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Thermodynamic studies of the interaction at the solid/liquid interface between metal ions and cellulose modified with ethylenediamine

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Abstract

The chelate molecule, ethylenediamine, has been incorporated onto the surface of cellulose by sequential reaction of cellulose fibres with phosphorous oxychloride followed by the chelating agent. The modified material (CelNN) retained its fibrous nature and was shown to be efficient at adsorbing divalent metal cations from water by complexation. Adsorption isotherms were determined for suspensions of CelNN in metal ion solutions of different concentrations, and the data were adjusted to fit the modified Langmuir equation. The maximum numbers of moles of Cu^{2+}, Ni^{2+} and Zn^{2+} adsorbed per gram of modified cellulose were 1.64×10^{-3}, 5.25×10^{-4} and 1.06×10^{-3}, respectively. The thermodynamic effects related to the adsorption of metal ion onto the cellulose surface were determined by calorimetric titration. Gibbs free energy was spontaneous for all interactions. The adsorption processes all exhibited endothermic enthalpy values and were accompanied by increases in entropy.

Keywords: Cellulose fibre; Metal ion adsorption; Calorimetry

1. Introduction

Heavy metal contaminants are often present in the wastewater effluents produced by industries involved in, for example, metal processing (particularly finishing and plating), mining and tanning. In general, heavy metals are not biodegradable and tend to accumulate in living organisms [1–3]. In natural water supplies, even low concentrations of such contaminants may be harmful to wildlife and can be the cause of various diseases in human beings [3,4]. For this reason, the monitoring of local water sources for heavy metal content is of paramount importance in ensuring the well-being of a given community [5]. However, in order accurately to determine concentrations of metal cations at trace levels, it is often necessary to carry out a pre-concentration step, typically involving specific adsorption of analyte onto a solid substrate [6]. In this respect, cellulose is a particularly attractive support since it is available at low cost as a renewable feedstock, and presents excellent mechanical and thermal resistance, and thermal and dimensional stability [7,8]. Furthermore, the active hydroxyl group present on C6 of each monomeric unit of cellulose (Fig. 1) has the ability to react with appropriate groups of organic ligands. In this manner, the surface of cellulose may readily be modified, through low-cost chemical processes, to produce materials with considerable ion exchange capacity [9,10].

The aim of the present study was to examine the adsorption from aqueous solution of divalent metal ions (Cu^{2+}, Ni^{2+} and Zn^{2+}) by a novel form of cellulose fibre, the surface of which had been modified with ethylenediamine. An understanding of the thermochemical characteristics of the adsorption interaction was developed by determination of the calorimetric adsorption data at the solid/liquid interface.

2. Experimental

2.1. Chemicals

Reagent grade cellulose fibre and phosphorus oxychloride were purchased from Merck, and ethylenediamine and xylene were from Aldrich: reagents were used without prior purification.

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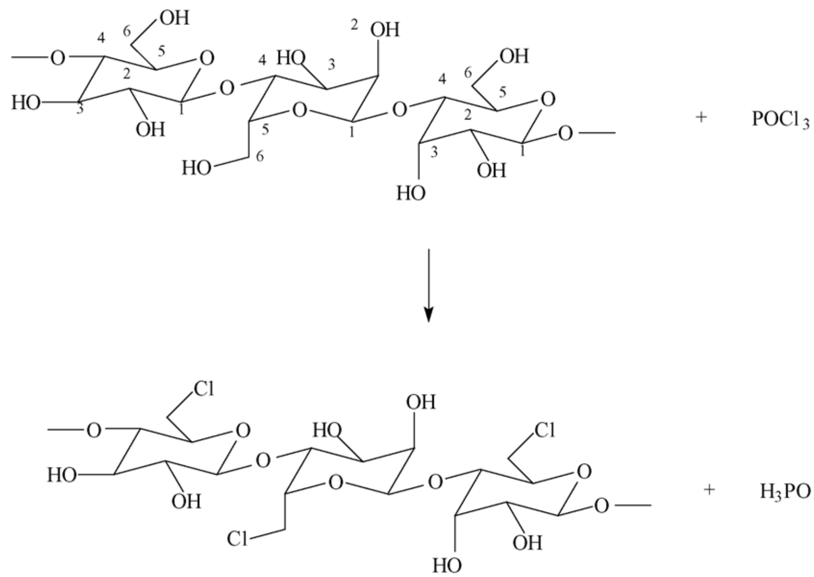

Fig. 1. The modification of cellulose by reaction with phosphorous oxychloride to give the precursor cellulose (CelCl).

2.2. *Synthesis of modified cellulose*

Cellulose fibre (6.0 g) was suspended in xylene (50.0 ml) and stirred mechanically for 1 h at 70 °C under an atmosphere of dry nitrogen. Phosphorus oxychloride (10.0 ml) was added dropwise to the resulting suspension, and the reaction mixture maintained under the same conditions for 24 h in order to obtain the precursor cellulose, CelCl (Fig. 1) [11]. Subsequently, ethylenediamine (5.0 ml) was added to the reaction mixture and the whole maintained under the same conditions for a further 24 h in order to yield the final product, CelNN (Fig. 2). The resulting solid material was washed with ethanol and water, and dried under vacuum at room temperature.

2.3. *Characterisation of modified cellulose*

The amount of ethylenediamine incorporated into the cellulose was determined by Kjeldahl analysis. In order to study the morphology of CelNN, samples were coated with carbon using a Balzer model MED 020 metalliser and subsequently examined by scanning electron microscopy performed on a JEOL model JSM-6360 LV instrument [12].

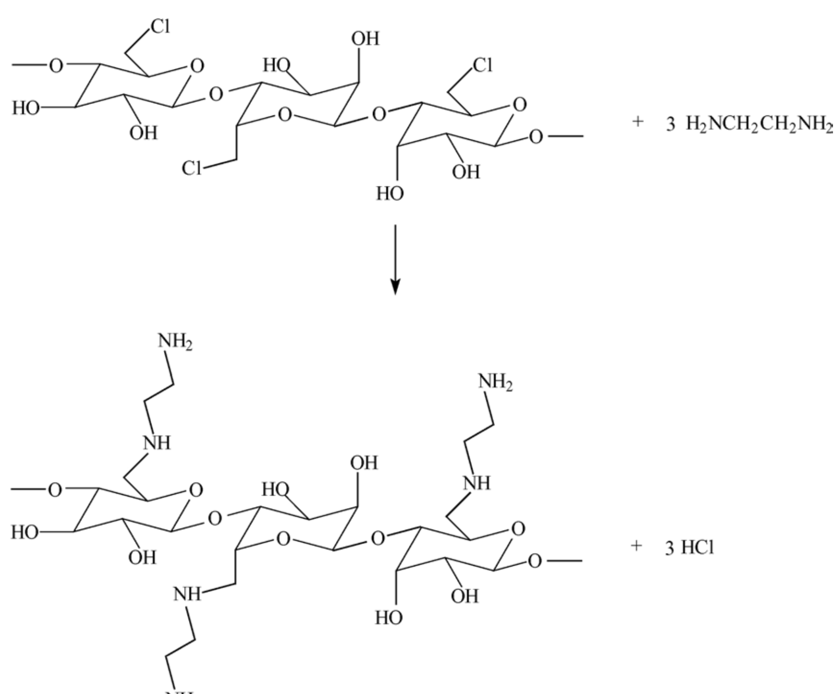

Fig. 2. Reaction between precursor cellulose (CelCl) and ethylenediamine to produce the modified cellulose CelNN.