element that exists in the environment mainly combined with other element (primarily oxygen, sulfur and the halogens). Thallium is used as a catalyst, in making alloys, optical lenses, low temperature thermometers, dyes and pigments in scintillation counters. Thallium is also used as medicines, rodenticides and insecticides [1]. By exploiting and machining mineral, thallium enters and contaminates environment. Therefore, it is important to remove the trace amounts of thallium and strictly controlled for preventing its pollution to humans and environment [2].

At present, it has been reported that thallium can be effectively removed from aqueous solution by iron powder method [3], activated alumina and ion exchange [4], manganese dioxide, ferrihydrite adsorption [5], silica gel [6], polyurethane foam [7],

active carbon [8], etc. Besides, John Peter et al. [9] indicated that modified *Aspergillus niger* biomass was also an emerging and attractive method for the removal of thallium from aqueous solutions. In this paper, nano- Al_2O_3 as sorbent was used to remove thallium from aqueous solutions for the first time.

The nanometer material is a new functional material [10], which has attracted much attention due to its special properties. Most of atoms on the surface of the nanoparticles are unsaturated and can easily bind with other atoms. Nanoparticles have high adsorption capacity. Besides, the operation is simple, and the adsorption process rapid. So there is a growing interest in the application of nanoparticles as sorbents [11].

2. Experimental

2.1. Apparatus

UV–vis–NIR Cary 5000(VARIAN Co., US) was used to measure the concentration of Tl^{3+} . A S-3C Model pH meter (Shanghai Precision Scientific Instrument Co., China) was used for measuring the pH of solutions. A model KQ-100B

* Corresponding author. Tel.: +86 24 62202380; fax: +86 24 62202380.
E-mail address: zhanglei63@126.com (L. Zhang).

ultrasonic cleaner (Kunshan Ultrasonic Instrument Co., China) and a model TDL80-2B centrifugal machine (Shanghai Anting Scientific Instrument Co., China) were used throughout.

2.2. Reagents

A stock solution of Tl(III) (1.000 mg mL^{-1}) was prepared by dissolving 1.3030 g of TlNO_3 (Beijing NCS Analytical Instruments Co., China) with some doubly distilled water and 2 mL concentrated nitric acid, then oxidized by saturated bromine water, finally diluted to a 1 L volumetric flask with 0.12 mol L^{-1} HCl .

All of the other reagents including Triton X-100 solution (1%), Cadion 2B ($5.0 \times 10^{-4} \text{ mol L}^{-1}$), ammonia, ammonium chloride, hydrochloric acid, nitric acid and sodium hydroxide, were of analytical grade and obtained from Shanghai Xinzhong Chemical Reagent Co., China. Doubly distilled water was used throughout experiments. Nano- Al_2O_3 ($\gamma\text{-Al}_2\text{O}_3$) that was used as sorbent in this study was provided from Zhoushanmingri Nanometer Material Co., and its particle size was about 10 nm .

2.3. Procedure

The adsorption experiments were carried out in a series of 50 mL Erlenmeyer flasks containing 0.03 g nano- Al_2O_3 and 10.0 mL of 10.0 mg L^{-1} thallium solution at $\text{pH } 4.5$. If necessary, an appropriate volume of 0.1 mol/L HCl or NaOH solutions was used to adjust the pH of the solution after addition of nano- Al_2O_3 . The solid/liquid phases were separated by centrifuging at 3000 rpm . The adsorption percentage (Ads.%) was calculated as

$$\text{Ads.}\% = \frac{(C_i - C_a)}{C_i} \times 100 \quad (1)$$

where C_i and C_a are the initial and the final concentration of Tl(III) in solution phase, respectively.

Adsorption isotherm studies were carried out with different initial concentrations of Tl(III) while maintaining the sorbent dosage at constant level. In order to inspect any adsorption of thallium on the container surface, control experiments were carried out without the sorbent. It was found that no adsorption occurred on the container wall.

Kinetic experiments were conducted using a known weight of the sorbent dosage at the range $2\text{--}40^\circ\text{C}$. After regular intervals of time, suitable aliquots were analyzed for thallium concentration. The rate constants were calculated using the conventional rate expression.

The thermodynamic parameters for the process of adsorption were determined at a particular temperature. This procedure was repeated at three different temperatures ranging from 2 to 40°C . In this experiment, it was found that Tl(III) ions would be desorbed from nano- Al_2O_3 , when the temperature of the system was more than 40°C . Therefore, all the temperatures of the procedure were controlled at less than 40°C .

3. Results and discussion

3.1. Effect of pH

In this study, knowledge of pH was important because the pH of solution influences the distribution of active sites on the surface of nano- Al_2O_3 . At the higher pH , the OH^- on the surface of nano- Al_2O_3 provides the ability of binding cations. The decrease of pH leads to the neutralization of surface charge, and OH^- is displaced from the surface. When the surface of nano- Al_2O_3 carries positive charges, it begins to adsorb anions.

Fig. 1 shows the effect of pH on the adsorption of Tl(III) by nano- Al_2O_3 , which indicates that the recovery of thallium increases with an increase in pH from 1 to 5. The effect of pH on Tl(III) adsorption can be explained by the following reasons. The surface charge is neutral at isoelectric point (IEP), which pH_{IEP} value is 9 for nano- Al_2O_3 . The surface of sorbent carries positive charges at pH value lower than IEP, which enhances electrostatic force of attraction with TlCl_4^- (In the studied system, the main chemical species of thallium(III) in solutions is TlCl_4^- [12]). As a result, the process of sorption takes place more easily in $\text{pH } 3\text{--}4.5$, so the adsorption percentage of Tl(III) was higher. In $\text{pH } 1\text{--}2$, there is a balance reaction: $\text{H}^+ + \text{HTlCl}_4 \rightleftharpoons \text{HTlCl}_4$, the main chemical species of thallium(III) is HTlCl_4 [13,14], so the adsorption percentage of Tl(III) was lower.

However, at $\text{pH} > 5$, with the increase of OH^- in solutions Cl^- in TlCl_4^- was gradually replaced by OH^- . And $[\text{TlCl}_2(\text{H}_2\text{O})_3]^-$, $[\text{Tl}(\text{H}_2\text{O})_4(\text{OH})_2]^+$, $[\text{Tl}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ [15] and so on, were formed in solutions, which is not favor of adsorption of thallium(III). Therefore, $\text{pH } 4.5$ was chosen for adsorption of Tl(III) in the experiment, and the adsorption percentage was calculated to be 99.56% at $\text{pH } 4.5$.

3.2. Adsorption kinetic model

The models of adsorption kinetics were correlated with the solute uptake rate; hence these models are important in water treatment process design. In this study, for a batch of reactions,

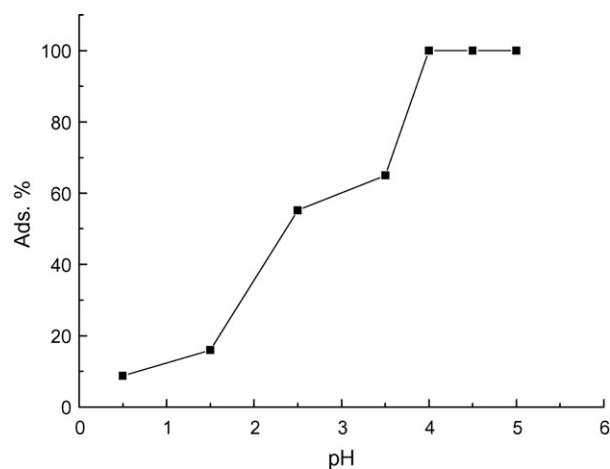


Fig. 1. Effect of pH on the adsorption efficiency of Tl(III) on nano- Al_2O_3 ; 30 mg of nano- Al_2O_3 ; $C_{\text{Tl(III)}} 10.0 \text{ mg L}^{-1}$; static time 10 min ; temperature $20 \pm 0.1^\circ\text{C}$.

Table 1
Kinetic parameters for Tl(III) adsorption on nano-Al₂O₃ at the different temperatures

<i>T</i> (K)	<i>k</i> ₁ (min ⁻¹)	<i>q</i> ₁ (mg g ⁻¹)	<i>r</i> ₁	<i>k</i> ₂ (g mg ⁻¹ min ⁻¹)	<i>q</i> ₂ (mg g ⁻¹)	<i>r</i> ₂
275	1.53	0.87	0.992	7.23	3.07	0.999
293	3.80	1.58	0.966	11.89	3.09	0.998
313	1.60	1.32	0.989	20.22	3.15	0.999

Indicates that model parameters are statistically significant (*t*-test) at 95% confidence level.

the adsorption dynamics was followed by conducting the adsorption of Tl(III) on nano-Al₂O₃ at optimized pH and the sorbent dosage.

Experiments were performed in order to investigate the kinetics of thallium removal by nano-Al₂O₃.

The sorption kinetics may be described by the pseudo-first-order Lagergren rate model. The equation is as follows [16]:

$$\ln(q_1 - q_t) = \ln q_1 - k_1 t \quad (2)$$

where *q*₁ and *q*_{*t*} are the amounts of Tl(III) adsorbed on the sorbent (mg g⁻¹) at equilibrium and at time *t*, respectively, and *k*₁ is the rate constant of the first-order adsorption (min⁻¹). The straight-line plots of ln(*q*₁ - *q*_{*t*}) against *t* were used to determine the rate constant, *k*₁ and correlation coefficient, *r*₁ values of the Tl(III) under different concentration range were calculated from these plots.

The Ho's pseudo-second-order model may also describe the kinetics of sorption of thallium on nano-Al₂O₃. Thus, the kinetic rate law can be rewritten as follows [17]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \quad (3)$$

where *k*₂ is the rate constant of second-order adsorption (g mg⁻¹ min⁻¹). The straight-line plots of *t*/*q*_{*t*} against *t* have been tested to obtain rate parameters and it suggests the applicability of this kinetic model to fit the experimental data.

The validity of both kinetic models is checked. The results of the kinetic parameters for Tl(III) adsorption are listed in Table 1. Based on the correlation coefficients, the adsorption of Tl(III) is best described by the pseudo-second-order equation.

It was possible to calculate the activation energy for adsorption employing Arrhenius equation for the rate constant [18] based on the result in Table 1. Arrhenius equation is as follows:

$$k = A \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

where *A* is the frequency factor (min⁻¹), *E*_{*a*} the activation energy (kJ mol⁻¹), *R* is the ideal gas constant (J mol⁻¹ K⁻¹), *T* the absolute temperature (K).

Eq. (4) can be converted into Eq. (5) by taking logarithm

$$\ln k = \ln A - \left(\frac{E_a}{RT}\right) \quad (5)$$

Thus, *E*_{*a*} could be obtained from the slope of the line plotting ln *k* vs. 1000/*T* (Fig. 2) and the estimated *E*_{*a*} for Tl(III) adsorption on nano-Al₂O₃ was 19.02 kJ mol⁻¹.

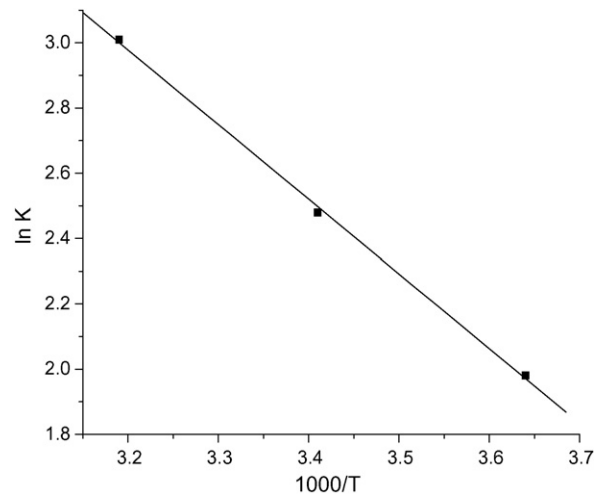


Fig. 2. Plot of ln *k* vs. 1000/*T* (the points correspond to 275, 293, 313 K); 30 mg of nano-Al₂O₃; C_{Tl(III)} 10.0 mg L⁻¹; pH 4.5.

3.3. Adsorption isotherm and adsorption capacity

The equilibrium adsorption of Tl(III) on nano-Al₂O₃ as a function of the initial concentration of Tl(III) is shown in Fig. 3. There was a gradual increase of adsorption for Tl(III) ions until the equilibrium was attained. Adsorption isotherm is important to describe how solutes interact with the sorbent. The Langmuir and Freundlich models are often used to describe equilibrium sorption isotherms. The most widely used Langmuir equation,

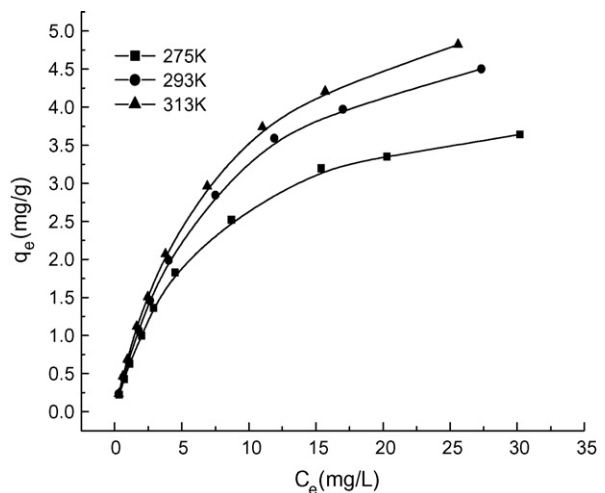


Fig. 3. Isotherm of Tl(III) adsorption on nano-Al₂O₃ at different temperatures (275, 293, 313 K); 30 mg of nano-Al₂O₃; the initial Tl(III) concentration range was 1.0~35.0 mg L⁻¹; static time 10 min; pH 4.5.

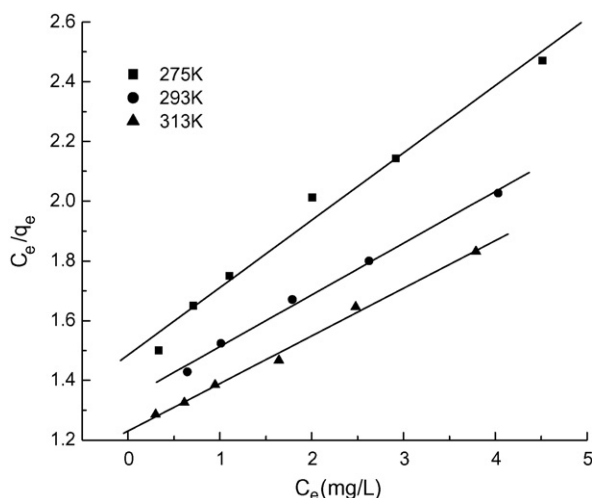


Fig. 4. Langmuir adsorption isotherm at different temperatures (275, 293, 313 K); 30 mg of nano- Al_2O_3 ; the initial Tl(III) concentration range was 1.0–10.0 mg L^{-1} ; static time 10 min; pH 4.5.

which is valid for monolayer sorption on a surface with a finite number of identical sites, is given by:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{K_{\text{ads}}}{q_{\max}} \quad (6)$$

where q_{\max} is the maximum adsorption at monolayer (mg g^{-1}), C_e is the equilibrium concentration of Tl(III), q_e is the amount of Tl(III) adsorbed per unit weight of nano- Al_2O_3 at equilibrium concentration (mg g^{-1}) and K_{ads} is the Langmuir constant related to the affinity of binding sites (mg L^{-1}). A linearized plot of C_e/q_e against C_e gives q_{\max} and K_{ads} (Fig. 4).

The widely used empirical Freundlich equation based on sorption on a heterogeneous surface is given by:

$$\lg q_e = \lg K_F + \frac{1}{n} \cdot \lg C_e \quad (7)$$

where K_F and n are Freundlich constants indicating sorption capacity (mg g^{-1}) and intensity, respectively. K_F and n can be determined from linear plot of $\lg q_e$ against $\lg C_e$ (Fig. 5).

The calculated results of the Langmuir and Freundlich isotherm constants are given in Table 2. Fig. 4 shows that the adsorption of Tl(III) on nano- Al_2O_3 was correlated well ($R > 0.99$) with the Langmuir equation as compared to Freundlich equation under the concentration range studied. The maximum adsorption capacity of thallium ions on nano- Al_2O_3 was 4.44 mg g^{-1} , 5.78 mg g^{-1} , and 6.28 mg g^{-1} at 2 °C, 20 °C and 40 °C, respectively.

Table 2
Langmuir and Freundlich isotherm constants and correlation coefficients at the different temperatures

T (K)	Langmuir			Freundlich		
	q_{\max} (mg g^{-1})	K_{ads} (mg L^{-1})	R	K_F (mg g^{-1})	n	R
275	4.44	6.61	0.992	0.56	1.23	0.919
293	5.78	7.72	0.997	0.65	1.20	0.961
313	6.28	7.75	0.998	0.69	1.16	0.985

Indicates that model parameters are statistically significant (t -test) at 95% confidence level.

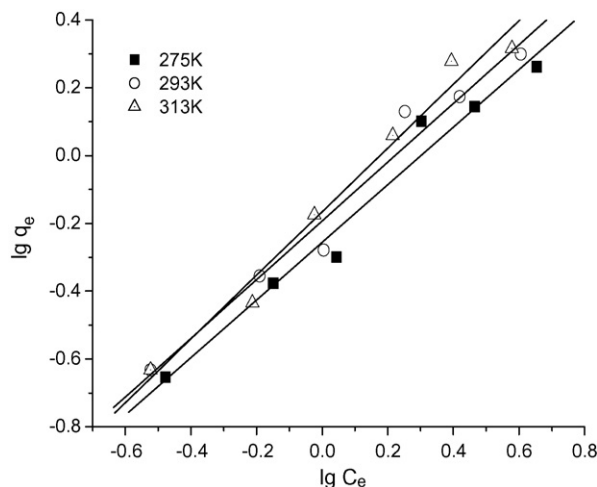


Fig. 5. Freundlich adsorption isotherm at different temperatures (275, 293, 313 K); 30 mg of nano- Al_2O_3 ; the initial Tl(III) concentration range was 1.0–10.0 mg L^{-1} ; static time 10 min; pH 4.5.

3.4. Thermodynamic studies

The experiments were carried out at 275, 293 and 313 K for different concentrations, respectively. The values of ΔH^0 were calculated from the slopes and intercepts of linear regression of $\ln C$ vs. $1/T$ using the Clausius-Clapeyron equation [19,20]

$$\ln C = \frac{\Delta H^0}{RT} + D \quad (8)$$

where C is the equilibrium concentration of Tl(III) in solution (mg/L) and D is the intercept of the plot of $\ln C$ vs. $1/T$. ΔH^0 was assumed to be constant for a constant surface coverage.

To calculate the values of the other parameters (ΔG^0 , ΔS^0) the following equations were used:

$$K_C = \frac{C_{\text{Be}}}{C_{\text{Ae}}} \quad (9)$$

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

$$\Delta S^0 = \frac{(\Delta H^0 - \Delta G^0)}{T} \quad (11)$$

where C_{Be} and C_{Ae} are the equilibrium concentrations of Tl(III) on the sorbent and solution, respectively, K_C is the equilibrium constant, ΔS^0 is standard entropy, ΔG^0 is standard free energy. Table 3 represents the estimated thermodynamic parameters for Tl(III) adsorption.

Table 3
Thermodynamic parameters for the adsorption of Tl(III) on nano-Al₂O₃

T (K)	275	293	313
K_c	1.21	1.48	1.64
ΔG^0 (kJ mol ⁻¹)	-0.44	-0.96	-1.29
ΔH^0 (kJ mol ⁻¹)		6.47	
ΔS^0 (kJ mol ⁻¹ K ⁻¹)	0.0251	0.0254	0.0258

Indicates that model parameters are statistically significant (*t*-test) at 95% confidence level.

It can be seen from Table 3 that positive ΔH^0 indicates that the adsorption reaction of Tl(III) on nano-Al₂O₃ is endothermic. The free energy values for all the systems are negative, and decrease in the value of ΔG^0 with increase of temperature shows that the reaction is easier at high temperature. Metal ions in aqueous media are hydrated. When the ions get absorbed on the sorbent surface, water molecules previously bonded to the metal ion get released and dispersed in the solution; the results in an increase in the entropy [21].

3.5. The type of adsorption process

The D–R isotherm is more general than the Langmuir isotherm, because it does not assume a homogeneous surface or constant sorption potential [22]. The D–R equation is

$$q_e = q_m \exp(-K\varepsilon^2) \quad (12)$$

The linear form of Eq. (12) is

$$\ln q_e = \ln q_m - K\varepsilon^2 \quad (13)$$

The ε can be calculated from the equation

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (14)$$

The values of q_m and K were deduced by plotting $\ln q_e$ vs. ε^2 (Eq. (13), Fig. 6). The mean energy of adsorption (E) can be

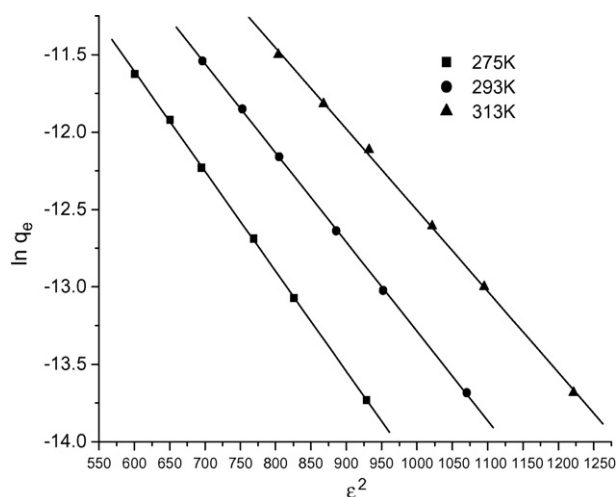


Fig. 6. D–R adsorption isotherm for Tl(III) adsorption on nano-Al₂O₃ at different temperatures (275, 293, 313 K); 30 mg of nano-Al₂O₃; the initial Tl(III) concentration range was 1.0–10.0 mg L⁻¹; static time 10 min; pH 4.5.

Table 4
D–R isotherm constants and correlation coefficients at the different temperatures

T (K)	K (mol ² kJ ⁻²)	q_m (mmol g ⁻¹)	E (kJ mol ⁻¹)	r
275	-0.0065	0.44	8.80	0.999
293	-0.0058	0.54	9.32	0.999
313	-0.0052	0.70	9.77	0.999

Indicates that model parameters are statistically significant (*t*-test) at 95% confidence level.

calculated from the equation

$$E = (-2K)^{-1/2} \quad (15)$$

where C_e is the equilibrium solution concentration, q_e is the amount of Tl(III) adsorbed at the equilibrium, q_m is the theoretical saturation capacity, ε is the Polanyi potential, E is the adsorption energy, K is a constant related to the adsorption energy.

The calculated results of the D–R isotherm constants are given in Table 4. The magnitude of the mean energy of adsorption (E) is often used to estimate the type of adsorption process. Accord to the experimental results, the value of E was calculated to be 9.32 kJ mol⁻¹, which was within the energy range of ion-exchange reactions, 8–16 kJ mol⁻¹ [23]. Therefore, the type of the adsorption of thallium on nano-Al₂O₃ is a chemical adsorption.

4. Conclusion

The experimental results indicate that nano-Al₂O₃ is an effective sorbent for the adsorption of Tl(III) from aqueous solutions. The percentage of Tl(III) removal from solution by nano-Al₂O₃ is close to 100% at pH 4.5. For all studied systems of kinetics, the pseudo-second-order model provides better correlation of the adsorption data than the pseudo-first-order model; this suggests that the rate-limiting step may be chemical sorption. The adsorption isotherms could be well fitted by the Langmuir and D–R adsorption isotherm equation. The thermodynamic parameters ΔG^0 , ΔH^0 and ΔS^0 are calculated, and the positive values of enthalpy confirm the endothermic nature of adsorption.

Acknowledgements

The authors greatly acknowledge the Education Department of Liaoning Province Science Foundation (No. 20060363) of China for financial support. The authors also thank our colleagues and other students participating in this work.

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