



# Dithiocarbamate-modified starch derivatives with high heavy metal adsorption performance



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## ARTICLE INFO

### Article history:

Received 6 July 2015

Received in revised form 18 August 2015

Accepted 21 August 2015

Available online 25 August 2015

### Keywords:

Modified starch

Dithiocarbamate

Heavy metal ions adsorption

Adsorption mechanism

## ABSTRACT

In this work, three types of dithiocarbamate (DTC)-modified starch derivatives including DTC starch (DTCS), DTC enzymolysis starch (DTCES) and DTC mesoporous starch (DTCMS) were developed, which showed the significant heavy metal adsorption performance. The adsorption ability of these three DTC modified starch derivatives followed the sequences: DTCMS > DTCES > DTCS. In single metal aqueous solutions, the uptake amount of heavy metal ions onto the modified starches obeyed the orders: Cu(II) > Ni(II) > Cr(VI) > Zn(II) > Pb(II). The adsorption mechanism was proved by the chelating between DTC groups and heavy metal ions through the pH effect measurements. A monolayer adsorption of Langmuir isotherm model for the adsorption of Cu(II) onto DTCMS was well fitted rather than the multi-layer adsorption of Freundlich isotherm model. The adsorption kinetics of Cu(II) onto starch derivatives was found to be fit well with the pseudo-second-order model. Additionally, in the presence of EDTA, the adsorption ability and uptake amount of heavy metal ions onto these three DTC modified starch derivatives is identical with the results obtained in the absence of EDTA.

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## 1. Introduction

Heavy metals have been excessively released into the environment through industrial wastewaters due to the rapid industrializations, which has created a major global environmental concern (Wan Ngah & Hanafiah, 2008). Several treatment technologies for heavy metals removal have been investigated extensively, such as chemical precipitation, ion-exchange, adsorption, membrane filtration, electro-chemical treatment technologies, etc. (Fu & Wang, 2011). Among these methods, adsorption is generally preferred because of its high efficiency, easy handling, and availability of different adsorbents (Schmuhl, Krieg, & Keizer, 2001). Thus, it is demanded for seeking the optimal adsorbents with low cost and high adsorption efficiency for heavy metal removal.

Starch is an abundant, low-cost, and renewable natural polymer, which plays an important role in our daily life. Recently, the application of starch and its modified derivatives in wastewater treatment has received more attentions, particularly, in heavy metals removal field (Ding, Zhao, & Li, 2011; Igura & Okazaki, 2012; Sancey et al., 2011; Wang, Song, Li, & Zhou, 2012; Yang, Wei, Wan & Meng, 2011). Dithiocarbamate (DTC) is a common functional group for

capturing heavy metal ions from effluents. Some studies have been done by introducing DTC group into natural materials to improve their heavy metal adsorption ability. Silica-supported DTC adsorbent (SiO<sub>2</sub>-DTC) was synthesized by anchoring the chelating agent of macromolecular DTC (MDTC) onto the chloro-functionalized silica matrix (SiO<sub>2</sub>Cl) and served as a new adsorbent for Pb(II), Cd(II), Cu(II), and Hg(II) removal from aqueous solution. The adsorption capacities were found to be 0.34, 0.36, 0.32, and 0.40 mmol g<sup>-1</sup> for Pb(II), Cd(II), Cu(II), and Hg(II), respectively (Bai et al., 2011). The DTC-anchored polymer/organosmectite composites were fabricated by modified smectite nanocomposites with carbon disulfide to combine the DTC functional groups with the nanolayer of organoclay. The obtained maximum adsorption capacities of heavy metal ions were 170.7 mg g<sup>-1</sup> for Pb(II); 82.2 mg g<sup>-1</sup> for Cd(II) and 71.1 mg g<sup>-1</sup> for Cr(III), respectively (Say, Birlik, Erdemgil, Denizli, & Ersöz, 2006, 2008). Ammonium pyrrolydine dithiocarbamate (APDC), which is a non-specific chelating agent and can form very stable metal complexes with metallic ions, was used to modify the surface of *Symphoricarpus albus* (*S. albus*) to develop a modified biosorbent for Pb(II) removal. The maximum monolayer biosorption capacities were found to be  $2.62 \times 10^{-4}$  mol g<sup>-1</sup> for Pb(II) onto the modified *S. albus* (Tunali Akar, Arslan, & Alp, 2012).

Enzymolysis-starch (ES) refers to the formation of spherical starch with hollow structure by pouring raw enzymes into farinaceous solution below the gelatinization temperature of starch (Whistler, 1991). The enzymolysis is one of the most widely used

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methods for the pretreatment of starch. This method can improve the reactivity of starch and ultimately modify the starch to meet various demands such as resistant starch (González-Soto, Agama-Acevedo, Solorza-Feria, Rendón-Villalobos & Bello-Pérez, 2004; Le et al., 2009; Lin, Wang, & Chang, 2009), slowly digestible starch (Guraya, James, & Champagne, 2001; Shin et al., 2004), and porous starch (Apinan et al., 2007).

Normally, the method that combines sol-gel and solvent exchange is used to dissolve the starch at gelatinization temperature so that the dense network structure of starch can be unfolded completely (Atkin, Abeysekera, Cheng, & Robards, 1998), followed by fast cooling the dissolved starch to retrograde back into crystal (Shamai, Shimoni, & Bianco-Peled, 2004). Then the crystallized colloid starch is slowly added into the ethanol and dried to remove the water (Li, Xiang, & Ni, 2004; Miao et al., 2008), which can obtain the mesoporous starch (MS) with high specific surface area.

Based on the aforementioned methods, in this work, three different types of DTC modified starch derivatives including DTC starch (DTCS), DTC enzymolysis starch (DTCES) and DTC mesoporous starch (DTCMS) are synthesized for heavy metal removal. The structures and morphologies of these three DTC modified starch derivatives are characterized by Fourier transform infrared spectra (FTIR), scanning electron microscope (SEM), Brunauer–Emmett–Teller (BET) and elemental analysis. The adsorption characters of each starch derivative are investigated toward five heavy metal ions, including Cu(II), Ni(II), Cr(VI), Zn(II), and Pb(II). The effects of solution pH values and EDTA on the adsorption of heavy metal ions are systematically explored. The room temperature equilibrium isotherms are studied by the Cu(II) concentration change with the different treatment times. Furthermore, the adsorption mechanism of heavy metals onto DTC modified starch derivatives is also discussed.

## 2. Materials and methods

### 2.1. Materials

Corn starch (food-grade quality) was provided by Shangdong Jincheng Co., Ltd. Glucoamylase,  $\alpha$ -amylase, cupric nitrate, nickel(II) nitrate hexahydrate, potassium dichromate, lead(II) nitrate, zinc chloride were purchased from Shanghai Reagents Company. All of these chemicals were analytical grade and used without any treatment. All heavy metal ion aqueous solutions were prepared using deionized water.

### 2.2. Characterizations

The concentration of heavy metal ions was determined by Agilent-3510 atomic absorption spectrophotometer (AAS) system. SEM images were performed on a scanning electron microscope (Philips XL-30 system). Fourier transform infrared spectroscopy (FTIR) was recorded on Nicolet FTIR NEXUS spectrometer with KBr pellets in the 4000–500  $\text{cm}^{-1}$  regions with resolution of 4  $\text{cm}^{-1}$ . Specific surface area was measured by  $\text{N}_2$  adsorption isotherm using a Micromeritics ASAP2000 instrument and obtained by equation of BET (Brunauer–Emmett–Teller). Elemental analysis was conducted by a Carlo Erba A1110 organic element analyzer.

### 2.3. Preparation of adsorbents

#### 2.3.1. Preparation of DTCS

DTCS was synthesized as reported previously (Li, Xiang & Ni, 2004). Briefly, the as-received starch and epichlorohydrin (ECH) was reacted in diluted NaOH solution (0.16  $\text{mol L}^{-1}$ ) to form the cross-linked starch (CS). Then the dried CS was mixed with ECH in

the presence of  $\text{HClO}_4$  to prepare the intermediate, etherified cross-linked starch (CHCS). After that, the dried CHCS was further reacted with acyclic polyamine to produce cross-linked amino-starch (CAS) in basic solution. Finally, a reaction was occurred between CAS and  $\text{CS}_2$  to obtain DTCS in an alkaline medium. The preparation procedure of DTCS is shown in Fig. 1(a).

#### 2.3.2. Preparation of DTCES

The as-received starch was firstly treated with the mixture of glucoamylase and  $\alpha$ -amylase to obtain ES. Then cross-linked amine enzyme-hydrolyzed starch (CAES) was prepared by modification of diethylenetriamine onto ES, and the detailed methods were same as the synthesis process of CAS. After that, a 2.0 g of CAES was weighed into three-necked flask and contacted with ethanol (60 mL) and high-purity water (5 mL) in the ice-water bath. After completely mixed, NaOH solution (10 mL, 40 wt%) was slowly added dropwise and stirred for 2 h. Then a mixture of  $\text{CS}_2$  (3 mL) and ethanol (15 mL) was added dropwise under the magnetic stirring. Later, the mixture solution was kept in the oil bath at 45 °C for 16 h, followed by rising temperature to 50 °C to remove the unreacted  $\text{CS}_2$ . The reaction mixture was then filtered, and successively washed with HCl (1 wt%), NaOH (1 wt%), and deionized water. Finally, the products were dried at 50–60 °C in a vacuum oven.

#### 2.3.3. Preparation of MS

MS was synthesized as previous literature (Budarin et al., 2006). Firstly, the as-received starch (5.0 g) was added into deionized water (500 mL), then the solution was magnetically stirred for 15 min with temperature at 30, 40, 50, 60, 70, 80, and 90 °C to dissolve the starch, respectively, followed by magnetic stirring for another 30 min at 100 °C to obtain the gelatinized starch. The fully dissolved starch solution was kept at 5 °C in a refrigerator until it became colloidal form. Later, ethanol (400 mL) was poured into the starch colloid and dried at 50 °C to obtain MS powder.

#### 2.3.4. Preparation of DTCMS

The synthesis procedure of DTCMS was same as that of the DTCS. The yellow powder DTCMS was obtained after the procedure of etherification, amination, and graft with  $\text{CS}_2$  of the cross-linked MS.

Firstly, the cross-linked MS was synthesized by reacting MS (10 g) with 8 mL ECH in 200 mL diluted NaOH solution under 25 °C. After 18 h, the pH value was adjusted to 6–7 using HCl (0.1 M). The reaction mixture was filtered and washed with deionized water. Then the acquired cross-linked MS was dried at 50 °C in a vacuum oven.

The dried cross-linked MS (8.5 g) was suspended in a mixture of ECH (60 mL) and  $\text{HClO}_4$  (0.3 mL, 60 wt%). Then the mixture was heated to 80 °C and kept for 18 h under magnetic stirring. After reaction was completed, the intermediate etherified cross-linked MS (CHCMS) was filtered, then washed with ethanol, deionized water, and dried at 50 °C under vacuum for 24 h.

CHCMS (2.5 g) was dissolved into 150 mL deionized water, followed by adding of 15 mL diethylenetriamine (DETA). This mixture was magnetically stirred for 30 min at 60 °C and then heated to 80 °C for 4 h. After that, the reaction mixture was filtered, washed with HCl (1 wt%), NaOH (1 wt%), and deionized water, successively. Finally, the cross-linked amino mesoporous starch (CAMS) was dried at 50 °C in a vacuum oven for 24 h.

CAMS (2.0 g) was added into a flask containing methanol (60 mL) and deionized water (10 mL). Then the 30 mL of 40 wt% NaOH solution was poured into above mixture solution and a mixture of  $\text{CS}_2$  (6 mL) and ethanol (20 mL) was added for 16 h of magnetic stirring at 45 °C. Finally, the obtained DTCMS was washed with ethanol, methanol, and acetone successively, and dried at 50 °C in a vacuum oven for 24 h.

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