Study on the Adsorption Properties of L-Alanine Modified Chitosan for Cesium Ion in Aqueous Solution

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Abstract—The chitosan was modified with L-alanine, which was used for the adsorption of cesium ion in aqueous solution. The results showed that: chitosan modified with L-alanine can remove cesium ions in the solution. When the initial concentration was kept as 150mg.L^{-1}, the optimal adsorption conditions were: The adsorption time is 100 min, the adsorption capacity was 29.502 mg/g; the adsorption temperature is 25°C, the adsorption capacity was 30.742mg/g; dosage of adsorbent was 0.1g, the adsorption capacity of 61.234 mg/g; pH was 8, the adsorption capacity of 30.121mg/g.

Keywords-Alanine; Modified; Chitosan; L-alanine; Adsorption; Cesium ion

I. INTRODUCTION

The water pollution is now a great challenge for the survival of human beings. Among them, the pollution of metal ions, such as Copper, Lead, Zinc, Chromium, Cadmium, Strontium, and Cesium and so on, causes more and more serious environmental problem [1-5].

Chitosan has been widely used as a kind of biomass adsorbent [6, 7], especially in the adsorption of heavy metal ion [8-11]. Chitosan molecule backbone has the active gene -NH_2 and –OH, which can be modified by inserting special groups to Chitosan. Due to the strong activity of -NH_2, chitosan moleculars can crosslink with glutaraldehyde, and then react with propylene oxide through nucleophilic addition. This process will insert active chlorine into the chitosan molecules; at last the carboxyl group of L-Alanine molecules could be inserted into chitosan molecules by the activity of chlorine atoms. The final product has carboxyl group, which has better affinity to metal ions and will benefit to the adsorption of Cs^+ ion in aqueous solution [12].

II. EXPERIMENT

A. Materials

Materials used in the experiments are obtained from Chengdu Kelong Reagent Company.

B. Experimental Methods

1) *Chitosan modification*

The chitosan was first dissolved into 2% acetic acid solution, and then sodium hydroxide solution was added slowly with constant stirring, at last a gel-like material formed. The gel like material was washed to neutral using deionized water and then dried at 45°C. Then 50 mL of methanol and 50% glutaraldehyde solution was added to the gel-like material at room temperature with stirring within 4 hours, and reacted for 6 hours at 55 °C and then filtrated. The filtration was washed with ethanol for 2-3 times. Then epoxy chloropropane, 2 mol/L NaOH solution, 10% dimethyl sulfoxide solution at 40°C were added into the filtration and stirred for 5 hours, stewing for some time and filtrated with Buchner funnel. The precipitation was then washed with deionized water to neutral and then drying at 30°C and obtained epichlorohydrin modified chitosan. 2 mol/L NaOH solution added into 2.0g L-alanine, and then 1mol/L pH=10.5 phosphate buffer solution was added into this solution together. After the above solution was entirely dissolved, epichlorohydrin modified chitosan was added and react for 24 hours with stirring at 70°C. Then the reaction solution was washed to neutral with deionized water, drying at 45 °C and gained the final product L-alanine modified chitosan [13-15].

2) *Cesium Ion of Adsorption Experiment*

Add 0.2 g L-alanine modified chitosan and 50 mL Cs^+ solution into 250 mL conical flask, and then sealed the flask and placed it on the constant temperature oscillator for planned time to finish the adsorption experiments. Centrifugating the suspension fluid after the adsorption experiment and extracting the clear liquid at upper level for latter experiments. Cesium ion concentration was determined by atomic absorption spectrophotometer.

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III. RESULTS AND DISCUSSION

A. *Characteristics of Modified Chitosan*

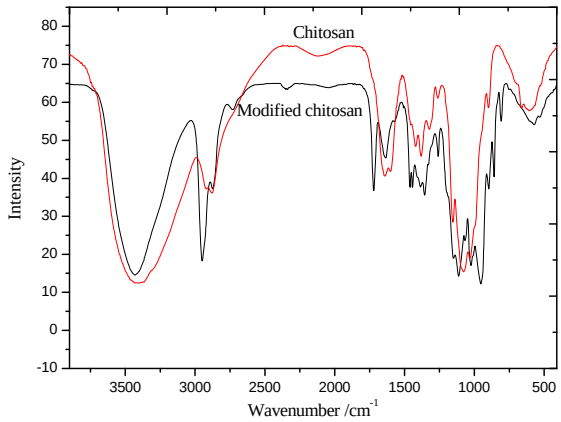
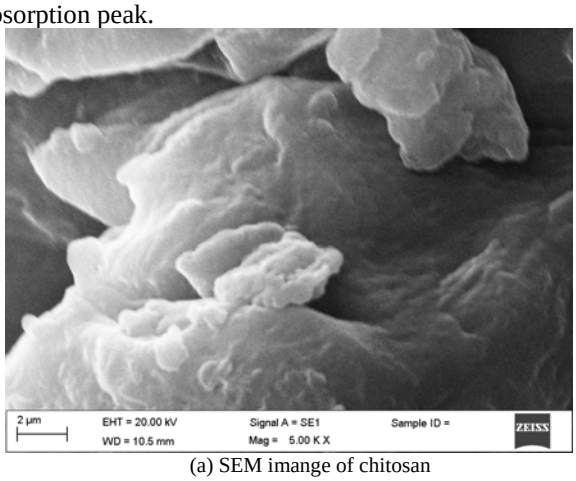
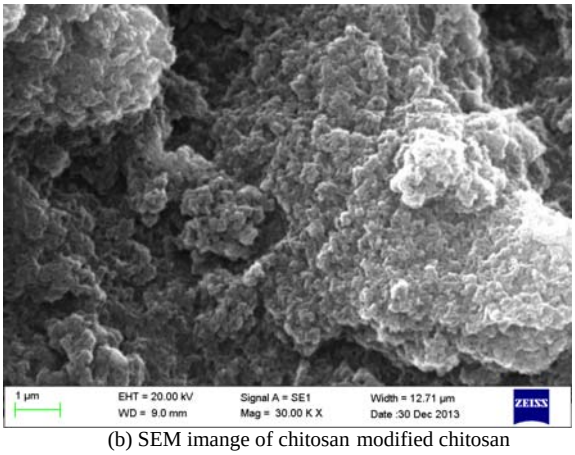


Figure 1 IR spectra of chitosan and modified chitosan

Fig.1 is IR spectra of chitosan and modified chitosan. Absorption band at 3428.81 cm^{-1} is a combination of the O-H stretching and N-H stretching vibration. Absorption peaks at 2881.12 cm^{-1} is attributed to -C-H bond stretching vibration; while the strong absorption band at 1641.12 cm^{-1} and 1602.55 cm-1 are related to the amide CO stretching vibration and NH_2 of vibration absorption, respectively. After modification, the absorption band of NH, OH (carboxyl and chitosan) stretching vibration remain almost the same as chitosan, so the hybrid absorption peak at 3432.67 $cm^{-1}$and an -C-H bond stretching vibration peak at 2874 cm^{-1}still exist. But compared to the infrared spectra of chitosan, the absorption peak at 2950 cm^{-1} increased apparently, and the absorption peak at 1355 cm^{-1} which is related with the $-CH_3$ bending vibration peak appeared, indicating that L-alanine modified chitosan microspheres have been effectively prepared. the original strong absorption peaks at 1602.55 cm^{-1}($-NH_2$) disappeared, indicating that the $-NH_2$ group in chitosan crosslinked with glutaraldehyde successfully. A strong absorption peak at 1720 cm^{-1} appeared after L-alanine modification means the amino group was added into the chitosan backbone as this absorption band is belong to of C=O stretching vibration absorption peak.



(a) SEM imange of chitosan



(b) SEM imange of chitosan modified chitosan

Figure 2. SEM photograph of Sample

Fig.2 is the SEM photograph of chitosan and modified chitosan, and it shows that the modified chitosan is more porous than the chitosan. The porous structure of L-alanine modified chitosan means bigger specific surface and is in favor of adsorption of metal ion.

B. *Adsorption Properties of Modified Chitosan*

1) *Effect of adsorption time on adsorption properties*

Fig.3 shows that the modified chitosan has a certain adsorption capacity to Cs^+ in aqueous solution. When the time lasted from 20 min to100 min, the curve slope rose and the adsorption amount increased from 28.870 mg/g to 29.502 mg/g. but when the adsorption time extended to120min, the modified chitosan adsorption capacity of Cs^+ ion decreased to 29.451 mg/g, The reason for the decrese of adsorption capacity may lies in the saturation of adsorption and desorption. Fig.4 is the adsorption kinetics of modified chitosan to Cs^+ ion.

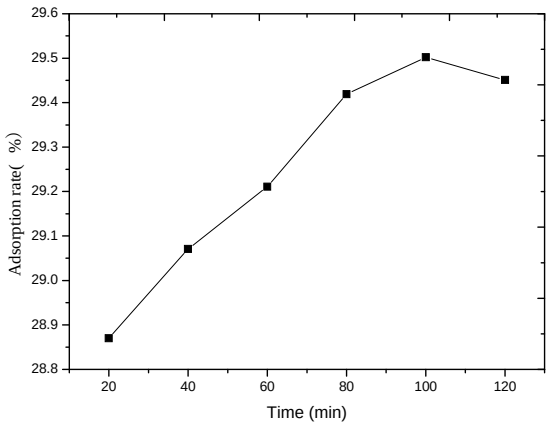
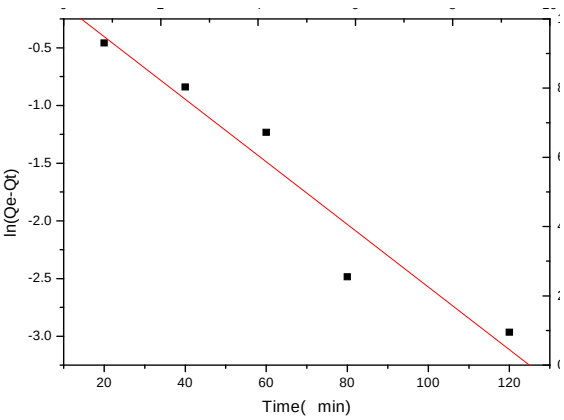
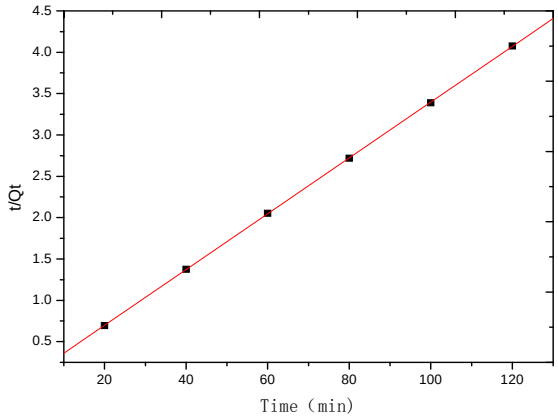


Figure 3. Effect of adsorption time on adsorption properties



(a) Pseudo first order kinetic fitting curve



(b) Quasi two order kinetic fitting curve

Figure 4. Adsorption kinetics of modified chitosan

TABLE I. KINETIC FITTING PARAMETERS

Pseudo first order kinetic parameters			
$q_{e(exp)}$ / $mg{\cdot}g^{-1}$	k_1/min^{-1}	$q_{e(cal)}$ / $mg{\cdot}g^{-1}$	R^2
29.502	0.02713	1.1494	0.9338
Quasi two order kinetic parameters			
	$K_2/min{\cdot}mg{\cdot}g^{-1}$	$q_{e(cal)}$ / $mg{\cdot}g^{-1}$	R^2
	0.04984	29.6384	0.9999

From Fig.4 and Tab.1, we can see that the test value of adsorption capacity of modified chitosan on Cs^+ ion is 29.502mg/g. This value is close to the calculation results of quasi second-order kinetic equation. Moreover, the linear correlation R^2 of quasi second order kinetics is higher than that of the pseudo first-order kinetics. So the adsorption process of L-alanine modified chitosan to Cs^+ ion should follows the quasi second-order dynamics [16].

2) *Effect of adsorption temperature on adsorption properties*

From Fig.5, it can be seen that experimental temperature will affect the adsorption capacity. The adsorption capacity and adsorption rate decreased from 30.742 $mg{\cdot}g^{-1}$ at 25°C to 28.102 $mg{\cdot}g^{-1}$ at 60 °C. But when the temperature rose from 60 °C to 90 °C, the adsorption capacity only has small change.

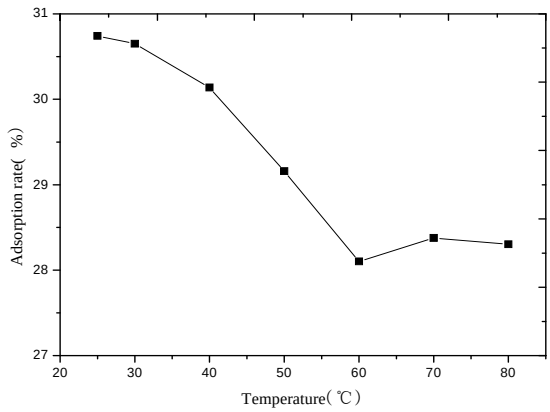


Figure 5. Effect of temperature on adsorption property

3) *Effect of pH value on adsorption properties*

From Fig.6, we can see that the pH value of the solution has a certain effect on the adsorption efficiency. When the pH value of the solution changed from 4 to 8, the adsorption capacity increased from 25.475 $mg{\cdot}g^{-1}$ to 30.121 $mg{\cdot}g^{-1}$. The experimental results showed that the alkaline environment is conducive to the adsorption of Cs^+ ion for modified chitosan.

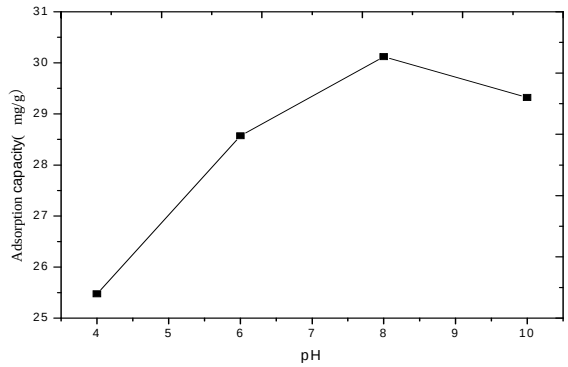


Figure 6. Effect of pH value on adsorption properties

4) *Effect of adsorbent dosage on adsorption properties*

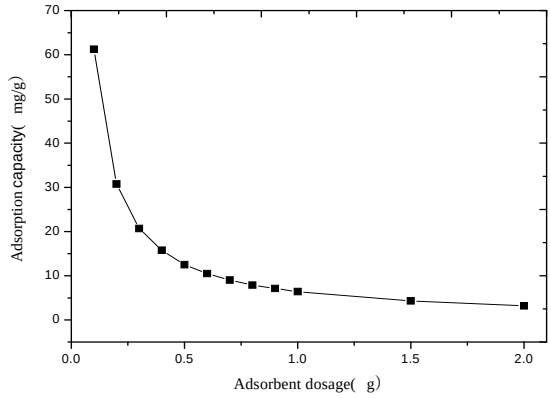


Figure 7. Effect of adsorbent dosage on adsorption properties

Fig.7 shows that the amount of adsorbent has a great influence on the adsorption capacity. The adsorption capacity decreases with the increase of the dosage of the adsorbent. When the dosage of the adsorbent is 0.1 g, the adsorption capacity can reaches to 61.234 $mg{\cdot}g^{-1}$, but when the dosage of the adsorbent is 0.6 g, the adsorption

capacity decreases to 10.495 mg·g^{-1}; and then when the dosage of the adsorbent rises to 2 g, the adsorption capacity only has about 5mg.g^{-1}.

5) *Effect of initial concentration on adsorption properties*

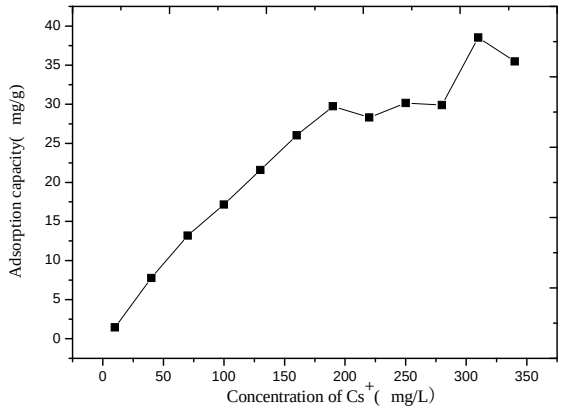


Figure 8. Effect of initial concentration on adsorption properties

From Fig.8, it can be seen that the adsorption capacity increases first and then became mild with the increase of Cs^+ ion concentration. When the concentration of Cs^+ ion was 10 mg·L^{-1}, the adsorption capacity was the smallest value of 1.450 mg·g^{-1}. When the ion concentration of Cs^+ increased from 10 mg·L^{-1} to 190 mg·L^{-1}, the adsorption capacity increased rapidly. When the Cs^+ ion concentration is between 190 mg·L^{-1} and 280 mg·L^{-1}, the adsorption curve is flat, and the adsorption capacity slowed down and maintained at a stable level.

The adsorption of solid and liquid system usually complies with Langmuir isothermal adsorption equation [7]. Then isothermal adsorption equation is obtained by Fig.9 as "(1)"and the correlation degree is 0.9812.

$$Y=0.02541X+0.89449 \qquad R^2=0.9812$$

The correlation degree R^2 is close to 1, indicates that the adsorption process accords with the Langmuir isotherm adsorption equation.

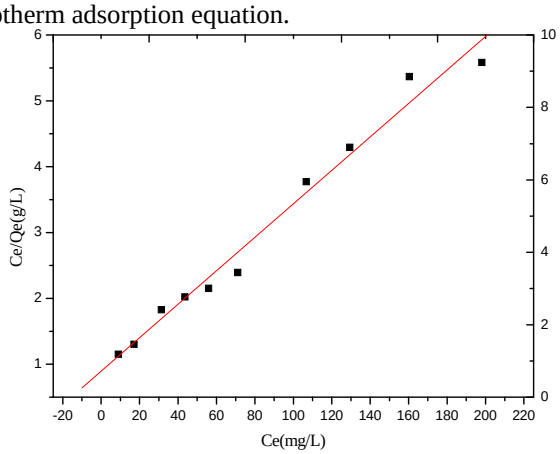


Figure 9. Isothermal adsorption curve fitting

IV.CONCLUSIONS

The chitosan was modified with L-alanine, which can remove cesium ion in the solution. The results obtained in this paper can provide a reference for the treatment of Cs^+ ion in radioactive wastewater.

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