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Incorporation of dithiooxamide as a complexing agent into cellulose for the removal and pre-concentration of Cu(II) and Cd(II) ions from natural water samples

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ABSTRACT

The present study describes the incorporation of a complexing agent, dithiooxamide, into microcrystalline cellulose for use in the pre-concentration of Cu(II) and Cd(II) ions from aqueous samples. The FTIR spectrum of the adsorbent exhibited an absorption band in the region of 800 cm^{-1}, which confirmed the binding of the silylating agent to the matrix. Elemental analysis indicated the amount of 0.150 mmol g^{-1} of the complexing agent. The adsorption data were fit to the modified Langmuir equation, and the maximum amount of metal species extracted from the solution, N_s, was determined to be 0.058 and 0.072 mmol g^{-1} for Cu(II) and Cd(II), respectively. The covering fraction ϕ, which was 0.39 and 0.48 for Cu(II) and Cd(II), respectively, was used to estimate a 1:2 (metal:ligand) ratio in the formed complex, and a binding model was proposed based on this information. The adsorbent was applied in the pre-concentration of natural water samples and exhibited an enrichment factor of approximately 50-fold for the species studied, which enabled its use in the analysis of trace metals in aqueous samples. The system was validated by the analysis of certified standard (1643e), and the adsorbent was stable for more than 20 cycles, thus enabling its safe reutilization.

1. Introduction

Cellulose is the most abundant polymer in nature and can be obtained from different sources, such as plants and bacteria. Because of the great abundance of chlorophyllous plants, the production of paper and paper products on an industrial scale is performed using chemical reactions for the extraction and bleaching of cellulose. On a smaller scale, cellulose can also be obtained in thin films [1] and from some bacteria [2–4], and the use of cellulose in the production of biofuel ethanol has also recently been investigated [5,6].

Because it is the most abundant biopolymer, cellulose has also been proposed as a potential material for use in, for example, solid-phase extraction procedures for the removal of toxic metal species in aqueous samples [2,7–9]. The ability of cellulose to serve in this capacity is the result of the presence of hydroxyl groups in its structure that are capable of undergoing chlorination and/or silylation reactions. Such reactions result in a reactive structure that contains chlorine atoms distributed along the polymer chain. Chlorinated and/or silylated cellulose can undergo reactions with a vast number of molecules that contain nitrogen, sulfur, phosphorus, and carboxylic acids, among others.

After the modification reactions, molecules that contain basic centers (atoms with pairs of free electrons) and groups that can act as ion exchangers are incorporated into the structure of cellulose, and the resulting cellulose can therefore be used for the solid-phase extraction of metal species.

This type of procedure enables the easy separation of analytes (metal species) from the matrix and ensures that quantification is achieved with greater accuracy. Currently, numerous chemically modified organic [9–13] and inorganic [14–17] materials are being used in pre-concentration systems. In many cases, these systems reduce the cost of analysis, which can be conducted using inexpensive equipment.

Many complexing agents are used in co-precipitation and/or precipitation systems to separate and remove metal species in aqueous and non-aqueous samples [18–21]; however, because the analyte and the complexing agent are in the same phase as the matrix, separation can be a complicated and time-consuming step.

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Dithiooxamide is a complexing agent that is generally used in the spectrometric determination of certain metals in solution, including copper, iron, nickel, and cobalt, among others.

Consequently, this study was aimed at the incorporation of the dithiooxamide molecule into the structure of commercial cellulose and the use of the resulting material for the solid-phase extraction of copper and cadmium in aqueous samples. The synthesized material was characterized using infrared spectroscopy and elemental analysis in relation to variables related to the adsorption process. The material was used in the pre-concentration of metal species in natural water samples, and the results were compared with those obtained using certified reference materials (CRM 1643e).

2. Materials and methods

2.1. Reagents and solutions

All metal solutions were prepared using the respective high-purity salts (Merck, Germany) and were dissolved in ultrapure water (Elga system, Purelab). The standard solutions used in atomic absorption spectrometry were prepared by dilution of 1000 mg L^{-1} stock solutions. Solutions of HNO_3, HCl and $H_3C_2O_2H$ acids were prepared by dilution of the concentrated solutions (Carlo Erba). Diluted NaOH solutions were prepared by dilution of the concentrated base (Merck, Germany) in ultrapure water. The complexing agent, dithiooxamide (Sigma–Aldrich), was used without prior treatment or purification. Commercial cellulose (Sigmacell Cellulose Type 50, St. Louis, USA) was used without prior treatment, except for drying.

2.2. Preparation of modified cellulose (Cel-DTX)

Initially, 5.0 g of commercial cellulose was placed in a vacuum oven at 373.15 K for 24 h to remove possible adsorbed water molecules. Then, 5.0 g of cellulose was suspended in 50 mL of dimethylformamide (DMF) in a reaction flask, to which 10 mL of a silylating agent, 3-chloropropyltrimethoxysilane, was added; the reaction was kept under a nitrogen atmosphere and refluxed at 423.15 K in a glycerin bath for 48 h. The resulting product was washed with DMF, left in a Soxhlet extraction system with ethanol for 24 h and oven dried at 423.15 K. In the second stage of the reaction, 3.0 g of the complexing agent, dithiooxamide, was dissolved in DMF, and cellulose with the silylating agent (Cel-CPTS) was subsequently added. The mixture was stirred and heated (423.15 K) for 48 h. After this time, the final product (cellulose modified with dithiooxamide (Cel-DTX)) was washed with DMF, left in a Soxhlet extraction system for 24 h with ethanol and oven-dried. The product was kept in a desiccator until it was used. A diagram of the reaction steps is shown in Fig. 1.

2.3. Equipment

During the adsorption experiments, the samples were stirred in an end-over-end mixer in 50-mL Falcon tubes (Sardest). The metal species were determined using an atomic absorption spectrometer (Shimadzu AA6800) equipped with a flame or graphite-furnace module, as appropriate. The monochromator of the equipment was adjusted to 324.7 and 228.8 nm, which are the most sensitive resonance lines for copper and cadmium, respectively. The infrared spectra were obtained using a Nicolet Nexus 670 spectrometer; samples were scanned 200 times at a resolution of 4 cm^{-1}, and the pellets were prepared with 1.0 mg of sample mixed with 500 mg of KBr. Elemental analysis were performed on an EA 1110 CHNS-O analyzer from CE Instruments using 2.2 mg of material.

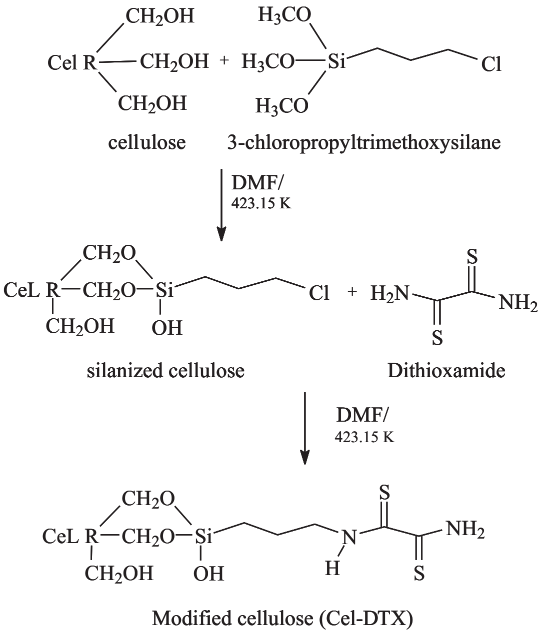

Fig. 1. Diagram of the commercial cellulose modification reaction with the dithiooxamide (rubeanic acid) molecule.

2.4. Adsorption experiments

All experiments related to adsorption studies were conducted using 40 mg of Cel-DTX. Initially, kinetic studies were performed to verify the time required for the adsorption sites to become saturated and for the system to reach equilibrium. This study was performed using 20 mL aliquots with concentrations of 10 mg L^{-1} of the metal species and with different periods of dynamic contact (1–180 min). The adsorption capacity as a function of time was calculated according to Eq. (1):

$$N_f = \frac{ni - ns}{m} \tag{1}$$

where ni is the amount of metal ion (mmol) in the initial solution, ns is the amount of metal ion (mmol) in the supernatant and m is the mass (0.04 g) of Cel-DTX used.

The effect of the solution pH on the adsorption of metal species was examined by changing the pH from 1.0 to 6.0 using 20 mL of the 10.0 mg L^{-1} solutions of the metal species and 40 mg of Cel-DTX. The pH levels of the solutions were adjusted with diluted solutions of NaOH and HNO_3, and the mixtures were stirred for 10 min. The N_f values for all pH values were calculated using Eq. (1).

The experiments to determine the maximum adsorption capacity were conducted using 20 mL of the metal solutions with different initial concentrations (10–600 mg L^{-1}), and the pH was adjusted to approximately 6.0. After 10 min of stirring, the solutions were filtered, and the adsorption capacity was determined using Eq. (1). The concentration of metal species in the initial solutions and in the supernatant was determined using flame atomic absorption spectrometry (FAAS).

2.5. Pre-concentration

The pre-concentration system was constructed using peristaltic pumps to control the flow and Tygon tubes to transport the solutions (eluents, samples and standards). The column was built using 0.003 g of Cel-DTX, which was packed into a section of the Tygon tube. The internal diameter of the Tygon tube was 2.86 mm. The mini-column was closed on both ends with glass wool.