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Adsorption behavior of Hg^{2+} in aqueous solutions on a novel chelating cross-linked chitosan microsphere

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ABSTRACT

In this study, cross-linked chitosan microspheres (CCTS) was synthesized from chitosan and epichlorohydrin (ECH), then, 2-(chloromethyl) benzimidazole (CBM) was introduced to modify CCTS as the ligand. The resulting CBM-chitosan was characterized by EA, FTIR and TGA, and tested for metal adsorption. Results showed that CBM-chitosan has a relatively high selectivity toward Hg^{2+}. Equilibrium data were fitted well with Langmuir isotherms with the maximum adsorption capacity of 257.8 mg/g for Hg^{2+}. Both kinetics and thermodynamic parameters of the adsorption process were obtained. The data indicated that adsorption process was exothermic spontaneous reaction and kinetically proceeded according to Second-order kinetics model. CBM-chitosan can be eluted effectively using 1.0 mol/L HCl solution and it has a potential use for separation and preconcentration of Hg^{2+} ions from contaminated natural waters.

1. Introduction

The pollution of water resources due to the indiscriminate disposal of transition metals has been causing worldwide concern for the last few decades. It is well known that some metals can have toxic or harmful effect on many forms of living organism. They are known to induce severe diseases like nervous system damage and even cancer. Such as, mercury targets the central nervous system causing mental and motor dysfunctions, as demonstrated by the Minamata Bay disease generated by the presence of mercury in the food chain (Muzzarelli, 2011). Therefore, transition metal detection and removal for contaminated water seems to be particularly important.

Effective treatments of industrial waste streams and toxic spills containing transition metals depend on the rapid removal of metal ions. The main techniques that have been widely used to remove transition metals from industrial effluents are chemical precipitation, complexation, ion exchange, evaporation, electrodeposition, liquid–liquid extraction, membrane separation, advanced oxidation processes, electrolysis, reverse osmosis and biological treatment. However, these methods are ineffective or expensive, especially when the transition metal ions are present in the wastewater at low concentrations. In contrast, the adsorption as an economical, effective and widely used method of transition metals ions removal has attracted a lot of interest for water treatment. The great advantages of this method over others are simple operation, waste less, easy metal recovery and the good reusability of the adsorbent (Benassi et al., 2006; Monier & Abdel-Latif, 2012; Ng, Cheung, & McKay, 2003; Vasconcelos, Fávere, Gonçalves, & Laranjeira, 2007). Due to the technical and economical point of view, now much attention has been focused on low cost adsorbents, such as chitosan, for the removal of metal ions.

Chitosan, which is usually obtained by alkaline deacetylation of chitin, a natural chelating polymer found in the exoskeletons of crustaceans such as crabs, prawns, shrimps and lobsters, which are waste products of the seafood processing industries. Chitosan has many excellent properties such as abundance, non-toxicity, hydrophilicity, biodegradability, adsorption properties, and wide application potential (Chiou & Li, 2003; Muzzarelli & Rocchetti, 1974; Wu, Tseng, & Juang, 2001; Zhou, Wang, Liu, & Huang, 2009). It is well known that chitosan is effective in the adsorption of transition metals because of the high content of $-NH_2$ groups and $-OH$ groups, which can serve as coordination sites. However, chitosan is soluble in acidic solutions and its applications are limited. Several methods have been used to modify natural chitosan either physically or chemically in order to improve the adsorption capacity. Crosslinking with glutaraldehyde (GLA), epichlorohydrin (ECH), ethylene glycol diglycidyl ether (EGDE), genipin and triphosphate (TPP) can be cited as examples of chitosan chemical modifications.

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These reactions are done in order to prevent from dissolving in acidic solutions or to improve metal sorption properties. It must be taken into account that cross linking can reduce the adsorption capacity. Such as, chitosan was cross-linked with both epichlorohydrin and triphosphate and the maximum adsorption capacities for Cu^{2+} was 130.72 mg/g (Laus & Fávere, 2011); HPAM-chitosan gel beads were prepared and they were demonstrated to be an effective adsorbent for removal of Cu^{2+}, Pb^{2+}, and Hg^{2+} from aqueous solutions, the adsorption capacities of Cu^{2+}, Pb^{2+}, and Hg^{2+} were 43.8 mg/g, 350.1 mg/g, and 102.3 mg/g, respectively (Cao, Tan, Che, & Xin, 2010). Therefore, in order to increase the adsorption capacity, it is necessary to introduce further modification for cross-linked chitosan. Heterocycle ligands usually contain different kinds of donor atoms, and the electronic and steric effects of these atoms in the heterocycle ligands may make them more selective for specific metal ion adsorption.

In this work, we have successfully designed a new chitosan microsphere (CBM-chitosan) containing 2-(chloromethyl) benzimidazole functional groups which has good application to the separation and preconcentration of Hg^{2+} from aqueous solutions. Elemental analysis (EA), Fourier transform infrared spectroscopy (FTIR) and thermo gravimetric analyzer (TGA) were used to characterize the novel microspheres. The synthesis conditions such as reaction solvent, reaction temperature, and molar ratio of reagents have been optimized. Meanwhile the influence of experimental parameters such as pH, temperature and time on Hg^{2+} adsorption has been revealed. The data of adsorption kinetics and thermodynamics were investigated. CBM-chitosan microsphere is expected to be a chelating microsphere with high adsorption uptake and selectivity for Hg^{2+}, and it was supposed to be widely applied to determination of metal ion in waters and foods.

2. Experimental

2.1. Materials

Chitosan as powder was purchased from JinKe Biological Co., Ltd. Zhejiang, the degree of deacetylation was reported to be 87% by the manufacturer. Epichlorohydrin (ECH) was purchased from Chemical Reagent Factory of Shanghai. CBM was purchased from J & K Chemical Technology Co., Ltd. of Shanghai. Salts and reactive solvents including N, N-dimethylformamide (DMF), 1,4-dioxane and toluene were purchased from the Sinopharm Group Chemical Reagent Co. Ltd., China. The standard stock solutions were prepared by dissolving an appropriate amount of salts in deionized water, respectively. Acetic acid-sodium acetate (NaAc-HAc) (pH 3.0–5.5) was employed as the buffer solution to control the pH of the solutions. All other reagents were of analytical grade.

A Mettler Toledo Delta 320 pH meter was used for measuring pH of solutions. C, H and N elements were analyzed by Elemental Analyzer Vario EL. IR spectra for the samples were obtained from a Nicolet 380 FTIR spectroscopy. The thermo-gravimetric analysis was investigated using Mettler TGA/DSC1 simultaneous thermal analyzer (with a temperature range of 50–1000 °C, heating rate of 20 °C/min, and atmosphere of N_2). Batch experiments were carried out in the DSHZ-300A temperature constant shaking machine.

2.2. Preparation of novel cross-linked chitosan microsphere

The CBM-chitosan microsphere was synthesized in two major steps:

2.2.1. The synthesis of cross-linked chitosan

The preparation of cross-linked chitosan CCST was carried out according to the following procedures: 0.5 g chitosan was fully dissolved in 12.5 mL 4% acetic acid in a 100 mL three-necked flask, and then added 55 mL liquid paraffin. After 10 min stirred at 350r/min, the mixture was heated to 55 °C and added two drops span-80 to emulsified for 10 min. When the temperature reached 60 °C, 1.5 mL of formaldehyde solution was added. 1.5 h later, added slowly dropwise, 5% NaOH solution at constant pressure dropping funnel in order to kept alkaline. The temperature was raised to 70 °C added slowly dropwise 1.5 mL epichlorohydrin solution with constant pressure dropping funnel for 5 h. Then cross-linked chitosan microspheres (CCTS) were suction filtered carefully and washed thoroughly with petroleum ether, anhydrous ethanol and distilled water. 0.78 g CCTS was obtained after dried in a vacuum at 50 °C.

2.2.2. The further modification of cross-linked chitosan

Deprotected CCTS was prepared by the following steps: CCTS was treated with 50 mL 1 mol/L HCl at 70 °C for 9 h, caustic and pickling, washed with distilled water until neutral, and dried in a vacuum at 50 °C.

20 mg deprotected CCTS moved into a 100 mL three-necked flask with 20 mL reaction solvent and soak overnight. Adding the mass ratio of the ligand reagent (CBM) and stirring at 70 °C, 80 °C, 90 °C or 100 °C in the catalyst and under nitrogen for 12 h (please take the corresponding protection measures). After completion reaction, the modified chitosan microspheres soaked and washed with reaction solvent until the washing liquid was colorless, washed thoroughly by acetone, ether, ethanol, distilled water, and then soaked with NaOH solution, washed with distilled water until neutral, soaked with HCl solution washed with water until neutral, dried under vacuum at 50 °C to spare.

2.3. Adsorption experiment

Batch adsorption experiments were conducted by 15.0 mg CBM-chitosan in 100 mL conical flasks containing 20 mL buffer solution with different pH (pH = 5.5, 5, 4.5, 4, 3.5, 3). After shaken in a shaker at constant temperature for 24 h, 10 mL standard metal ion solution was put in. The upper layer liquid was taken for analysis by UV spectrophotometer until adsorption equilibrium reached. With respect to the kinetic tests, the aqueous samples were taken at preset time intervals and the concentrations of metal ions were similarly measured.

The adsorption capacity (Q_e) and distribution coefficient (D) were calculated with the following formulas, respectively (Fethiye & Erol, 2006; Xiong & Yao, 2009):

$$Q_e = \frac{(C_0 C_e)V}{m} \quad (1)$$

$$D = \frac{Q_e}{C_e} \quad (2)$$

where C_0 (mg/mL) and C_e (mg/mL) are the initial and equilibrium metal ion concentrations, respectively, V (mL) is the total volume of solution, and m (g) is the mass of the microspheres.

Column experiments were conducted in a fixed-bed mini glass column (3 mm inner diameter × 30 cm long) with 100.0 mg of microspheres. The CBM-chitosan in the column was presoaked for 24 h (the height was 8.5 cm) before the experiment was started. Hg^{2+} ion solution of 0.10 mg/mL and flow rate 0.10 mL/min was passed continuously through the stationary bed of sorbent in upflow mode to avoid channeling of the effluent. The samples in the outlet were taken at the preset volume intervals and the concentrations of metal ions were similarly determined as above. The adsorption capacity (Q_e) was calculated with the following formula (Tabakci & Yilmaz, 2008):

$$Q_e = \int_0^{v} \frac{(C_0 - C_i)}{m} dV \quad (3)$$

where C_0 (mg/mL) and C_i (mg/mL) are the influent and effluent metal ion concentrations, respectively; V (mL) for the outflow of the liquid volume; m (g) is the mass of the microspheres.

2.4. Desorption

Desorption experiments were performed immediately following the completion of the adsorption experiments.

2.4.1. Batch desorption

At the end of adsorption experiments, the exhausted solids were separated from the aqueous solution by filtration, washed by deionized water and were stirred with different eluent solutions of various concentrations, oscillating to balance at constant temperature. The final metal ion concentration in the aqueous phase was similarly analyzed as above. Desorption ratio was calculated from the ratio between the amount of metal ions adsorbed on the microspheres and that in the elution medium.

$$E\ (\%) = \frac{(C_d V_d)}{(C_0 - C_e)V} \times 100 \quad (4)$$

where C_d (mg/mL) is the balance metal ion concentration of the desorption liquid; V_d (mL) is the desorption solution volume. C_0, C_e and V (mL) for the outflow of the liquid volume.

2.4.2. Column desorption

In order to wash out unabsorbed metal ions, flush microspheres five times with optimal pH NaAc-HAc buffer solution. Then column desorption experiments carried on by use the preferred desorption conditions obtained in the batch desorption experiments. The samples in the outlet were taken at the preset volume intervals and the concentrations of metal ions were similarly determined as above, until the concentration of metal ions in the effluent is zero.

3. Results and discussions

3.1. Synthesis of novel cross-linked chitosan microspheres

The effect of different solvents, reaction temperatures and molar ratio on the synthesis process was investigated. Due to the boiling point (152.8 °C, 110.8 °C and 101.4 °C), the reaction solvent DMF, toluene and 1,4-dioxane were chosen respectively 100 °C was selected as the maximum temperature of reaction, and the other temperatures were 90 °C, 80 °C and 70 °C. Mass ratio of the cross-linked chitosan microspheres and ligand were chosen as 1:1, 1:2, 1:3, 1:4 and 1:5, respectively.

The optimal synthesis conditions were determined according the change of N element content. Maximum nitrogen content (20.83%) was obtained when the reaction solvent was DMF, mass ratio was 1:5 and temperature was 100 °C. However, before modified, the nitrogen content of CCTS was only 5.15%. The average diameter of the CBM-chitosan was about 300 μm.

3.2. Infrared spectra and thermo-gravimetric analysis of CBM-chitosan

As shows in Fig. 1(a), the appearance of CBM characteristics bands near 3411 cm^{-1} was due to the N—H stretching vibrations of amine and secondary amine groups. Absorption peak at 1623 cm^{-1}, 1593 cm^{-1} and 1440 cm^{-1} indicated the presence of the aromatic ring. The absorption peak at 698 cm^{-1} was caused by the C—Cl stretching vibration. Fig. 1(b) shows that CBM-chitosan absorption peak at 3429 cm^{-1} was strengthened, absorption peak at 1585 cm^{-1} suggested that there's hardly any primary amine NH bending vibration, at 1623 cm^{-1} and 1440 cm^{-1} appears the benzene ring characteristic absorption peaks, there was no absorption peak of C—Cl near at 698 cm^{-1}, indicated the substitution reaction between chitosan primary amine and chloromethyl of the ligand.

TGA curves for CCTS, CBM and CBM-chitosan are shown in Fig. 1(c). Two decomposition steps are observed in the curves. The first step, from 220 to 370 °C, CCTS's weightlessness became evident, because skeleton began to decomposition; for CBM, weight loss was 45.6% and fast; the weight loss ratio of CBM-chitosan was higher. The second step, beginning at about 370 °C, decomposition of CCTS became flatten gradually; weightlessness ratio of CBM was fast and then became slower relatively; for CBM-chitosan, weight loss was evident but slower, which due to decomposition of grafted ligand and chitosan. These indicated that CBM-chitosan has good thermal stability.

3.3. Batch studies

3.3.1. Influence of pH

The pH of the aqueous solution is an important parameter in adsorption processes (Xiong, Yao, & Wu, 2008). In this study, the influence of pH on the adsorption behavior of CBM-chitosan for Hg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+} was studied in the pH range of 3.0–5.5. The results were illustrated in Fig. 2. It suggested that CBM-chitosan has much higher affinity toward Hg^{2+} than the other four kinds of metal ions from aqueous solutions indicating a high selectivity. The optimal adsorption condition of the metal ions was obtained at pH 4.5 for Hg^{2+}.

3.3.2. Adsorption kinetics

The kinetics of adsorption that describes the solute uptake rate is one of the most important characteristics that define the efficiency of sorption. The kinetic sorption data was treated with two simplified kinetic models including First-order kinetics model and Second-order kinetics model. The First-order kinetics model (Ho & McKay, 1999; Keskinkan, Goksu, Basibuyuk, & Forster, 2004) is expressed as follows:

$$\log(Q_e - Q_t) = \log\ Q_e - \frac{K_1 t}{2.303} \quad (5)$$

where k_1 (min^{-1}) is the First-order kinetics rate constant of adsorption, and Q_e (mg/g) and Q_t (mg/g) are the amounts of metal ion adsorbed at equilibrium and time t (min), respectively.

The Second-order kinetics model (Ho, Ng, & McKay, 2001) is expressed as follows:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (6)$$

where k_2 (g/(mg min)) is the Second-order kinetics rate constant of adsorption.

As shown in Table 1, the experimental data for adsorption of Hg^{2+} on CBM-chitosan showed better correlation coefficient for Second-order kinetics model (Jha, Van, Lee, Jeong, & Yoo, 2009).

3.3.3. Adsorption isotherms

The equilibrium adsorption isotherm is fundamental in describing the interactive behavior between the adsorbate and adsorbent. In this study, both models were used to describe the relationship between the adsorbed amount of Hg^{2+} ions and its equilibrium concentration in solution at three separate temperatures (288 K, 298 K and 308 K).

The expression for the Langmuir isotherm (Langmuir, 1918) is:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \quad (7)$$

where Q_e (mg/g) is the equilibrium Hg^{2+} ions adsorption capacity, C_e (mg/mL) is the equilibrium Hg^{2+} ions concentration in solution,

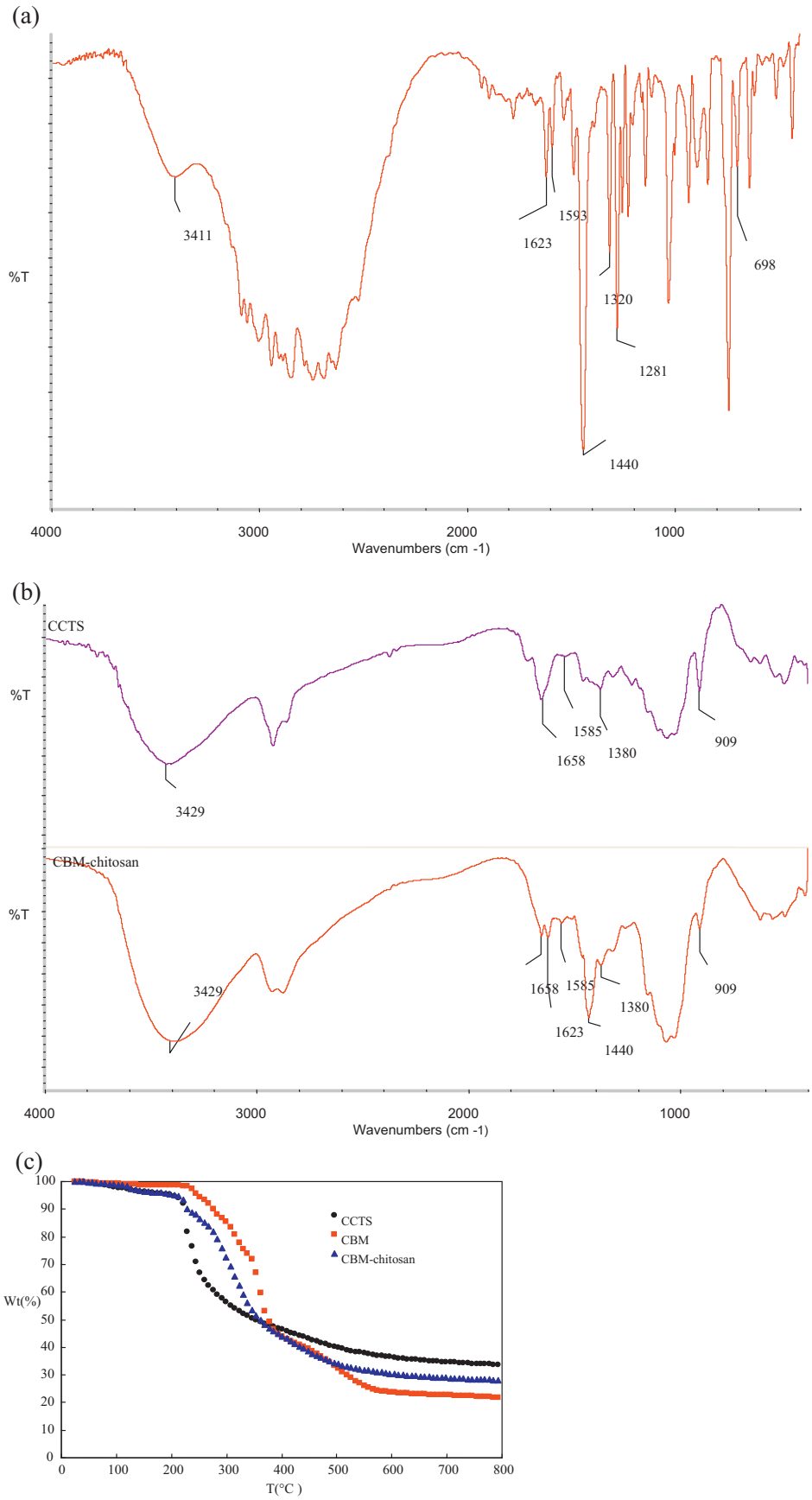

Fig. 1. IR spectra of CBM (a); IR spectra of CCTS and CBM-chitosan (b); TGA of CBM, CCTS and CBM-chitosan (c).

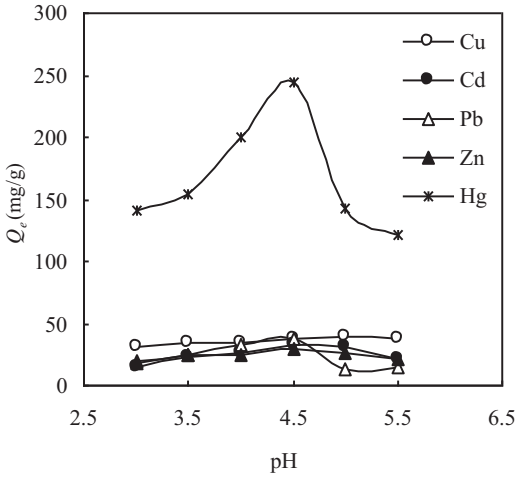

Fig. 2. Adsorption capacity of CBM-chitosan in different pH.

Q_m (mg/g) is the theoretical monolayer adsorption capacity of the adsorbent, b is the Langmuir constant and related to the free energy of adsorption.

Langmuir isotherm assumes that the adsorption occurs at specific homogeneous adsorption sites within the adsorbent. Furthermore, it assumes monolayer adsorption and maximum adsorption occurs when adsorbed molecules on the surface of the adsorbent form a saturated layer. All adsorption sites involved are energetically identical and the intermolecular force decreases as the distance from the adsorption surface increases.

Unlike the Langmuir isotherm model, the Freundlich isotherm expresses adsorption at multilayer and on energetically. Freundlich isotherm (Freundlich, 1906) can be expressed as follows:

$$lg\, Q_e = lg\, K_f + \frac{1}{n} lg\, C_e \quad (8)$$

where K_f is Freundlich constant and n (dimensionless) is the heterogeneity factor.

According to the results that show in Fig. 3(a) and (b), higher R^2 values ($R^2_{288\,K} = 0.9989$, $R^2_{298\,K} = 0.9988$, $R^2_{308\,K} = 0.9984$) were obtained from Langmuir model for Hg^{2+} than from the Freundlich model ($R^2_{288\,K} = 0.9974$, $R^2_{298\,K} = 0.9434$, $R^2_{308\,K} = 0.9204$), suggesting the applicability of Langmuir model to this system. This indicates that the adsorption of Hg^{2+} ions by CBM-chitosan is monolayer-type.

3.3.4. Thermodynamic parameters

Adsorption experiments to study the effect of temperature on Hg^{2+} adsorption by CBM-chitosan were carried out at 288, 298 and 308 K separately. Thermodynamic parameters such as standard free energy change (ΔG), standard enthalpy change (ΔH) and standard entropy change (ΔS) were calculated by using the following equations (Ünlü & Ersoz, 2006):

$$lg\, D = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \quad (9)$$

$$\Delta G = \Delta H - T\Delta S \quad (10)$$

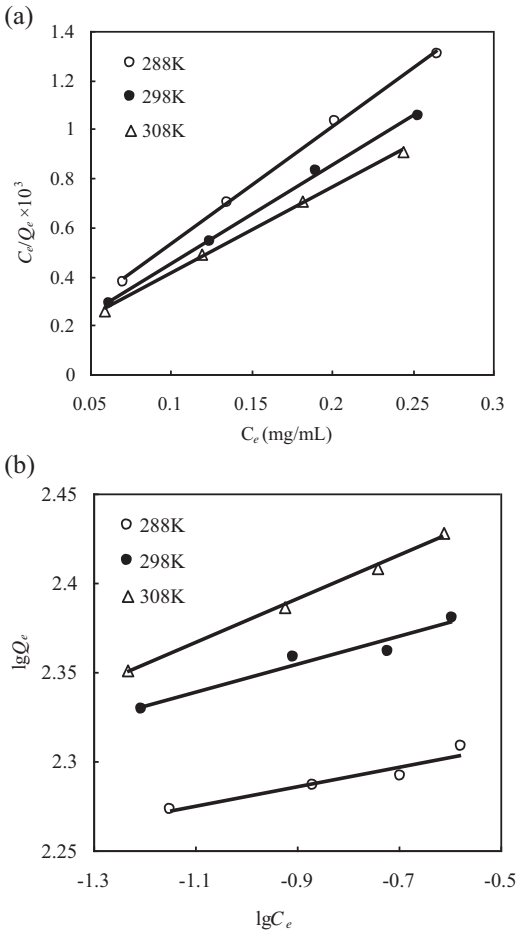

Fig. 3. Langmuir isotherm and Freundlich isotherm curves of Hg^{2+}.

Table 2
Thermodynamic parameters calculated for adsorption of Hg^{2+} on CBM-chitosan at different temperatures.

T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)
288	−15.9	13.3	101.6
298	−16.9		
308	−18		

where R is the gas constant (8.314 J/(mol K)), and T is the absolute temperature. The plot of lg D versus $1/T$ gives the straight line from which ΔH and ΔS were calculated. Then the free energy variation, ΔG was obtained from equation.

The results are tabulated in Table 2. As presented in the table, the negative ΔG values at given temperatures indicate the spontaneous nature of the adsorption and confirm the feasibility of the adsorption process. The positive value of ΔH reveals that the adsorption is endothermic in nature. The enthalpy change value is 13.3 kJ/mol, indicating that physisorption and chemisorption coexist during adsorption process. Positive ΔS value of Hg^{2+} adsorption process

Table 1
The First-order and Second-order kinetics constants for adsorption of Hg^{2+} on CBM-chitosan.

T (K)	First-order			Second-order		
	k_1 (min^{-1})	Q_e (mg/g)	R^2	k_2 (g/mg min)	Q_e (mg/g)	R^2
288	0.0055	257.2	0.9709	3.98×10^{-7}	227.6	0.9912
298	0.0053	268.3	0.9670	2.38×10^{-7}	262.4	0.9927
308	0.0055	283.5	0.9943	1.21×10^{-7}	283.5	0.9964

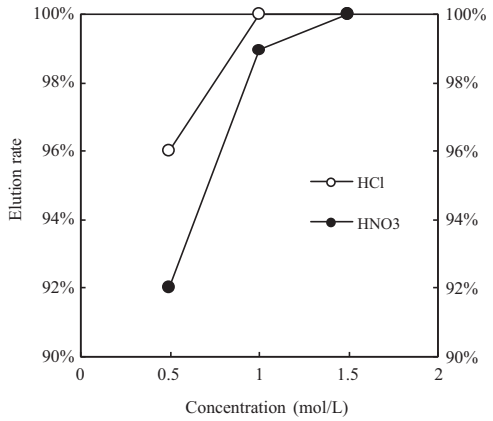

Fig. 4. Elution test of CBM-chitosan for Hg^{2+}.

indicates an irregular increase of the randomness at CBM-chitosan interface during adsorption.

3.3.5. Elution

Desorption performance of the adsorbent material is closely related to the recovery of metal ions. It can be used to judge property of adsorbent. For repeated use of an adsorbent, adsorbed metal ions should be easily desorbed under suitable conditions. In this work, desorption of the adsorbed mercury ions from CBM-chitosan was studied. The mercury ions loaded onto CBM-chitosan were eluded with HCl and HNO_3 in various concentrations, respectively. The results were shown in Fig. 4, as can be seen from the figure, among the two kinds of eluents, HCl solution offered the best performance. Maximum recovery of Hg^{2+}, at 100%, was achieved with a 1.0 mol/L HCl solution under the experimental condition.

3.4. Column studies

3.4.1. Dynamic adsorption curve

The performance of packed beds is described through the concept of the breakthrough curve. It shows the loading behavior of Hg^{2+} to be removed from solution in a fixed bed. It is usually expressed in terms of adsorbed Hg^{2+} concentration (C_{ad} = inlet Hg^{2+} concentration (C_0) outlet Hg^{2+} concentration (C_e)) or normalized concentration defined as the ratio of effluent Hg^{2+} concentration to inlet Hg^{2+} concentration (C_e/C_0) as a function of time or volume of effluent for a given bed height. Successful design of a column adsorption process requires prediction of the concentration versus time profile or breakthrough curve for the effluent. The maximum sorption capacity of CBM-chitosan is also in design.

To experiment, the standard concentration of Hg^{2+} ions was 0.1 mg/mL, the flow rate was 0.1 mL/min, the samples in the outlet were taken at the preset volume intervals and the concentrations of metal ions were similarly determined as above. Until the concentration of metal ions in the effluent $C_e = C_0$. As shown in Fig. 5(a), the breakthrough point of adsorption at 100 mL, when $V < 100$ mL, the metal ions were almost completely adsorbed, $V = 600$ mL, Hg^{2+} was almost completely outflow, this suggested that the dynamic adsorption has reached saturation. The maximum dynamic adsorption capacity for Hg^{2+} was 257.8 mg/g.

3.4.2. Dynamic desorption curve

It was essential to elute adsorbed solute efficiently from CBM-chitosan. When the dynamic adsorption reached saturation, desorption experiment was performed in the same column. The samples in the outlet were taken at the preset volume intervals and the concentrations of metal ions were similarly determined as above, until the concentration of metal ions in the effluent is zero.

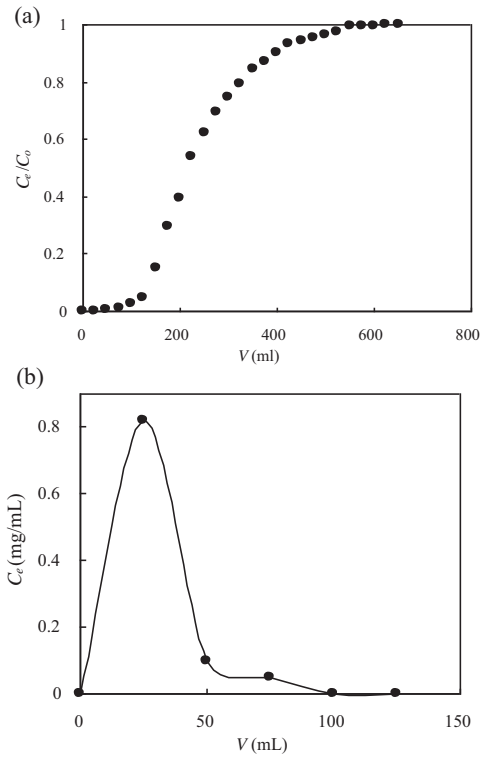

Fig. 5. Breakthrough and desorption curves of Hg^{2+}.

From Fig. 5(b), when the eluate of the effluent reached 100 mL, CBM-chitosan was eluted completely. This is an important property of the adsorbent material, and to lay some foundation for its practical application.

4. Conclusion

A novel chelating cross-linked chitosan microsphere has been synthesized and well characterized by FTIR and EA, and it was successfully employed as a novel adsorbent material for separation and preconcentration of Hg^{2+} from aqueous solution carried out through batch and column methods. Kinetics and thermodynamic studies indicated that the adsorption process was endothermic spontaneous reaction and kinetically proceeded according to Second-order kinetics model. In addition, the adsorption process proceeds followed the Langmuir isotherm. The microsphere can be eluted effectively using 1.0 mol/L HCl solution and was supposed to be widely applied to determination of metal ion in waters and foods.

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