



# Synthesis of a carbamide-based dithiocarbamate chelator for the removal of heavy metal ions from aqueous solutions



Zhili Li <sup>a,b,\*</sup>

<sup>a</sup> School of Chemistry & Chemical Engineering, Guangxi University, Nanning 530004, China

<sup>b</sup> Guangxi Bossco Environment Technology Co., Ltd., Nanning 530007, China

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## ABSTRACT

This study was carried out to develop a carbamide-based dithiocarbamate (CDTC) chelator for the removal of heavy metal ions from wastewater. Its structural properties were characterized by FT-IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR. Results confirmed the functional groups of –HNC(=S)S– existed. The adsorption isotherms showed CDTC had a high adsorption capability for Zn (119.8 mg/g) and Cu (63.1 mg/g). It exhibited a distinctive selectivity for the removal of metal ions (Cu<sup>2+</sup> > Zn<sup>2+</sup> > Cr<sup>3+</sup> > Pb<sup>2+</sup> > Cd<sup>2+</sup>) as they coexisted. The influence of initial pH of wastewater for the removal efficiency of metal ions was also investigated and a pH > 7 was preferred.

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## 1. Introduction

Many heavy metals, such as lead, copper, zinc, cadmium, and chromium, have been discharged into the environment by industries including metal plating facilities, mining operations, battery manufacturing, paints, pigments, etc. Pollution by heavy metals is currently of great concern, due to their non-biodegradability and tendency to accumulate in living organisms, causing various diseases and disorders [1]. Such as an excessive intake of copper over 1.0 mg/L from drinking results in hemochromatosis and gastrointestinal catarrh diseases because it is accumulated in the livers of human and animals [2]. The trivalent chromium (Cr<sup>3+</sup>) has been reported it affects human erythrocyte membrane to a great extent and could decrease immune system activity [3]. Consequently, in many countries, more strict legislation has been introduced to control water pollution. Various governments have set the maximum prescribed limits for the discharge of heavy metal ions into aqueous systems.

For that reason, the removal of heavy metal ions from waters and wastewaters is important in terms of protection of public health and environment. Adsorption is one of the most effective processes for wastewater treatment, which industries employ to reduce hazardous metal ions or other contaminants in wastewater. Many adsorbents have been widely used to adsorb heavy metal ions from wastewaters, such as activated carbon [4], zeolite [5],

and other adsorbents [6–10]. They generally have high metal adsorption capacity but also have limitations such as high operational costs and always producing large volume of secondary hazardous contaminants that are difficult to be treated. Therefore, intensive studies have been carried out to develop more effective and inexpensive adsorbents for removal of heavy metal ions from wastewater. Dithiocarbamate (DTC), which includes micromolecules with single and multiple dithiocarbamate groups and macromolecules with multiple dithiocarbamate groups, is such a substance that has attracted more and more interests from scientific researchers and industrial engineers for the treatment of wastewater containing heavy metal ions, for it can strongly bind with various heavy metal ions and yield excellent removal of heavy metal ions due to the strong tendency of sharing electrons between N, S elements and heavy metal ions [11,12]. Generally, micromolecular chelators with dithiocarbamate groups have strong chelating abilities and forms flocs rapidly, making them popular research topics in recent years. Micromolecular DTC is usually synthesized from amino compounds and carbon disulfide under alkaline environment [13–15], including diethylenetriamine, ethylenediamine, diethylamine, etc., which have the limitations of being volatilizable, very expensive, not easily available and toxic [16–18]. To address these problems, we have begun to develop dithiocarbamates that are derived from easily available, simple reagents with low cost, easily obtained, non-toxic and that are specifically designed to adsorb various heavy metal ions from aqueous solutions or wastewaters.

In this work, a new micromolecular chelator with binary dithiocarbamate groups (CDTC) was prepared from carbamide, which was widely available, non-toxic and inexpensive, with

\* Correspondence address: School of Chemistry & Chemical Engineering, Guangxi University, Nanning 530004, China. Tel.: +86 15578150040; fax: +86 771 4960252.  
E-mail address: [cezli@foxmail.com](mailto:cezli@foxmail.com)

carbon disulfide under alkaline environment. The CDTC structure was characterized by FT-IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy. The adsorption performance of CDTC toward  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Pb}^{2+}$ , which are known to be common heavy metal ions from wastewater, was also investigated including adsorption kinetics, adsorption isotherms, effects of pH and competitive adsorption. This work provided a simple and feasible approach to obtain a high performance and low cost dithiocarbamate and allowed it to be easily converted to practical usage.

## 2. Experimental

### 2.1. Materials

Carbamide, carbon disulfide, sodium hydroxide and metal nitrates were all reagent grad and were purchased from Xiongrun Chemicals (Nanning, China). They were used as obtained.

### 2.2. Synthesis of CDTC

The micromolecular CDTC with binary functional groups was synthesized as follows: (i) 26.0 g carbamide and 100 mL distilled water was poured into a flask bottle equipped with a thermostated water bath, a motor stirrer, a thermometer, a dropping funnel, and a reflux condenser. It was kept at environmental temperature for 30 min with stirring and then a NaOH solution was added to adjust the pH to 10.5; (ii) carbon disulfide with a mole ratio 2.2:1 to carbamide (the dosage was predetermined to ensure the  $-\text{NH}_2$  groups of carbamide taking part in the reaction with carbon disulfide) was then added dropwise as this is an exothermic reaction. The resulting mixture was then heated to  $40^\circ\text{C}$  or 3 h to maximize the conversion of carbamide to a dithiocarbamate. After that, the reaction mixture was cooled to ambient temperature and was extracted with acetone and ethanol (v/v: 50/50). Finally, a red brown powder, i.e., CDTC was obtained after drying under vacuum at  $45^\circ\text{C}$  overnight. The CDTC chelator was prepared from carbamide as depicted in Fig. 1.

### 2.3. Characterizations of CDTC

The structural properties of CDTC were investigated with FT-IR and NMR spectroscopy. FT-IR spectroscopy was recorded on a FT-IR spectrophotometer (Thermo Nicolet 510, USA) using a KBr disk containing 1% finely ground samples. The IR spectra of solid samples were recorded in the range of  $4000\text{--}450\text{ cm}^{-1}$  wavenumbers.

The solution-state  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were carried out on a Varian 600 MHz NMR spectrometer at  $25^\circ\text{C}$ . The sample was dissolved in dimethyl sulfoxide- $d_6$  (DMSO).

### 2.4. Adsorption experiments

Aqueous solutions of heavy metals involving lead, copper, zinc, cadmium, and chromium ions were prepared with initial concentrations for each ions ranging from 5 mg/L to 200 mg/L. The batch adsorption test for removal of the single heavy metal ion was performed as follows. Using one set of sealed flasks, 0.08 g CDTC samples were added to 250 mL of the ions solutions with

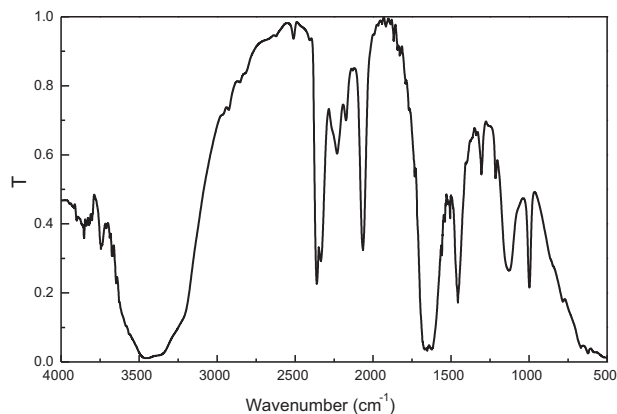


Fig. 2. FT-IR spectrum of CDTC.

different initial concentrations. The mixtures in the flasks were stirred to guarantee a good dispersion of the materials and placed in a water bath at  $30 \pm 0.5^\circ\text{C}$  for a suitable time to allow complete equilibration. The mixtures were filtered with a microsyringe. The concentrations of the initial and residual heavy metal ions were determined by an inductively coupled plasma optical emission spectrometry (ICP-OES, optima 5300DV, Perkin Elmer, USA). The adsorption amounts of CDTC ( $A_e$ , mg/g) for heavy metal ions were calculated by the following equation:  $A_e = \frac{V(C_0 - C_e)}{m}$  where  $C_0$  and  $C_e$  (mg/L) were the initial and final concentrations of heavy metal ions in the flasks, respectively;  $V$  was the volume of the solution (L), and  $m$  was the mass of dry CDTC used (g).

Kinetic adsorption was conducted at 303 K (ion solutions with 50 mg/L, 0.05 g CDTC/100 mL) in a conical flask. At predetermined time intervals, 4 mL volumes of supernatant solutions were pipetted from the conical flask, and samples were filtered with a microsyringe. The concentration in the aqueous solution was determined by ICP-OES. In addition, the influence of pH value of heavy metal ions solutions on adsorption was also investigated. The initial pH values of the solutions were adjusted from 3 to 10 with 0.1 M  $\text{HNO}_3$  and 0.1 M NaOH. The competitive adsorption of heavy metal ions from their mixture was further investigated. Aqueous solutions containing the five metal ions were treated with CDTC following the procedures mentioned above.

## 3. Results and discussion

### 3.1. Characterizations of CDTC

Fig. 2 shows the FT-IR spectrum of the CDTC. As expected, the typical peaks could be found from Fig. 2: the wide peak at  $3300\text{--}3500\text{ cm}^{-1}$  was assigned to N-H stretching. The strong peak at  $1650\text{ cm}^{-1}$  was due to C=O stretching. The C-N stretching was indicated by the peak at  $1450\text{ cm}^{-1}$ . The peaks correlated with S were also found in this curve: C=S stretching was indicated by the peak at  $1140\text{ cm}^{-1}$ . C-S stretching was indicated by the peak at  $990\text{ cm}^{-1}$ . The results from FT-IR demonstrated the synthesis of urelyene-dithiocarbamate was successfully achieved.

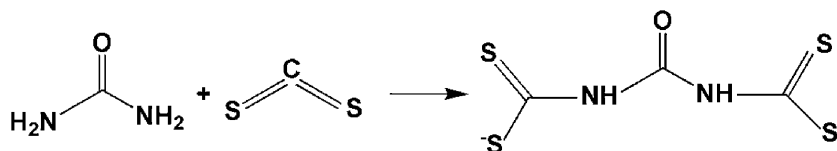


Fig. 1. Illustration for the synthesis of carbamide-based dithiocarbamate.

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