

## Preparation and adsorption properties of cyclodextrin modified chitosan inclusion compound crosslinked by glutaraldehyde

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### Abstract

Based on indirect acylation method and direct acylation method,  $\beta$ -CD/CTS cross-linking inclusion compound material was prepared by using glutaraldehyde as cross-linking agent. Effects of preparation methods and preparation conditions on the loading capacity of  $\beta$ -CD were studied. Adsorption properties of the cross-linking inclusion compound for phenol contaminant and formaldehyde contaminant were also investigated. The results showed that the loading contents of  $\beta$ -CD was up to 551.08  $\mu\text{mol/g}$  when the mass ratio of CTS and  $\beta$ -CD was 1:2. Compared with indirect acylation method, the loading contents of the  $\beta$ -CD-CTS cross-linking inclusion compound prepared by the direct acylation method was significantly higher. In addition, the adsorption properties of the cross-linked inclusion compound prepared by the direct acylation method were better than those of unmodified chitosan and the cross-linked inclusion compound prepared by the indirect acylation method.

### Keywords

Adsorption properties; chitosan; cyclodextrin; inclusion compound; cross-linking.

### 1. Introduction

In recent years, biodegradable chitosan (CTS), which modified as microspheres, porous films and composite materials, has been widely used in fields of water treatment and adsorption due to good flocculation, forming-film, adsorption and chelation [1-3]. However, the adsorption effect is not ideal because of bad mechanical properties and instability for adsorption material.

$\beta$ -cyclodextrin ( $\beta$ -CD) is a cyclic oligosaccharide built of 7 D-glucose units which are attached by  $\alpha(1-4)$  bonds to form torus-like structures. Their cavities, which are of a hydrophobic nature, provide an ideal binding for drugs of adequate size by Van der Waals force, hydrogen bonding force and hydrophobic force, such as aromatic small organic molecules [4].  $\beta$ -CD has been widely used as the adsorption capacity for contaminant or hemoglobin because  $\beta$ -CD used as host molecules can form inclusion compound with guest molecules [5-7]. However, the use of  $\beta$ -CD as an adsorbent is limited due to its inherent water solubility [6].

### 2. Experimental Procedure

#### 2.1 Materials

CTS (the degree of deacetylation: 85%) was purchased by Jinan Haidebei Marine Biological Engineering co., Ltd.  $\beta$ -CD and hemoglobin were supplied by Aladdin and  $\beta$ -CD was recrystallized and dried under vacuum at 100 °C for 24 h. Glutaraldehyde (GA) was purchased by Tianjin Kemiou Chemical Reagent Co., Ltd. All other chemicals were of analytical grad and used without further purification.

#### 2.2 Preparation of the $\beta$ -CTD/CS Inclusion Compound

The  $\beta$ -CTD/CS inclusion compound were prepared by indirect method and direct method.

Indirect method: 1 g CTS and appropriate  $\beta$ -CD were dissolved in 1 mol/L HCl aqueous solution and stirred rapidly until forming homogeneous solution. 25% GA (W/V) (the molar ratio of GA and  $\beta$ -CD

was 3:1) were added rapidly into the solution and the mixture solution were reacted for 2 h at 85 °C. The reaction mixture were allowed to react further for 0.5 h after neutralizing with a 1.0 mol/L NaOH solution to pH 7~8. The precipitation were washed to neutral with distilled water and then washed with 10 mL of acetone for 2~3 times. The product was frozen-dried and the  $\beta$ -CTD/CS inclusion compound were obtained.

Direct method: The appropriate CTS and  $\beta$ -CD were dissolved in 60 mL 0.05 mol/L acetic acid and stirred rapidly until forming homogeneous solution. 12.56 ml of 25% GA (w/v) was added rapidly to the solution. The mixture was allowed to stir until complete gelation and allowed to react further for 1 h before neutralizing with a 0.2 mol/L NaOH solution to pH 6~7. The product was washed with deionized water and acetone, respectively. Then the product was frozen-dried and the  $\beta$ -CD/CTS inclusion compound were obtained.

### 2.3 Structure Characterization

The FTIR spectra of the  $\beta$ -CD/CTS inclusion compound prepared by indirect method and direct method were obtained with a Bruker EQUINX 55 of German measuring in the range of 4000~500  $\text{cm}^{-1}$ .

### 2.4 Measurement of B-CD Loaded Capacity

25.00 mg of  $\beta$ -CD/CTS inclusion compound and 5 mg of  $\alpha$ -amylase were added into 15 mL taper bottle and hydrolyzed at 50°C water bath for 4 h. 25.00 mg of  $\beta$ -CD/CTS inclusion compound and 5 mg of  $\alpha$ -amylase were added into 15 mL taper bottle and hydrolyzed at 50°C water bath for 4 h. The hydrolyzed solution were transferred to the 50 mL volumetric flask and diluted with water to 50 mL. 1 mL hydrolyzed solution, 1 mL distilled water, 1 mL 8% phenol and 5 mL  $\text{H}_2\text{SO}_4$  were added into 15 mL volumetric flask, and diluted with water to 15 mL after standing 30 min at 25 °C. The resulting solution were analyzed by measuring the absorbency at a wavelength of 490 nm. The  $\beta$ -CD loaded capacity was calculated according to glucose contents based on the working curve.

### 2.5 Adsorption Properties of the B-CD/CTS Inclusion Compound for Phenol

Each 30 mL phenol solution with concentration of 25 mg/L was added respectively into four centrifugal tubes, a tube was a blank control group, a tube was added into 15 mg CTS, a tube was added into 15 mg  $\beta$ -CD/CTS inclusion compound prepared by indirect method, a tube was added into 15 mg  $\beta$ -CD/CTS inclusion compound prepared by direct method. The four tubes were took into the constant temperature table and absorbance of the samples were tested for each one hour at 220 nm, until concentration of the phenol solution was no change.

### 2.6 Adsorption Properties of the B-CD/CTS Inclusion Compound for Formaldehyde

Each 30 mL formaldehyde solution with concentration of 20  $\mu\text{g}/\text{mL}$  was added respectively into four centrifugal tubes, a tube was a blank control group, a tube was added into 15 mg CTS, a tube was added into 15 mg  $\beta$ -CD/CTS inclusion compound prepared by indirect method, a tube was added into 15 mg  $\beta$ -CD/CTS inclusion compound prepared by direct method. The samples of the four tubes were taken into the constant temperature table and then taken into another tube which had been first taken in into prepared pentanedione solution(5 mL). The mixture solutions were heated for 6 min at  $58 \pm 1$  °C water bath and absorbance of the samples were tested for each one hour at 412 nm, until concentration of the formaldehyde solution was no change.

## 3. Results and Discussion

### 3.1 Chemical Structure of the Inclusion Compound

FTIR spectrum of CTS,  $\beta$ -CD and  $\beta$ -CD/CTS inclusion compound were performed as illustrated in [Fig.1](#). It could be seen from the figure that the characteristic absorption peaks of C-H groups for  $\beta$ -CD/CTS inclusion compound were enhanced to compare with that of C-H groups at 2881  $\text{cm}^{-1}$  for CTS and that of C-H groups at 2926  $\text{cm}^{-1}$  for  $\beta$ -CD. The characteristic absorption peaks of  $-\text{NH}_2$

groups for inclusion compound were weakened to compare with that of  $\text{-NH}_2$  groups at  $1596\text{ cm}^{-1}$  for CTS. The cross-linked reaction and structure for the  $\beta\text{-CD/CTS}$  inclusion compound was shown in Fig.2.

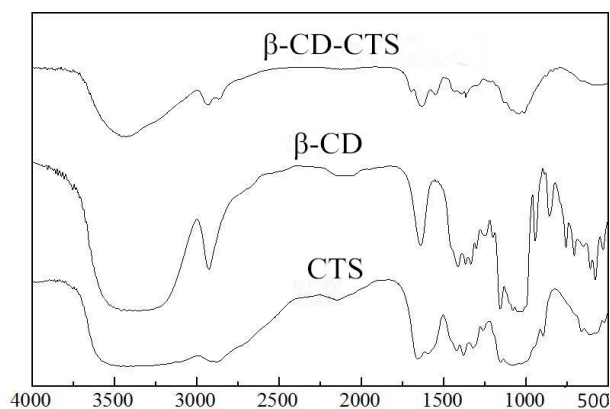


Fig. 1 FTIR spectra of CTS,  $\beta\text{-CD}$  and  $\beta\text{-CD/CTS}$  cross-linked inclusion compound

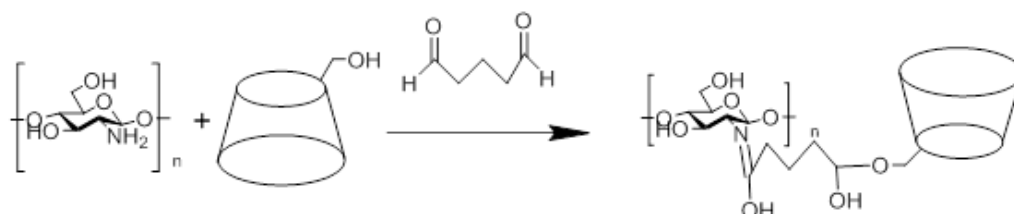


Fig.2 Scheme of cross-linked reaction and structure for the  $\beta\text{-CD/CS}$  inclusion compound

### 3.2 B-CD Loading Capacity of the Inclusion Compound

Effects of preparation methods and preparation conditions on the loading contents of  $\beta\text{-CD}$  were studied and showed in Table 1. The results showed that the loading contents of  $\beta\text{-CD}$  was up to  $551.08\ \mu\text{mol/g}$  when the mass ratio of CTS and  $\beta\text{-CD}$  was 1:2. Compared with indirect acylation method, the loading contents of the  $\beta\text{-CD-CTS}$  cross-linking inclusion compound prepared by the direct acylation method was significantly higher.

Table 1.  $\beta\text{-CD}$  immobilization contents of  $\beta\text{-CD/CTS}$  inclusion compound

Preparation method and condition (CTS: $\beta\text{-CD}$ mass ratio)	$\beta\text{-CD}$ immobilization contents ( $\mu\text{mol/g}$ )
direct acylation method, 1:1	330.58
direct acylation method, 1:2	551.08
direct acylation method, 1:3	501.71
indirect acylation method, 1:5	276.28
indirect acylation method, 1:6	391.46
indirect acylation method, 1:7	368.43

### 3.3 Adsorption Properties of the B-CD/CTS Inclusion Compound for Phenol and Formaldehyde

Adsorption properties of the cross-linking inclusion compound for phenol contaminant and formaldehyde contaminant were also investigated and present in Fig.3 and Fig.4. Compared with pure CTS, the adsorption properties of the cross-linked inclusion compound for phenol contaminant and formaldehyde contaminant were improved obviously. For example, the adsorption property of

the pure CTS for phenol contaminant was 47.6% within 3 h but that of the cross-linked inclusion compound was up to 76.7%. At the same time, the adsorption property of the pure CTS for formaldehyde contaminant was 8.2% within 2 h but that of the cross-linked inclusion compound was up to 20.7%. In addition, the adsorption properties of the cross-linked inclusion compound prepared by the direct acylation method were better than those of unmodified chitosan and the cross-linked inclusion compound prepared by the indirect acylation method.

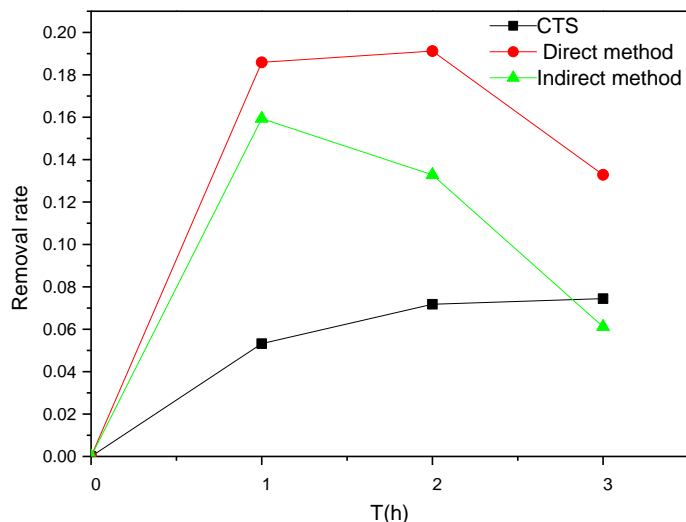


Fig.3 Adsorption properties of CTS and  $\beta$ -CD-CTS inclusion compound for phenol solution

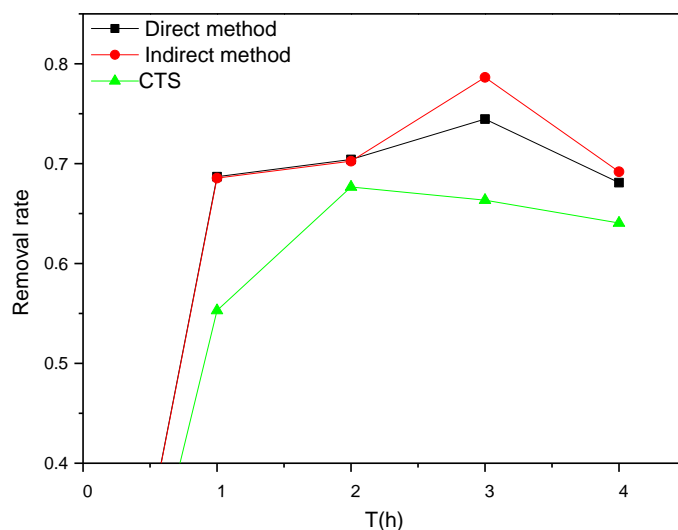


Fig.4 Adsorption properties of CTS and  $\beta$ -CD-CTS cross-linked inclusion compound for formaldehyde

#### 4. Conclusion

Based on indirect acylation method and direct acylation method, a novel inclusion compound material was prepared by using glutaraldehyde as cross-linking agent. The preparation methods and preparation conditions had effect on the loading capacity of  $\beta$ -CD. Compared with pure CTS, the adsorption properties of the cross-linked inclusion compound for phenol contaminant and formaldehyde contaminant were improved obviously.

#### Acknowledgements

This work was supported by the National Nature Science Fund of China (No. 31000446), and the Fundamental Research Funds for the Central Universities (No. 21612440).

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