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Adsorption properties of gold onto a chitosan derivative

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ABSTRACT

In order to find a material which can be used for the recovery of Au(III), a chitosan derivative was synthesized by carboxymethylation and grafting sulfur groups onto cross-linked chitosan backbone. Adsorption studies were carried out at different pH values to optimize the pH condition. Batch method was conducted to study the effects of parameters such as reaction time, initial metal concentration and temperature on Au(III) sorption. The maximum adsorption affinity for Au(III) was found to be 8.32 mmol/g at pH 4.0, 25 °C. The results of kinetic study showed that the adsorption reaction followed the pseudo second order model. The derivative showed high adsorption ability and reusability toward Au(III). All results suggested that the chitosan derivative had potential to be utilized in the recovery of Au(III) from aqueous medium.

1. Introduction

Scarcity of precious metals including gold, silver, platinum and palladium makes their recovery valuable and significant. To avoid more precious metals being mined, efforts are made to recover them from various sources such as ores, electronic waste, computer scrap and aqueous wastes. Several technologies have been developed to recover precious metals, including precipitation [1], ion exchange [2] and adsorption [3–6]. Among all the applied technologies, adsorption has been focused more and more on its high efficiency and is probably the most suitable for treating large volumes of aqueous wastes economically [7–11].

Chitosan is a popular adsorbent available to remove precious metals from aqueous medium, and also might provide an environmental advantage for its degradability [12]. Chitosan has great potential to deal with a variety of aquatic pollutants, especially heavy metals, because it contains a large number of amino and hydroxyl functional groups [13]. Compared to other biomaterials, chitosan is an attractive alternative because of its good chemical stability, excellent chelation capacity, high selectivity [14] and low toxicity. Natural chitosan could be modified by several methods to enhance its adsorption ability toward precious metals [15,16]. In this study, we synthesized a chitosan derivative and studied the adsorption behavior of the derivative toward gold in aqueous solution. ICP-OES was used to determine the metal ion concentration and both kinetic and thermodynamic data were also investigated.

2. Experimental

2.1. Materials and instrumentation

Chitosan with 80 mesh, 96% degree of deacetylation and average-molecular weight of 6.36 × 105 was purchased from Qingdao Baicheng Biochemical Corp. (China). All the other chemicals and reagents used in this study were from Sigma Chemicals Co. Standard solution of gold (1000 mg/L) for ICP-OES was obtained from Beijing NCS Analytical Instruments Co. Ltd. Metal ions of nitrate form was used and all the chemicals used were of analytical grade.

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Thermo-Fisher, iCAP6300 radial) was used to determine the concentration of metal ions. Neblizer size: 0.1 ml/min; Repeats = 3; Flush time = 23 s; RF Power = 1100 w; Pump rate = 16 rpm; View height = 13 mm.

2.2. Synthesis of the chitosan derivative

(1) 3 g chitosan and 50 ml of 50 wt% NaOH solution were added into a flask to swell and alkalize at room temperature for 24 h. 7.5 g of monochloroacetic acid was dissolved in 40 ml of isopropanol, and then added drop-wise to the flask containing the alkalized chitosan after filtration for 30 min. The mixture was reacted for 8 h at room temperature and then the filtrate was obtained and dissolved in 150 ml of water. 2.5 M HCl was added to it to adjust its pH to 7, and then the solution was centrifuged to remove the precipitate. 600 ml of anhydrous ethanol was added and the precipitate was carboxymethyl chitosan.

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(2) 9.0 g of thiourea was dissolved in 60 ml distilled water. A 51.3 ml of (50%) glutaraldehyde solution was added to thiourea solution in a flask. The mixture was reacted for 3 h on a water bath at 323 K, and then the product of step (1) was dissolved in 50 ml distilled water and added to the mixture of the flask. The reaction was continued under vigorous stirring for 8 h at 343 K. The product was washed several times with dilute sodium hydroxide, distilled water and acetone, respectively, and then was dried at 333 K for 3 h and weighed about 9.18 g. The particle size fraction between 0.1 and 0.5 mm was sieved and used in this study.

2.3. Adsorption experiments

The experiments were performed by placing 0.1 g of the product in a series of flasks containing 100 ml 1×10^{-2} mol/L metal ion solution. 0.1 mol/L HNO_3 and 0.1 mol/L NaOH were used to adjust the solution to the desired pH, and then the flasks were shaken at 300 rpm for 12 h at 25 °C. The metal ion concentration of the filtrate of each flask was obtained for further study.

The kinetic study was performed by placing 0.1 g of the chitosan derivative in a series of flasks containing 100 ml of Au(III) solution with initial concentration of 1×10^{-2} mol/L and pH 4.0. The contents of the flasks were shaken at 25 °C. Five milliliters of samples were taken at scheduled time intervals to analyze the change of Au(III) concentration.

The effect of initial concentration was studied by placing 0.1 g of the product in Au(III) solution with various initial concentrations ranging from 0.002 to 0.012 mmol/L at 25 °C and pH 4.0. The thermodynamic study was also performed at 25, 35, 45 and 55 °C.

2.4. Desorption studies

The chitosan derivative after Au (III)-adsorption experiments were gathered and washed with deionized water. Then batch method were carried out for desorption of Au (III) using different concentrations of thiourea, HCl and thiourea–HCl solutions. The chitosan derivative after desorption was reused and the process was repeated for five times.

3. Results and discussion

3.1. The pH effect on Au(III) sorption

Because there was colloidal precipitate of $Au(OH)_3$ formed above pH 4 which avoided studying the adsorption of Au(III) ions in basic media [17], we mainly studied the pH effect ranging from 1.0 to 4.0. The point of zero charge (pH_{ZPC}) of this derivative was found to be 4.5. In Fig. 1, when the pH rises, the adsorption of Au(III) increases until reaching a maximum value around pH 4.0. In the literature, there are several mechanisms used for explanation of the adsorption of precious metals onto chitosan derivatives, such as ion exchange, electrostatic attraction and chelation. In this study, chelation can explain the adsorption behavior very well. Due to the existence of free lone pairs of electrons on nitrogen and sulfur atoms, it is possible for the derivative and metal to form a relatively stable complex [18,19].

SEM micrograph of the derivative is shown in Fig. 2. The diameters of most of the synthesized derivative particles are below 0.5 mm. The derivative particle has irregular shape, and also there are holes in each particle. The existence of the holes in the derivative particles could help gold ion adhere onto the derivative.

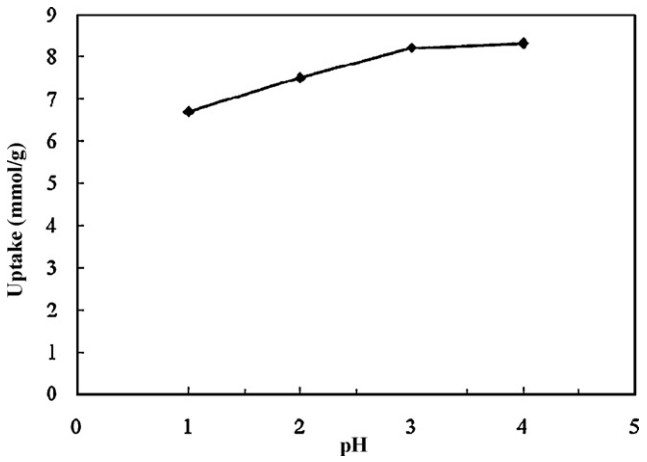

Fig. 1. Effect of pH on the uptake of Au(III).

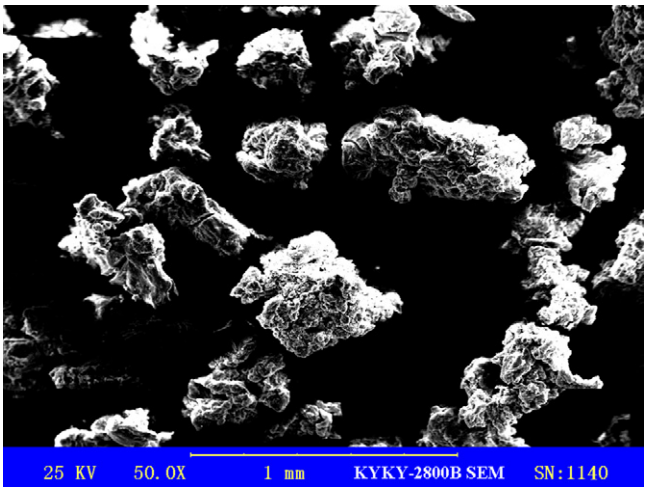

Fig. 2. SEM micrograph of the chitosan derivative.

3.2. Adsorption kinetics

In Fig. 3, it is clearly seen that the uptake of Au(III) could reach the maximum value 8.32 mmol/g within 3.5 h. In our former study, the kinetic mechanism for this chitosan derivative to adsorb metal ions like mercury and silver follows pseudo second order kinetic model. Therefore, we still use pseudo second order model in this study to evaluate the adsorption process of Au(III).

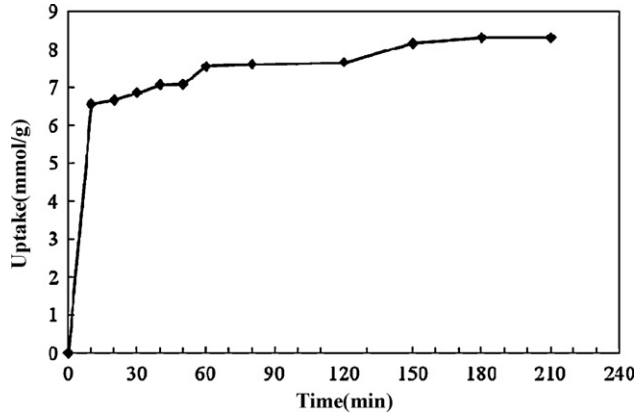

Fig. 3. Influence of time on the uptake of Au(III).

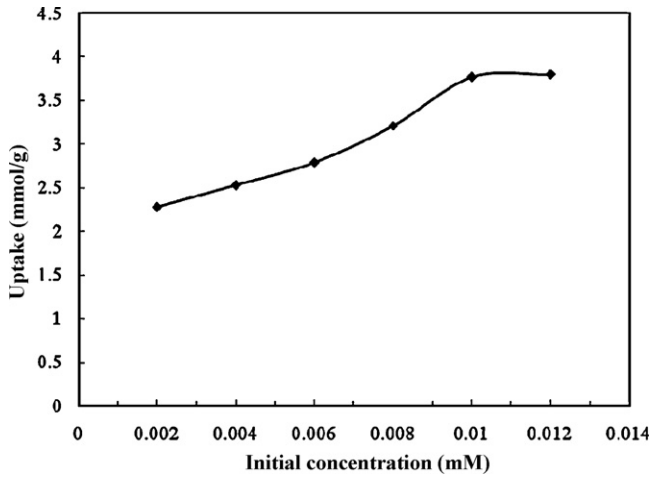

Fig. 4. The effect of initial concentration on the uptake of Au(III).

The pseudo second order model [20] is expressed as:

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

After calculated following the equation above, k_2 (rate constant of adsorption) is 0.016 g/(mmol min). q_e (the amount of metal ion adsorbed at equilibrium) is 8.47 mmol/g near the experimental data and the R^2 value is 0.997. t is reaction time and q_t is the amount of metal ion adsorbed at time t. Accordingly, the adsorption of Au(III) onto the derivative fits pseudo second order model very well, which implies the main adsorption mechanism may be chemical adsorption.

3.3. Adsorption isotherms

Fig. 4 shows the derivative's adsorption capacity for Au(III) in solution with various initial metal concentration. As the initial concentration increases, it is also seen that the uptake of Au(III) increases while slows down around 0.01 mmol/L. Fig. 5 shows the adsorption isotherms of Au(III) onto the chitosan derivative. The adsorption of Au(III) decreases as the temperature increases and the maximum uptake value was 8.32 mmol/g at 25 °C. The rearranged Langmuir equation is used to explain Au(III) adsorption [21].

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{max}} + \frac{1}{K_L Q_{max}} \quad (2)$$

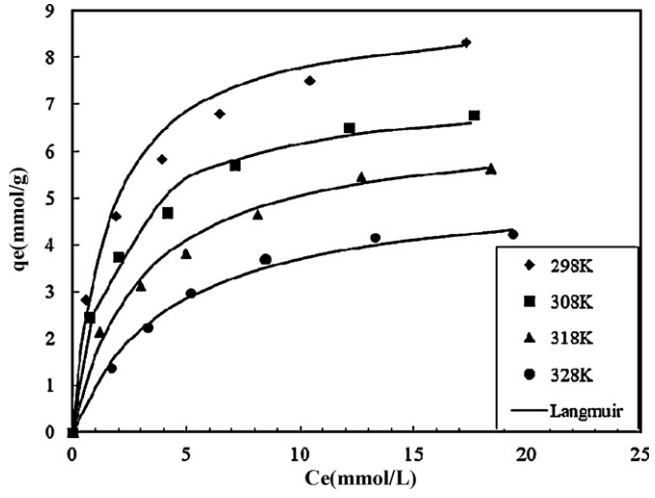

Fig. 5. Plots of Langmuir model for Au(III) adsorption.

Table 1
Data of Langmuir model for adsorption of Au(III).

Temperature (K)	Langmuir model		
	Q_{max} (mmol/g)	K_L (L/mmol)	R^2
298	8.27	0.623	0.9962
308	6.61	0.549	0.9948
318	5.65	0.330	0.9958
328	4.34	0.234	0.9926

Table 2
Maximum adsorption capacities for adsorption of Au(III) onto various adsorbents.

Absorbent	Adsorption capacity (mmol/g)
Chitosan derivatives [17]	3.0
Glycine modified crosslinked chitosan [23]	0.86
Chemically modified chitosan with magnetic properties [24]	3.6
L-Lysine modified crosslinked chitosan resin [25]	0.357
Chitosan derivative (this work)	8.32

where q_e (mmol/g) is the amount of metal ions adsorbed and C_e is the concentration of metal ions in solution (mmol/L) at equilibrium. Q_{max} is the theoretical saturated adsorption ability (mmol/g) and K_L is the Langmuir binding constant which represents affinity of binding sites (L/mmol). Table 1 listed the values of Q_{max} and K_L at different temperatures. All the results suggested that the Langmuir isotherm model can perfectly describe the adsorption isotherms.

The equilibrium parameter R_L could be calculated to identify whether the chitosan derivative is suitable for adsorption of Au(III):

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

where K_L is the Langmuir constant and C_0 is the initial metal concentration. The R_L value between 0 and 1 means the adsorption system is suitable [22]. In this study, the values of R_L at 25 °C lie between 0.993 and 0.998, which suggests the adsorption of Au(III) onto the chitosan derivative was favorable.

Table 2 compares the maximum uptake of the chitosan derivative for Au(III) with other chitosan adsorbents reported in the literature. The result demonstrated that the adsorption capacity of the derivative we synthesized was relatively higher than several other adsorbents.

3.4. Desorption and regeneration

Batch method was used to remove Au(III) from the chitosan derivative with various concentrations of HCl, thiourea and thiourea–HCl solutions. The desorption data was presented in Table 3, and it was found that 0.5 mol/L thiourea–2.0 mol/L HCl solution could remove Au(III) most effectively and the desorption efficiency was above 98%. The derivative after desorption was

Table 3
Desorption data.

Desorption agent	Desorption efficiency (%)
0.1 mol/L thiourea	30.75
0.3 mol/L thiourea	69.42
0.5 mol/L thiourea	80.90
1.0 mol/L thiourea	87.67
0.5 mol/L HCl	35.78
1.0 mol/L HCl	64.33
1.5 mol/L HCl	79.72
2.0 mol/L HCl	81.20
0.5 mol/L thiourea–2.0 mol/L HCl	98.91

reused and the results demonstrated that its adsorption capability was not significantly changed up to 5 cycles. The uptake of Au(III) was 8.32, 8.20, 8.15, 8.13 and 8.08 mmol/g, respectively. Therefore, the chitosan derivative we synthesized could be utilized for the recovery of Au(III) from wastewater or other aqueous medium.

4. Conclusions

A chitosan derivative was synthesized and its adsorption behavior of Au(III) from aqueous solution was investigated. The novel derivative showed high adsorption ability toward Au(III) and parameters like pH of solution, initial concentration of Au(III) and contact time all influenced the adsorption process. As illustrated in the experimental data, the derivative's adsorption process for Au(III) followed the pseudo second order kinetic model and conformed to the Langmuir equation. The 0.5 mol/L thiourea–2.0 mol/L HCl solution can effectively remove Au(III) and the adsorption capability of the derivative has no obvious change up to five cycles. This chitosan derivative we synthesized showed great potential in the recovery of Au(III) from aqueous solution.

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