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果胶对稀土金属 Ce^{4+} 的吸附研究

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摘 要：本文研究了低脂果胶对稀土金属铈离子的吸附性能. 研究了吸附时间、铈离子溶液的pH、吸附温度、果胶用量、铈离子浓度对果胶吸附容量的影响. 分别用 Langmuir 和 Freundlich 模型对吸附过程进行了分析. 根据吸附等温线，计算了相关的热力学和动力学参数，并用红外光谱对样品进行了分析. 结果表明，所研究的变量显著地影响果胶对铈离子的吸附容量，吸附前后果胶的红外光谱发生了明显的改变，说明吸附过程中可能发生了化学反应. 与 Langmuir 模型相比，Freundlich 模型更适合用来描述果胶对铈离子的吸附过程. 吸附过程遵循伪一级动力学方程. 焓变和熵变是吸附过程的驱动力.

关键词：果胶；铈离子；吸附；热力学；动力学
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Study on the adsorption of rare earth metal cerium ions (Ⅳ) by pectin

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Abstract: The adsorption of rare earth metal cerium ions by low fat pectin was determined. The effects of the adsorption time, pH of the cerium ion solution, adsorption temperature, dosage of pectin and concentration of cerium ions on the adsorption capacity of pectin were investigated. The adsorption process was analyzed by the Langmuir and Freundlich models. Using the adsorption isotherm, the related thermodynamic and kinetic parameters were calculated, and infrared spectrum analysis was performed. The results indicate that the variables studied significantly affect the adsorption of cerium ions by pectin and that the infrared spectra before and after adsorption are apparently different, implying that a chemical reaction may have occurred in the adsorption process. The Freundlich equation is better suited to describe the adsorption process compared to the Langmuir equation. The adsorption process is best described by a pseudo-first order kinetics equation. Enthalpy and entropy differences are the driving forces of the adsorption process.

Keywords: Pectin; Ceriumion; Adsorption; Thermodynamics; Kinetics

1 Introduction

Metal ions continue to play an increasing role in the pollution of water. Rare earth elements at high concentrations may have negative impacts on the aquatic ecosystem. Cerium, a rare earth ele-

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ment, affects the germination of seeds and physiological activity of seedlings. Cerium ions are beneficial at low concentrations for seed germination as well as seedling growth and development due to the replacement of copper and cadmium ions by cerium. However, a high concentration of cerium ions inhibits seedling growth and works in conjunction with copper and cadmium, leading to toxicological effects[1-5]. Thus, it is very important to recover cerium (IV) in water.

In recent reports, Yunnan Tuo Cha was used to adsorb cerium (IV) ions, and adsorption equilibrium was reached with an adsorption capacity of 7.95 mg/g at the optimal pH of 2.8 and adsorption temperature of 25 ℃ for 80 min [6]. Pectin is a natural polymer and a polysaccharide found in the cell walls of plants, a light yellow or white powder, soluble in aqueous solutions, weakly acidic and cohesive. Pectin is insoluble in glycerol and ethanol, stable at a certain acidities, and undergoes facile depolymerization in strongly acidic or alkaline environments. It is widely present in citrus fruits, apples, sugar beets among others and is widely used in the food industry. Pectin is mainly used as a coagulating agent, emulsifier, thickener and stabilizer. It is also used to adsorb heavy metal ions in the water treatment industry due to its strong adsorption capability as a natural adsorbent. Thus, pectin is also used as an antidote in the pharmaceutical industry [7-12]. In addition, due to its biochemical properties, pectin can also be used to reduce blood lipids and blood sugar as well as to produce health foods that control blood lipids, diabetes and other diseases [8]. Some studies have also shown that pectin exhibits obvious adsorption of Cu^{2+}, Pb^{2+} and Fe^{3+} [13], mainly due to the interaction between metal ions and the carboxyl functional groups on galacturonic acid in pectin. However, most studies on pectin's adsorbent properties have focused on the adsorption of common heavy metals and radioactive ions, and practical studies of the adsorption of rare earth metal ions are lacking. In this work, the adsorption of rare earth metal cerium ions by pectin was studied, suitable adsorption conditions were determined, and isothermal adsorption was also investigated, from which the related thermodynamic and kinetic parameters were calculated. This work may serve as a reference for the removal of rare earth metal ions in water pollution using pectin as the adsorbent.

2 Experiment

2.1 Determination of the standard curve between the concentration of cerium ions and absorbance

The concentration of cerium ions in solution was determined by the methyl green spectrophotometric method[14]. Different volumes (1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 mL) of a standard solution of cerium ions (10 ug/mL) were added to colorimetric tubes (25 mL), followed by the addition of 2.5 mL of a sulfuric acid solution (4.5 mol/L) and 5.0 mL of a methyl green solution (0.05 g/L). Finally, distilled water was used to dilute the solution to the standard scale, followed by shaking for 20 min for coloration. Using the blank reagent as a reference, the absorbance was determined by a 752 spectrophotometer at a maximum absorption wavelength of 465 nm. The standard curve between the concentration (C, mg/L) and absorbance (A) was plotted, giving the following standard curve equation and correlation coefficient (Eq. 1).

$$A = 0.03017 * C + 0.01233,\ R^2 = 0.99819 \tag{1}$$

2.2 Adsorption of cerium ions by pectin

Solutions of varying concentrations of cerium ions (50 mL) were added to beakers, and the pH value was adjusted with NaOH and HCl solutions. Pectin was then added to each beaker, which was sealed with plastic wrap, and a few holes were pricked with a needle. The adsorption time (10, 20, 30, 40, 60, 80 and 100 min), pH value (1, 2, 3 and 4), temperature (15, 25, 35, 45, 55 and 65 ℃), dosage of pectin (0.01, 0.02, 0.025, 0.03 and 0.04 g) and cerium ion concentration (5, 7.5, 10, 12.5 and 15 ug/mL) were investigated as variables for the adsorption of cerium (Ⅳ) ions by pectin.

3 Results and Discussion

3.1 Factors affecting adsorption

3.1.1 Effect of adsorption time Fig. 1 shows the effects of the adsorption time on the adsorption capacity of pectin. As seen from Fig. 1, in a certain range, the adsorption capacityincreases over time and the adsorption of cerium ions by pectin mainly occurs in the former 40 min. In the first 10 min, the change of the adsorption capacity is especially apparent, reaching 4.0 mg/g. However, the change is slow after 40 min, and the adsorption equilibrium is essentially reached at 80 min. The adsorption capacity at 40 min is 9.0 mg/g, and the adsorption capacity at adsorption equilibrium is 9.75 mg/g, meaning that the adsorption capacity at 40 min reaches 92.3% of that at adsorption equilibrium. That is to say, the adsorption of cerium (IV) ions by pectin is quite fast, supporting the potential application of pectin for adsorption of cerium ions in polluted water.

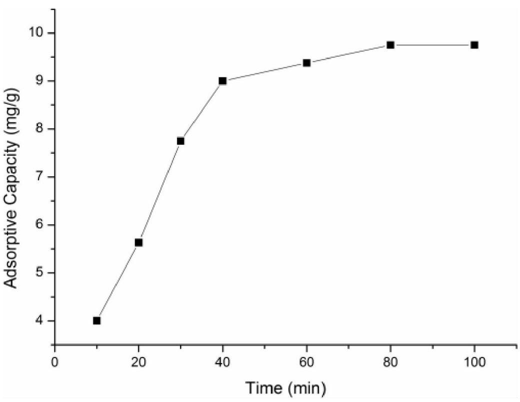

Fig. 1 Effects of the adsorption time on the adsorption capacity of pectin

3.1.2 Effect of the pH value Tab. 1 shows the effects of the pH value on the adsorption of cerium (IV) ions by pectin. It can be seen from Tab. 1 that with the increasing pH value in the initial solution, the adsorption capacity of pectin initially increases and then decreases. The adsorption capacity reaches 9.75 mg/g at the optimal pH of 2, which implies that a certain amount of acid aids the adsorption of cerium (IV) ions by pectin. However, the adsorption capacity falls to 1.13 mg/g when the pH is reduced to 1.0, implying that excess acid is not beneficial for the adsorption of cerium (IV) ions by pectin, which may be attributed to structural damage of pectin due to the hydrolysis of ester bonds under strongly acidic conditions. It has been reported that cerium ions began to generate $Ce(OH)_4$ precipitate when the pH value is greater than 5 [15]. Thus, the pH of the treated solution should be kept below 5 in practical applications.

Tab. 1 Effects of pH on the adsorption of rare earth metal cerium (IV) ions by pectin

pH	1	2	3	4
Adsorption capacity (mg/g)	1.13	9.75	7.33	4.88

3.1.3 Effect of temperature Fig. 2 shows the adsorption capacity of pectin relative to temperature. From Fig. 2, it is apparent that the adsorption capacity of pectin initiallyincreases and then decreases with increasing temperature. The maximum adsorption capacity reaches 15.13 mg/g when the temperature is 45 ℃, which indicates that a relatively high temperature promotes the adsorption of cerium (IV) ions by pectin. This phenomenon can also be explained by the following study. However, the adsorptive capacity decreases with further increases in temperature. This may be related to structural changes of pectin at temperatures higher than 45 ℃, resulting in a decreased absorption capacity. Thus, the temperature of the treated solution was controlled below 45 ℃ in the study.

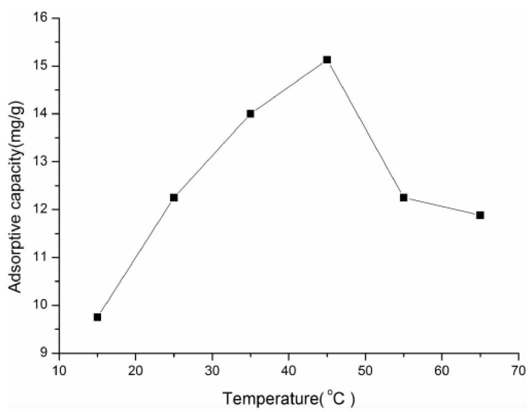

Fig. 2 Effects of the adsorption temperature on the adsorptive capacity of pectin

3.1.4 Effect of pectin dosage Fig. 3 shows the effects of the amount of pectin adsorbent on the adsorption capacity. As shown in Fig. 3, the adsorption capacity of pectindecreases gradually with the increasing pectin dosage. This may be because, with changes in pectin dosage, the total contact area between pectin and cerium ions increases and the active adsorption sites also increase. However, the concentration of cerium ions in solution decreases rapidly due to the fast adsorption by the increased amount of pectin. It is difficult to make full use of the adsorption of pectin due to the limited amount of cerium ions. As a result, the adsorption capacity of cerium ions per unit mass of pectin is reduced, and thus, the adsorption capacity of pectin drops continuously.

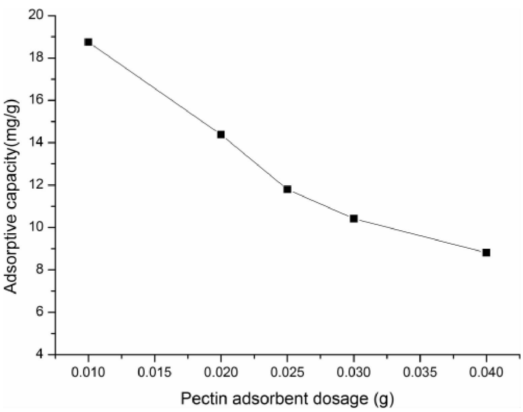

Fig. 3 Effects of the amount of pectin adsorbent on the adsorption capacity

3.1.5 Effect of the initial cerium ion concentration

Fig. 4 presents the effects of the initial cerium ion concentration on the adsorption capacity of pectin. As shown in Fig. 4, the adsorptive capacity of pectin graduallyincreases with the increasing cerium ion concentration when the other conditions remain unchanged (25 ℃, 100 min). The increase is quite obvious, which indicates that the concentration of cerium ions has a significant effect on the adsorption of cerium (IV) ions by pectin.

With the increasing concentration of cerium ions in solution, the cerium ion adsorption probability on the adsorbent surfaceis increased; however, the concentration gradient between the adsorbent surface and cerium ions in solution increases; therefore, the amount of cerium ions adsorbed on the surface of the adsorbent is increased when the adsorption equilibrium is reached.

3.2 Adsorption thermodynamics

3.2.1 The adsorption isotherm Static adsorption was conducted withpectin as the adsorbent at 45 ℃ for 100 min using various concentrations of cerium ions in the treated solution. The concentrations of cerium ions in the solution were tested when adsorption equilibrium was reached, and the adsorptive capacity was calculated based on the obtained data. At present, the most frequently used adsorption models are the Langmuir (Eq. 2) and Freundlich (Eq. 3) models [16]. The data of adsorption of cerium ion by pectin were analyzed by the Langmuir and Freundlich models, and the specific results are given in Fig. 5.

$$\frac{C_e}{Q_e}=\frac{1}{Q_m}C_e+\frac{1}{K_L Q_m} \tag{2}$$

$$\lg Q_e=\frac{1}{n}\lg C_e+\lg K_F \tag{3}$$

where C_e is the equilibrium concentration of the cerium ions solution; Q_e is the equilibrium adsorptive capacity of cerium ions; Q_m is the theoretical maximum adsorptive capacity of cerium ions; K_L is the Langmuir empirical constant; and n and K_F are the Freundlich constants indicating the relative adsorptive capacity and adsorption rate, respectively.

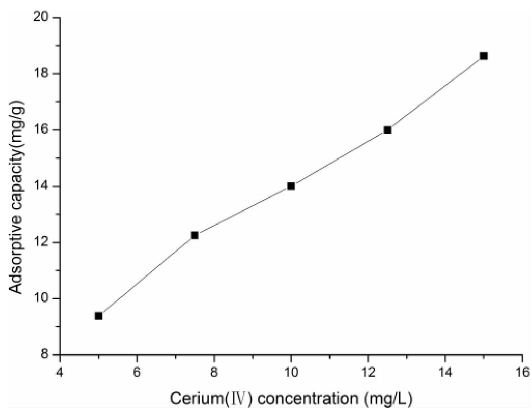

Fig. 4 Effect of the initial cerium ion concentration on the adsorption capacity of pectin

The Langmuir model[17] assumes that the maximum adsorption corresponds to a saturated monolayer of cations, all of the exchange sites are equivalent and the energy of adsorption is constant over all sites, and adsorption occurs at definite and localized sites. In contrast, the Freundlich model implies that adsorption occurs on a heterogeneous surface, where the adsorption sites exhibit a spectrum of different binding energies.

As seen from Fig. 5, when the Langmuir model was used to analyze the results of the adsorption equilibrium, C_e and C_e/Q_e show an approximate linear relationship, and the linear correlation coefficient (R^2) is 0.9363. Whereas, $\lg Q_e$ and $\lg C_e$ present a better linear relationship and R^2 is 0.97494 for the Freundlich model. The theoretical maximum adsorptive capacity Q_m was calculated to be 21.03 mg・g^{-1}, as shown in Table 2. Relatively speaking, the Freundlich equation is more suitable for describing the actual adsorption process. The parameters n and K_F are 2.78249 and 8.57788 L/g, respectively, according to the Freundlich equation. It has been reported that a $1/n$ of 0.1-0.5 suggests facile adsorption, while a $1/n$ greater than 2 implies difficult adsorption [18]. In this work, n = 2.78249 and indicates that the adsorption of cerium ions by pectin is facile, also supporting the potential application of pectin for adsorption of cerium ions in polluted water.

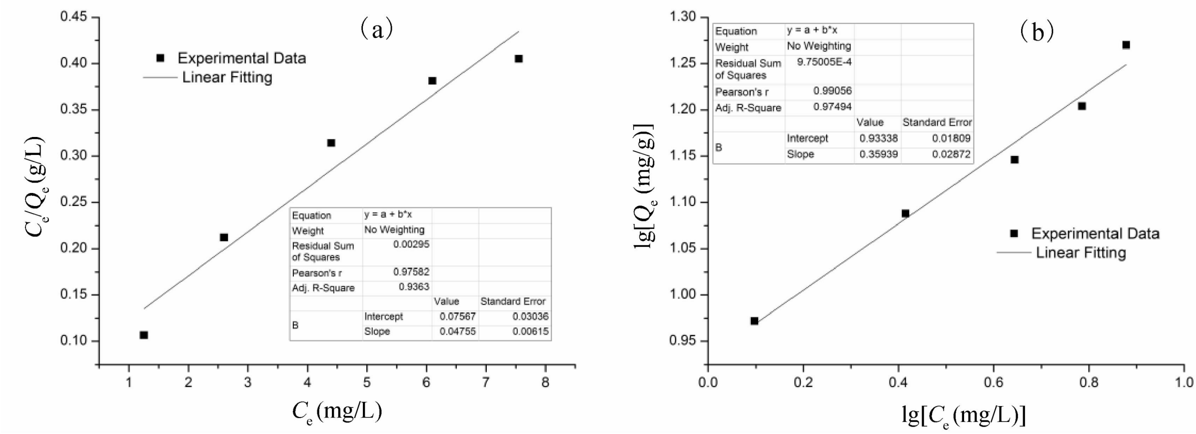

Fig. 5　The Langmuir (a) and Freundlich (b) isotherms of the adsorption of cerium (IV) ions by pectin

Tab. 2　Types of and parameters for the isothermal adsorption of cerium ions by pectin

Langmuir model			Freundlich model		
Q_m(mg/g)	K_L(L/mg)	R^2	n	K_F(L/g)	R^2
21.03	0.62823	0.9363	2.78249	8.57788	0.97494

3.2.2　ΔH of the adsorption　The equation of Clausius carat Dragon (Equation 4) was used.

$$\ln C_e = \Delta H/RT + K \quad (4)$$

where R is the gas constant (8.314 J・mol^{-1}・K^{-1}); T is the absolute temperature (K); C_e is the corresponding equilibrium concentration when the adsorption capacity is q_e (mg/L); ΔH is the enthalpy change of the adsorption process (kJ/mol); and K is the adsorption equilibrium constant.

The adsorption curve of pectin is shown in Fig. 6. The relationship between $\ln C_e$ and $1/T$ was linearly fitted, and the correlation coefficient R^2 is 0.98851. In addition, the adsorption enthalpy difference ΔH directly reflects the relative properties of the adsorption. The value of ΔH was calculated according to the slope of the fitted straight line, shown in Tab. 3. From Tab. 3, in can be seen that the correlation coefficient R^2, the adsorption equilibrium constant and ΔH are 0.98851, −2.90525 and 11.2579 kJ/mol, respectively, indicating that the adsorption process is an endothermic reaction. Consequently, in a certain range, the adsorptive capacity increases with increasing temperature, as presented in section 3.1.3.

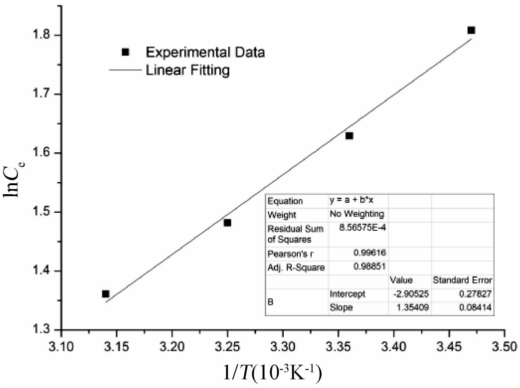

Fig. 6 The linear relationship of $\ln C_e$ and $1/T$

Tab. 3 Enthalpy change of adsorption of cerium ions by pectin

Adsorption equilibrium equation	R^2	K	ΔH/(kJ/mol)
$\ln C_e = -2.90525 + 1.35409\times10^3/T$	0.98851	−2.90525	11.2579

3.2.3 ΔG of the adsorption ΔG of the adsorption process was calculated according to a previously reported method using the following equation (Eq. 5) [18].

$$\Delta G = \int_0^x y dx / x \tag{5}$$

Where x, y, and ΔG are the adsorbed mass fraction in the equilibrium solution, adsorption isotherm equation, and change of the adsorption free energy, respectively.

Eq. 5 was induced into the Freundlich equation to obtain Eq. 6, from which ΔG was calculated at different temperatures, as shown in Tab. 4. It can be seen from Tab. 4 that the value of ΔG is negative, indicating that the adsorption process is a spontaneous irreversible process. The absolute value increases slowly when the temperature increases from 288 to 318 K, illustrating that the spontaneous trend of the adsorption process in this temperature range increases slightly with increasing temperature, which is in agreement with the analysis of the enthalpy change. The effects of the entropy and enthalpy factors on the ΔG of the adsorption reaction are contrary, while a complementary phenomenon exists in the adsorption process. The microscopic nature of this compensation relationship is related to intermolecular forces and the degrees of freedom in molecule motion [18].

$$\Delta G = -nRT \tag{6}$$

Tab. 4 The free energy change of adsorption of cerium ions by pectin

Adsorption equilibrium equation	$\ln C_e = -2.90525 + 1.35409\times10^3/T$			
T(K)	288	298	308	318
ΔG/(kJ/mol)	−6.6625	−6.8938	−7.1252	−7.3565

3.2.4 ΔS of the adsorption According to the Gibbs-Helmhotz equation (Eq. 7), the entropy changes of adsorption of cerium ions by pectin under different temperatures can be calculated, and the results are presented in Tab. 5.

Tab. 5 shows the entropy change ΔS of the adsorption of cerium ions by pectin. As seen from Tab. 5, in the range of 288-318 K, ΔS decreases with the increasing temperature. However, the trend is not obvious. It can be concluded that the adsorption temperature has little effect on ΔS of the adsorption process.

$$\Delta S = (\Delta H - \Delta G)/T \tag{7}$$

Tab. 5 Entropy change of adsorption of cerium ions by pectin

Adsorption equilibrium equation	$\ln C_e = -2.90525 + 1.35409\times10^3/T$			
T(K)	288	298	308	318
ΔS (J/(mol·K))	62.2236	60.9117	59.6854	58.5359

3.3 Adsorption kinetics

The kinetics of the adsorption of cerium ions by pectin at 298 K are shown in Fig. 7, and the adsorption kinetics curves were fitted with the pseudo-first and pseudo−second order adsorption kinetic equations (Eq. 8 and 9).

$$\ln(1-F_t) = -K_1 t/2303 \tag{8}$$

$$\ln(1-F_t^2) = -K_2 t/2303 \tag{9}$$

Where $F_t = q_t/q_e$ represents the adsorption fraction at time t; q_t and q_e are the adsorptive capacities at time t and at adsorption equilibrium, respectively; K_1 is a kinetic parameter of the pseudo-first order adsorption; and K_2 is a kinetic parameter of the pseudo-second order adsorption.

The kinetic fitting curves are shown in Fig. 7. The kinetic parameters of the adsorption of cerium ions by pectin were calculated based on the linear fitting parameters shown in Fig. 7 and in Tab. 6. From Tab. 6, it can be seen that the constants K_1 and R^2 are 132.58 and 0.95699, respectively, according to the kinetic equation of pseudo-first order adsorption, and the constants K_2 and R^2 are 117.25 and 0.95487, respectively, according to the kinetic equation of pseudo-second order adsorption. The linear correlation coefficients are relatively similar when the pseudo-first and pseudo-second order adsorptions are used to analyze the adsorption process. The adsorption of cerium ions by pectin is better described by the pseudo-first order adsorption kinetics equation, indicating that the adsorption time plays a relatively dominant role in the adsorption rate of pectin [18].

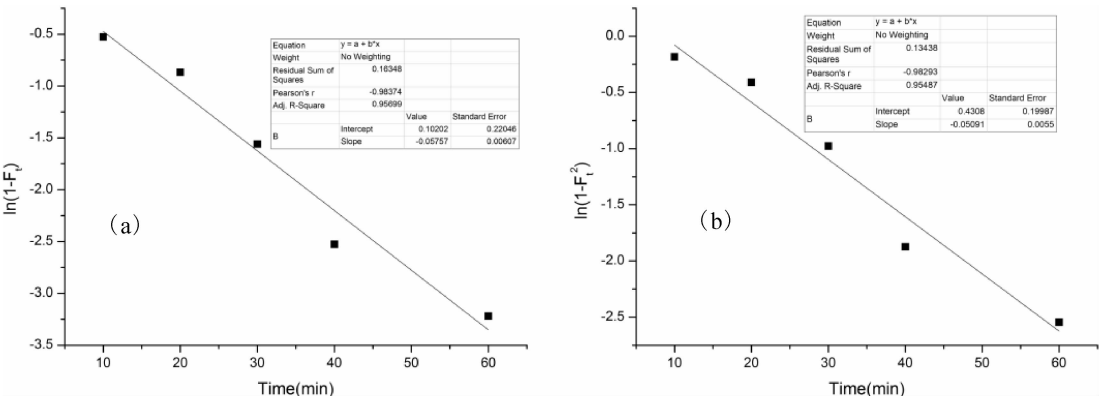

Fig. 7　Relationship between $\ln(1-F_t)$ and time (a, pseudo-first order adsorption), and $\ln(1-F_t^{\,2})$ and time (b, pseudo-second order adsorption)

Tab. 6　Kinetic parameters of adsorption of cerium ions by pectin

K_1	R^2	K_2	R^2
132.58	0.95699	117.25	0.95487

3.4　IR analysis

Fig. 8 shows the infrared spectra of pectin before (a) and after (b) the adsorption of cerium ions. The infrared spectrum of pectin is significantly different after the adsorption of cerium ions. The peak from 3750-3000 cm^{-1} corresponds to the O-H stretching vibration (V_{O-H}), which becomes steeper after adsorption compared with the peak prior to adsorption. The peak from 3000-2700 cm^{-1} is attributed to the C-H saturated stretching vibration (V_{C-H}). The peak from 1680-1500 cm^{-1} is assigned to the double bond stretching vibration of C=C ($V_{C=C}$). The peak from 1350-1200 cm^{-1} suggests the C-O bending vibration (V_{C-O}), which becomes sharper after adsorption. For the sample after the adsorption of cerium ions (b), the two peaks from 1250-1000 cm^{-1} are assigned to the C-O stretching vibration (V_{C-O}). One is attributed to the C-O-H on the sugar-ring and glycosidic C-O-C bond, and the other is attributed to the C-O-H of Gal A-carboxyl and C-O-R. It is apparent that the infrared spectrum of pectin changes significantly after the adsorption of cerium ions. The differences mentioned above show that a chemical reaction may have occurred between pectin and cerium ions during the process of adsorption.

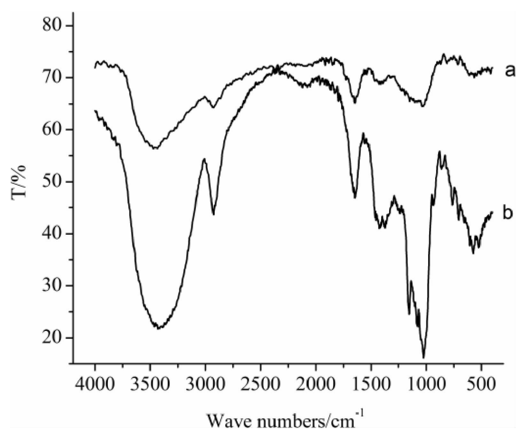

Fig. 8　Infrared spectra of pectin before (a) and after (b) adsorption of cerium ions

4　Conclusions

The adsorption performance of pectin on the rare earth metal cerium (IV) is related to the adsorption time, pH, temperature, dosage of adsorbent, and initial concentration of cerium (IV) ions. The adsorption capacity reaches 15.13 mg/g when the temperature, pH, dosage of pectin, concentration of cerium ions, and adsorption time are 45 ℃, 2, 0.02 g, 10 mg/L and 40 min, respectively. The Freundlich equation is better suited to describe the adsorption process compared with the Langmuir equation, and the adsorption process is better described by a pseudo-first order adsorption kinetics equation. Enthalpy and entropy changes are the driving forces of the adsorption.

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