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Separation of cellulose nanowhiskers from microcrystalline cellulose with an aqueous protic ionic liquid based on ammonium and hydrogensulphate

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ABSTRACT

Cellulose nanowhiskers (NWC) have several applications, but its achievement, when held by hydrolysis with strong acids, presents some undesirable aspects as their corrosivity, toxicity and low recovery rate. Recently, [BMIM][HSO₄] was proposed as an alternative, but its use has yet disadvantages, mainly due its toxicity and cost. In this sense, this work reports the separation of NWC from MCC by a synthesized protic ionic liquid 2-hydroxyethylammonium hydrogensulphate ([2-HEA][HSO₄]) potentially lower toxic than [BMIM][HSO₄], which can be easily produced by a low-cost procedure. A stable and polydisperse NWC aqueous suspension was formed exhibiting the birefringence flow typical of nanoparticle dispersions. TEM micrographies confirm needle-shape particles with high average aspect ratio of 50.23 ± 20.93 nm. A good thermal stability was achieved, with T_{max} of cellulose decomposition around 234 °C. No ionic liquid residues were observed in the NWC by FTIR analysis. The calculated crystallinity index and crystallite size were 54% and 17.2 nm, respectively. The ionic liquid used in the hydrolysis experiments was successfully recovered in 76.91 ± 0.13% yield, with a similar structure to that of the original ionic liquid. Therefore, [2-HEA][HSO₄] was successfully tested as a new, alternative and promising medium to separate cellulose nanowhiskers from cellulosic sources.

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1. Introduction

Cellulose nanocrystals shaped nanowhiskers (NWC) have been widely used in several technological applications, electronics devices, tissue engineering and food packaging, mainly due its optical, chemical and mechanical properties, besides it could be obtained from cellulosic renewable sources, a low-cost biopolymer highly abundant in the nature [1–3]. Considering the main problems involved with its production by acid hydrolysis with strong inorganic acids, as high corrosion, high toxicity and low-rate recovery, there were reported in the literature [4] researches with ionic liquids as alternatives to separate cellulose nanowhiskers from cellulosic matrices under less harsh conditions. As a general rule, ionic liquids are playing an increasingly important role in separation science [5] and have been tested in nanocellulose production technologies.

Protic Ionic Liquids (PILs) based on 2-hydroxyethylammonium ([2-HEA] cation were reported [6] as less toxic and safer for the terrestrial environment than the Aprotic Ionic Liquids (AILs), due its

potential for biodegradation in the soil. The AIL 1-butyl-3-methylimidazolium hydrogen sulphate ([BMIM][HSO₄]) and microcrystalline cellulose (MCC) have been the main ionic liquid and cellulose source, respectively, used in the studies reported until now [7–9]. Cellulose nanocrystals with dimensions of 50–300 nm in length and 14–22 nm in diameter and crystallinity higher than 80% were successfully prepared [7], as well 75–80 nm in length and 15–20 nm in diameter with an even greater crystallinity than 95.8% [8]. Higher ratio aspects were achieved in another work [9]: 146.8 ± 62 nm in length and 3.6 ± 1.8 diameter, but with a lower crystallinity (77%).

It was proposed a mechanism for MCC hydrolysis by [BMIM][HSO₄] [8] and the main contribution to cellulose hydrolysis and removal of amorphous regions is due the interaction between hydrogen sulphate anions and hydroxyl groups, so the cationic part has a secondary role in this process. Furthermore, elongation of the alkyl chain is known for the trend to increase the toxic effect of PILs [10]. In order to reduce the cited disadvantages, the 1-butyl-3-methylimidazolium cation was replaced by a 2-hydroxyethylammonium [2-HEA] cation, maintaining the anion responsible for the cellulose hydrolysis. As far as the authors of this paper are aware, the PIL [2-HEA][HSO₄] has not been previously

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studied for the manufacture of cellulosic nanowhiskers. The resulting PIL, which structure is shown in Fig. 1, tends therefore to be less corrosive and toxic than strong inorganic acids, another advantage is that due to the direct and simpler synthesis, this PIL tends to have a final lower cost if you compare with the IL based on [BMIM]:

In this work, [2-HEA][HSO₄] was synthesized and used as simple, efficient and low-cost alternative medium to separate cellulose nanowhiskers (NWCPIL) from MCC.

2. Materials and methods

2.1. Materials

MCC and monoethanolamine were purchased from Sigma Aldrich, while sulphuric acid was purchased from VWR Chemicals. All reactants used had high purity, greater than 90%.

2.2. Methods

2.2.1. Synthesis of [2-HEA][HSO₄]

The ionic liquid was synthesized by a neutralization reaction between monoethanolamine and sulphuric acid, as proposed in the literature [11]. The stoichiometric sulphuric acid diluted in water (3 ml of water per every 1 ml of H₂SO₄) was added by dropwise to a solution of amine in water (1 ml of water per every 1 ml of amine). The amine was placed in a jacketed reactor covered by a black shirt to avoid photodecompositions and equipped with a reflux condenser and an addition funnel containing diluted sulphuric acid. The reactor was connected to a thermostatic bath at low temperature of 10 °C. The acid was added dropwise to the reactor with mechanical stirring until reaction completion. In the end, the reaction system was kept stirred for 30 mins and then the PIL was collected. Water removal was partially performed with a vacuum pump, at 50 °C for 48 h. After hydrolysis, the ionic liquid was filtered to remove solid particles and the oven dried at 105 °C to determine the rate of recovery. This step was performed in duplicate. The Fig. 2 illustrates the system where has been occurred the synthesis.

2.2.2. Separation of NWCPIL from MCC

NWCPIL separation was adapted from a procedure proposed in the literature [8] to [BMIM][HSO₄]. They were produced from a solution with 10% mass fraction of MCC in [2-HEA][HSO₄]. MCC was slowly added into PIL, with vigorous mechanical stirring at 70 °C for 1.5 h. The reaction was quenched by adding 20 ml of cold water to the reaction mixture, which was centrifuged to separate the supernatant, rich in the PIL. The solid content resulting was washed with deionized water using various centrifugations to isolate NWCPIL in aqueous suspension. Before dialysis against water until a neutral pH, the suspension was filtered under vacuum to remove some solid non-hydrolyzed particles.

2.2.3. [2-HEA][HSO₄] characterization

In order to elucidate its chemical structure and evaluate its thermal stability in the hydrolysis conditions different techniques were used: ¹³C and ¹H Nuclear Magnetic Resonance (NMR) spectra were obtained on Avance DPX-250 MHz spectrometer by Bruker, where 20 mg of sample was dissolved into 0.5 ml of deuterated

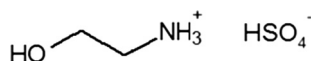


Fig. 1. Chemical structure of 2-hydroxyethylammonium hydrogensulphate ([2-HEA][HSO₄]).

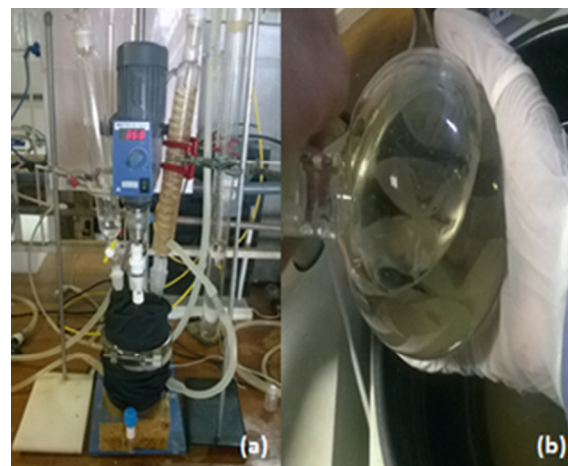


Fig. 2. Synthesis of [2-HEA][HSO₄]: (a) Reactor and experimental apparatus; (b) Ionic liquid yield as an aqueous solution.

water until complete dissolution, then a sample was transferred to 5 mm NMR tube. Infrared Spectroscopy (FTIR) measurements were carried out with the sample mixed with KBr in a tablet shape, on a Shimadzu spectrometer; model IR Prestige-21, transmittance mode, wavelength range of 4000–400 cm⁻¹. Thermogravimetric (TG) analysis was performed in a Seiko equipment, model Exstar TG/DTA6200, with about 6 mg of the pure sample previously dried in a furnace, from 25 to 1000 °C at a rate of 20 °C min⁻¹ under nitrogen flow of 100 ml min⁻¹. Differential Scanning Calorimetry (DSC) profile was obtained on a Shimadzu equipment, model DSC-50, where the sample was heated to 110 °C, after cooled to –100 °C under liquid nitrogen and then heated again until to 110 °C at a rate of 2 °C min⁻¹.

2.2.4. NWCPIL characterization

In order to evaluate the flow birefringence of the obtained NWCPIL, two films of crossed polarizers were attached in the lens of a professional digital camera. Polarizing films were adjusted to be perpendicular to each other, which were focused a direct light. The sample was photographed just after vigorous manual stirring. Transmission Electron Microscopy (TEM) was carried out in aqueous suspension, which was dripped onto 400 mesh copper grids covered with Formvar[®] film. Uranyl acetate solution 2 wt.% was used as contrast. TEM micrographies were recorded in a JEOL microscope; model JEM-1230, operating at 80 kV. To analyze the images (around 30 measurements), it was used the Image J[®] software. TG was performed with the sample in a solid state in a Seiko equipment; model Exstar TG/DTA6200, where About 6 mg of the samples, previously dried in a furnace, were analyzed from 25 to 1000 °C at a heating rate of 20 °C min⁻¹ under nitrogen flow of 100 ml min⁻¹. DSC analysis was carried out a Shimadzu equipment; model 51-H. About 10 mg of the solids, previously dried in a furnace, was analyzed from 25 to 600 °C at a heating rate of 20 °C min⁻¹ under nitrogen flow of 50 ml min⁻¹. FTIR analysis was carried out using a Shimadzu spectrometer; model IR Prestige-21, transmittance mode, wavelength range of 4000–400 cm⁻¹. The spectra was recorded using a tablet composed for solid NWCPIL diluted in KBr. X-ray diffraction (XRD) was carried out in a Shimadzu X-ray diffractometer; model XRD-6000, angle range of 5–30°. The crystallinity index (CrI) was calculated using Segal's method [7,12] (Eq. (1)):

$$CrI(\%) = \frac{I_{(002)} - I_{(am)}}{I_{(002)}} \times 100 \quad (1)$$

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