



## Immobilization of ethylene sulfide in aminated cellulose for removal of the divalent cations

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### ABSTRACT

Cellulose (Cel) was first chemically modified with thionyl chloride to increase its reactivity. In the next step CelCl was reacted with ethylenediamine (CelEn) and subsequently reacted with ethylene sulfide to obtain a solid substance, CelEnEs. The modification reactions were confirmed by elemental analysis, TG, XRD, <sup>13</sup>C NMR and FTIR. The chemically modified biopolymer CelEnEs had an order of divalent metal sorption of  $Pb^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+} > Cu^{2+} > Zn^{2+}$ , and the maximum adsorption capacities were found to be  $6.282 \pm 0.023$ ,  $5.783 \pm 0.015$ ,  $5.561 \pm 0.017$ ,  $4.694 \pm 0.013$ ,  $1.944 \pm 0.062$  and  $1.733 \pm 0.020$  mmol g<sup>-1</sup>, respectively. The equilibrium data were fitted to Langmuir, Freundlich and Temkin models, and in general, the experimental data best fit the Freundlich model. This newly synthesized biopolymer proved to be a chemically useful material for cations removal from aqueous solution.

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### 1. Introduction

The mere presence of a variety of metals such as copper, cadmium, lead, nickel and chromium in an aquatic environment is of great concern because they are toxic and do not biodegrade in nature. These metal ions may show acute toxicity to aquatic organisms and terrestrial life and cause remarkable adverse physiological effects in humans and animals. From this perspective, the need to reduce or eliminate these pollutants and minimize their adverse effects has led to a significant increase in recent decades in the number of investigations aimed at controlling these metals in the environment (Santana, Vieira, da Silva Filho, Melo, & Airoidi, 2010).

Currently, research has become more focused on developing new materials that have the ability to remedy this problem. Many studies use natural or synthetic materials whose roles during synthesis and in the process of removing the cations pollutants follow the requirements of green chemistry, which aims to reduce waste and optimize the wastewater treatment processes (Airoidi, 2008; Staudinger, 1920).

When seeking new materials, a natural source is undoubtedly the most exploited and becomes more attractive when the isolation process is less expensive, especially when it is used as we have found or when very few processing operations are necessary.

Additionally, certain chemical modifications enhance the utility of their surfaces (Airoidi, 2008).

In recent years, polymers that have attracted more interest such as cellulose, which comes from a variety of sources, and chitin, which is derived from crustaceans, mollusks, insects, fungi and other organisms (Airoidi, 2008; Staudinger, 1920).

Cellulose is the most abundant biopolymer and represents approximately  $1.5 \times 10^{12}$  tons of the total production of biomass per year. It is considered a source of almost inexhaustible raw material for environmentally safe and biocompatible products (Staudinger, 1920).

The molecular structure of cellulose consists of a carbohydrate polymer generated by repeating  $\beta$ -D-glucopyranose units, which are covalently linked by acetal functionalities between the equatorial OH group on carbon atom 4 (C4) and carbon atom 1 (C1), hence the name  $\beta$ -1,4-glucan. As a result, cellulose possesses an extensive linear chain polymer with a large number of hydroxyl groups (three groups per anhydroglucose unit (AGU)) and a thermodynamically preferred conformation 4C1 (a bond between carbons 4 and carbon 1).

Pure cellulose has very few applications compared to the diversity of applications of its changed form (Jorge & Chagas, 1988). That is why chemical changes are made; one of the main objectives for introducing structural modification is to increase its adsorption capacity for heavy metals in aqueous and non-aqueous media (Kamel, Hassan, & El-Sakhawy, 2006). Moreover, chemical modifications can be used to vary several other properties of cellulose, such as hydrophobicity or hydrophilicity, elasticity,

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adsorptivity, microbial resistance and heat and mechanical resistance (McDowall, Gupta, & Stannett, 1984).

Chemical modification of a polysaccharide surface follows the same principles as those established for other media, such as silica gel. However, the hydroxyl groups on cellulose are less reactive and the start of a chemical modification takes place at the primary hydroxyl found on carbon 6, which may occur through several different routes. However, modifications may also occur on the secondary hydroxyl groups present on carbons 2 and 3. The major modifications of cellulose occur through halogenation, oxidation, etherification and esterification (Martin, Sánchez-Chaves, & Arranz, 1999).

This study aimed to synthesize a new cellulose derivatives by incorporating ethylene sulfide into the polysaccharide chain through reaction of an available amino group, which was present from a previously reaction with ethylenediamine, that required prior chlorine anchoring to increase the reactivity of the cellulose surface. The derivative's capacity for adsorbing divalent cations from aqueous solution was studied using batchwise studies, and three models, the Langmuir, Freundlich and Temkin, were used to evaluate the obtained new isotherms after linear adjust.

## 2. Experimental

### 2.1. Materials

The microcrystalline cellulose (Cel) (Aldrich) was previously dried at a 373 K under vacuum for 24 h to remove any physically adsorbed water (Martin et al., 1999). Ethylenediamine (Vetec), thionyl chloride ( $\text{SOCl}_2$ ) (Chemiker), N,N-dimethylformamide (Vetec) and ethylene sulfide (Vetec) were used in the cellulose modification reactions. The nitrates of the divalent heavy metals (Vetec) were used in the adsorption process with deionized water.

### 2.2. Equipment and measurements

The content of chlorine, sulfur and nitrogen of the precursor cellulose and the chemically modified biopolymer were determined through elemental analysis on a Perkin Elmer, model 2400, elemental analyzer. The FTIR spectra of the samples as KBr pellets (1% sample) were obtained by accumulating 36 scans on a MB-series Bomem Spectrophotometer in the range of 4000–400  $\text{cm}^{-1}$ , with 4  $\text{cm}^{-1}$  of resolution. Solid-state  $^{13}\text{C}$  NMR spectra of the samples were obtained on an INOVA Varian spectrometer, using the CP/MAS technique, with pulse repetitions of 5 s and contact times of 1 ms; the measurements were recorded at 75.47 MHz, with magic angle spinning of 4 kHz. The x-ray diffraction patterns were obtained on a Shimadzu XD-3A diffractometer (35 kV, 25 mA), with a scan rate of 5°  $\text{min}^{-1}$  in the  $2\theta = 5\text{--}50^\circ$  range and nickel-filtered  $\text{Cu K}\alpha$  radiation, with a wavelength of 0.154 nm. The thermogravimetric curves were obtained using a Shimadzu TGA 50 apparatus, under an argon atmosphere at a flow rate of 1.67  $\text{cm}^3 \text{s}^{-1}$  and a heating rate of 0.167  $\text{K s}^{-1}$ . The amount of cation adsorbed was determined using a Perkin Elmer 3000 DV ICP-OES apparatus, and by determining the difference between the initial concentration in the aqueous solution and that found in the supernatant after the adsorption process. The reproducibility was checked by performing at least one duplicate run for each experimental point.

### 2.3. Chemical reaction

#### 2.3.1. Cellulose chlorination

A 10.0 g sample of cellulose (Cel) previously activated at 353 K for 12 h was suspended in 200.0  $\text{cm}^3$  of N,N-dimethylformamide (DMF). The 35.0  $\text{cm}^3$  of thionyl chloride ( $\text{SOCl}_2$ ) was slow added with mechanical stirring at 353 K. After the addition was complete,

the stirring was continued at the same temperature for an additional 4 h. The cellulose chloride (CelCl) obtained from this reaction was washed with several aliquots of a dilute ammonium hydroxide solution and the supernatant after each treatment was removed to restore the pH to neutral. To complete the washing step, the suspension was exhaustively treated with distilled water and acetone to ensure the DMF removed. The solid was then isolated by filtration and dried under vacuum at room temperature (Kobayashi, Sakamoto, & Kimura, 2011; Martin et al., 1999).

#### 2.3.2. Functionalization with organic molecules

The synthesis was performed without solvent under reflux for 4 h with 1.0 g of chlorinated cellulose (CelCl) and 5.0  $\text{cm}^3$  of ethylenediamine. At the end of the reaction, the solid was separated from the liquid by vacuum filtration and washed with deionized water to remove the excess reagent, and then, it was dried under vacuum at 353 K for 24 h. The material obtained was named CelEn (Kobayashi, Uyama, & Ohmae, 2001).

In the final step, 1.0 g of CelEn was reacted with 2.83  $\text{cm}^3$  of ethylene sulfide, and the mixture was kept under reflux with constant stirring for 4 h at 328 K. Subsequently, the material was filtered and washed with water to remove the unreacted ethylene sulfide, dried under vacuum at room temperature and named CelEnEs.

### 2.4. Adsorption experiments

The obtained solid, CelEnEs, was suspended in several metal salt solutions to evaluate its adsorptive capacity. All of the experiments were performed in duplicate, using a batch process in which approximately 20.0 mg of the chemically modified biopolymer (CelEnEs) was introduced into a series of polyethylene flasks containing 25.0  $\text{cm}^3$  of a metallic cations solution. The concentrations of the cation solutions ranged from approximately  $7.0 \times 10^{-4}$  to  $7.0 \times 10^{-2} \text{ mol dm}^{-3}$ .

The time chosen for the adsorption procedure was 6 h to ensure the best equilibrium condition, and the suspensions were stirred in an orbital bath at  $298 \pm 1 \text{ K}$ . The supernatant solutions were separated from the solid by filtration and aliquots were taken to determine the amount of remaining cations by ICP-OES.

The amount of cations adsorbed in the experiment ( $\text{mmol g}^{-1}$ ) was calculated using Eq. (1), where  $N_f$  is the number of moles adsorbed onto the modified cellulose,  $n_i$  and  $n_s$  are the number of moles in the initial solution and the supernatant after equilibrium, respectively, and  $m$  is the mass of the adsorbent used in each adsorption process (da Fonseca et al., 2004).

$$N_f = \frac{n_i - n_s}{m} \quad (1)$$

The experimental data were fit to three isotherm models: (i) the Langmuir model, which assumes that the sorption sites have similar energies and are gradually saturated in a monolayer behavior, (ii) the Freundlich model establishes the same sorption process occurs in a multilayer condition and (iii) the Temkin model assumes both of the previously described possibilities but that the solutes adsorb on the surface at the same time.

The parameters related to each model were obtained by linearly fitting the data according to the linear equation that corresponds to each model. Therefore, the parameters for the Langmuir isotherm are  $N_s$  the number of moles needed for the formation of the monolayer, and  $b$ , a constant related to the equilibrium constant, obtained from the linear fit of the experimental data to the modified Langmuir equation (Eq. (2)) (Langmuir, 1918).

$$\frac{C_s}{N_f} = \frac{1}{N_s b} + \frac{C_s}{N_s} \quad (2)$$

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