

Use Of Low-Cost Hydrated Hydrogen Sulphate Based Protic Ionic Liquids for Extraction of Cellulose Rich Materials from Common Wheat (*Triticum Aestivum*) Straw

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Abstract : Recently, the use of ionic liquids (ILs) for the preparation of lignocellulose derived cellulosic materials as alternatives to petrochemical feedstocks has been the focus of considerable research interest. While the technical viability of IL-based lignocellulose treatment methodologies has been well established, the high cost of reagents inhibits commercial feasibility. This work aimed to assess the technoeconomic viability of the preparation of cellulose rich materials (CRMs) using protic ionic liquids (PILs) synthesized from low cost alkylamines and sulphuric acid. For this purpose, the tertiary alkylamines, triethylamine, and dimethylbutylamine were selected. Bulk scale production cost of the synthesized PILs, triethylammonium hydrogen sulphate and dimethylbutylammonium hydrogen sulphate, was reported as \$0.78 kg⁻¹ to \$1.24 kg⁻¹. CRMs were prepared through the treatment of common wheat (*Triticum aestivum*) straw with these PILs. By controlling treatment parameters, CRMs with a cellulose content of ≥ 80 wt% were prepared. This was achieved using a *T. aestivum* straw to PIL loading ratio of 1:15 w/w, a treatment duration of 180 minutes, and ethanol as a cellulose antisolvent. Infrared spectra data and decreased onset degradation temperature of CRMs ($\Delta T_{ONSET} \sim 70$ °C) suggested the formation of cellulose sulphate esters during treatment. Chemical derivatisation can aid the dispersion of prepared CRMs in non-polar polymer/ composite matrices, but act as a barrier to thermal processing at temperatures above 150 °C. It was also shown that treatment increased the crystallinity of CRMs ($\Delta CrI \sim 40$ %) without altering the native crystalline structure or crystallite size (~ 2.6 nm) of cellulose; peaks associated with the cellulose I crystalline planes (110), (200), and (004) were observed at Bragg angles 16.0 °, 22.5 ° and 35.0 ° respectively. This highlighted the inability of assessed PILs to dissolve crystalline cellulose and was attributed to the high acidity ($pK_a \sim -1.92$ to -6.42) of sulphuric acid derived anions. Electron micrographs revealed that the stratified multilayer tissue structure of untreated *T. aestivum* straw was significantly modified during treatment. *T. aestivum* straw particles were disassembled during treatment, with prepared CRMs adopting a golden-brown film-like appearance. This work demonstrated the degradation of non-cellulosic fractions of lignocellulose without dissolution of cellulose. It is the first to report on the derivatisation of cellulose during treatment with protic hydrogen sulphate ionic liquids, and the potential implications of this with reference to biopolymer feedstock preparation.

Keywords : cellulose, extraction, protic ionic liquids, esterification, thermal stability, waste valorisation, biopolymer feedstock

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