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# Simple preparation of aminothiourea-modified chitosan as corrosion inhibitor and heavy metal ion adsorbent

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## ABSTRACT

By a simple and convenient method of using formaldehyde as linkages, two new chitosan (CS) derivatives modified respectively with thiosemicarbazide (TSFCS) and thiocarbohydrazide (TCFCS) were synthesized. The new compounds were characterized and studied by Fourier transform infrared spectroscopy, elemental analysis, thermal gravity analysis and differential scanning calorimetry, and their surface morphologies were determined via scanning electron microscopy. These CS derivatives could form pH dependent gels. The behavior of 304 steel in 2% acetic acid containing different inhibitors or different concentrations of inhibitor had been studied by potentiodynamic polarization test. The preliminary results show that the new compound TCFCS can act as a mixed-type metal anticorrosion inhibitor in some extent; its inhibition efficiency is 92% when the concentration was 60 mg/L. The adsorption studies on a metal ion mixture aqueous solution show that two samples TSFCS and TCFCS can absorb As (V), Ni (II), Cu (II), Cd (II) and Pb (II) efficiently at pH 9 and 4.

## 1. Introduction

As one of the most important and abundant natural polysaccharides next to cellulose and starch, chitosan (CS) has advantages of non-toxic, biocompatible and biodegradable, which is partially deacetylated derivatives obtained from chitin. This polysaccharide is composed of β-D-glucosamine and N-acetyl-β-D-glucosamine unit with a 1, 4-linkage. Deacetylated degree determines the amino amounts [1–3]. CS and its derivatives can be used as insecticidal [4], antifungal [5], antimicrobial materials [6] and anticoagulant [7]. In the field of tissue engineering, CS presents excellent biocompatibility [8] and enhances the biological performance of a biomaterial [9]. Some CS derivatives can act as potential carriers for gene transfection [10,11]. CS and their derivatives may be expansively utilized in many more fields [12,13]. Furthermore, the presence of a considerable percentage of free amine and hydroxyl groups on this natural polymer endows it anticorrosion properties [14] and good capability in the adsorption of pollutant [15–19].

CS is such an attractive material that many scientific teams have devoted themselves in searching new modification methods and new application of it. The key purpose of modification is to alter the functional groups of CS to match specific applications [20]. Modification procedures for CS were often handled at the two chemical active sites: hydroxy group at 6-site and amino group at 2-site. In order to amplify its application capability, new derivatives containing novel functional groups in CS structure await to be synthesized efficiently [21].

Recently, the development of inhibitors or adsorbents has been the subject of great interest especially from the point of view of their efficiency and applications [22,23]. Compounds containing heteroatom in the conjugated system have been particularly reported as efficient corrosion inhibitors [22,24], and these kinds of compounds can be used as chelate sorbents in dealing with waste water [25]. Thiosemicarbazide (TS) and thiocarbohydrazide (TC) are two useful compounds containing N=C=S heteroatom conjugated structure. They were widely used in pharmaceutical and materials science as chemical intermediate [26–29]. The derivatives of them were also employed as corrosion inhibitor and metal ion adsorbents in treated with heavy metal pollutants [30–33]. Literature has reported that chitosan derivatives modified with TC could stabilize silver and copper nanoparticles in their matrix [34,35]. By the methods of using formaldehyde as linkages, adsorbents containing TS groups were synthesized [36], and water soluble CS derivatives could be synthesized smoothly [37].

Based on the analysis above, we attempted to find a simple and convenient approach to synthesize some new CS derivatives containing TS or TC groups to cater for specific applications such as anticorrosion and heavy metal sorbents. In this work, we chose formaldehyde as linkages for its cheapness and easy accessibility to get active intermediates, and then the two new CS derivatives

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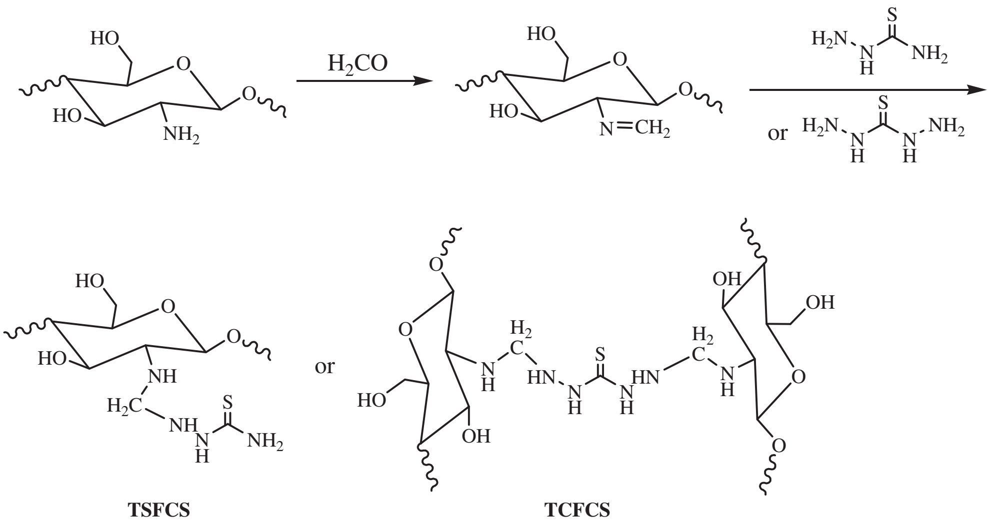

**Scheme 1.** Synthesis of TSFCS and TCFCS by using formaldehyde as linkages.

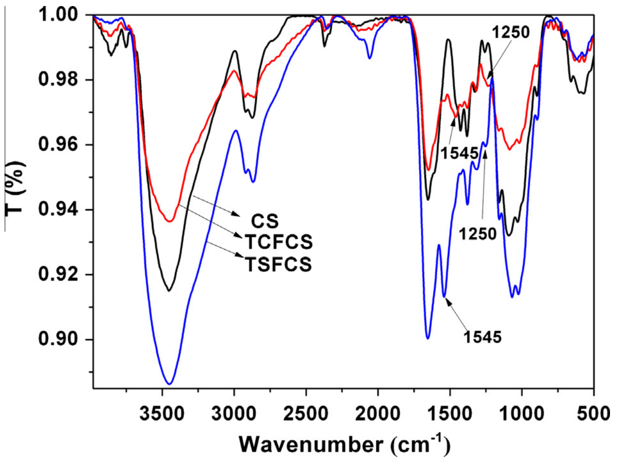

**Fig. 1.** Comparative FT-IR spectra of CS, TCFCS and TSFCS.

**Table 1**
Elemental analysis results of TSFCS TCFCS and CS.

| Sample | Elemental analysis (%) | | | | C/N |
|---|---|---|---|---|---|
| | C | H | N | S | |
| TSFCS | 36.23 | 5.70 | 15.07 | 5.36 | 2.40 |
| TCFCS | 37.62 | 6.12 | 12.69 | 2.37 | 2.96 |
| CS | 44.98 | 6.79 | 8.52 | – | 5.28 |

were synthesized and characterized. The preliminary tests of anticorrosion and heavy metal adsorption were also investigated.

## 2. Experimental

### 2.1. Materials

All compounds were of analytical grade and used as received. Chitosan (CS) was purchased from Sinopharm Chemical Reagents Co. Ltd. (Shanghai, China; the deacetylation degree was 90%). Thiosemicarbazide (TS) and thiocarbohydrazide (TC) were purchased from Solarbio Sci. & Tech. Ltd. (Beijing, China). Formaldehyde solution (37–40%) was purchased from Xilong Chem. Co. Ltd. (Chengdu, China). Deionized (DI) water (Milli-Q, Millipore, Bedford, MA) was used to prepare aqueous solutions. A heavy metal mixture solution contained As (V) (2.0 mg/L), Ni (II) (2.0 mg/L), Cu (II) (1.6 mg/L), Cd (II) (0.8 mg/L), Zn (II) (0.8 mg/L) and Pb (II) (8.0 mg/L) was prepared by diluting the standard stock solution purchased from Sigma–Aldrich (St. Louis, MO, USA).

### 2.2. Synthesis of modified CS

#### 2.2.1. Synthesis of TS modified chitosan (TSFCS)

Modification of CS with TS was accomplished by using formaldehyde as coupling link reagent. In a 100-mL round bottomed flask, CS (0.8 g) was added into a solution of 10 mL of ice acetic acid diluted in 30 mL DI water to form viscous solution. Subsequently, TS (0.45 g, 1 mol equivalent to pyranose ring) was added and stirred until the mixture changed to clear. After about 45 min, formaldehyde (1 mL) was added and mixed thoroughly for 12 h at room temperature to get gel like mixture. The obtained product TSFCS was neutralized with aqueous NaOH to form precipitates. The precipitates were filtrated and washed with DI water and ethanol several times, and then dried under vacuum to give TSFCS as pale powder.

#### 2.2.2. Synthesis of TC modified CS (TCFCS)

TCFCS was synthesized using CS (0.8 g) with TC (0.53 g, 0.5 mol equivalent to pyranose ring), formaldehyde (2 mL) as the reactants by the same methods mentioned above to give product as rufous powder.

### 2.3. Characterization

The Fourier transform infrared spectra (FT-IR) of CS, TSFCS and TCFCS were recorded in powder form by using a Nicolet 5700 instrument (Thermo Company, USA) over the wave number range of 4000–400 $cm^{-1}$ in KBr disks. Software OPUS viewer from Bruker Optics was used to analyze the spectra. The elemental analysis (C, H, N and S) was performed on a Thermo Scientific FLASH 2000 organic elemental analyzer (Thermo Fisher, Italy). Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with a TGA/DSCI analyzer (Mettler, Switzerland) between 20 and 500 °C with a 10 °C/min heating rate under a nitrogen flow rate of 20.0 mL/min. The samples were put into