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Coupling of ionic liquid treatment and membrane filtration for recovery of lignin from lignocellulosic biomass

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ABSTRACT

The work demonstrates the pretreatment of lignocellulosic biomass (Rice straw) in imidazolium based ionic liquids. Three different imidazolium based ionic liquids, 1-ethyl-3-methyl–imidazolium acetate, 1-methyl-3-octylimidazolium chloride and 1-butyl-3-methyl-imidazolium tetrafluoroborate were used to dissolve the lignocelluloses of rice straw and the dissolution process was optimised under several conditions viz. time, temperature and particle size of biomass. The dissolution process was investigated by characterizing the biomass before and after treatment by FTIR, XRD, SEM and Zeta Potential analysis. From the pretreated lignocelluloses, cellulose and lignin were separated using chemical methods. On the basis of investigations, the role of ionic liquids on dissolution of lignocelluloses and effect of different imidazolium based ionic liquids for the regeneration of cellulose and lignin were discussed. After the separation process ionic liquid was recovered using nano filtration membrane and was reused for further study.

1. Introduction

Biomass provides alternative and renewable energy resources for sustainable production of organic fuels and chemicals. Furthermore lignocellulosic biomass from agricultural residues, forestry wastes, waste paper and crops which is a renewable, relatively carbon-neutral source of energy has come under intense research scrutiny due to its potential use as a starting material for bioproducts from biofuels to specialty chemicals [1–3]. In this study rice straw (*Oryza sativa*) collected from the North East India, one of the hotspots of biodiversity of the world was considered as the lignocellulosic biomass for processing and recovery of value added product by greener approach. Various pretreatment options are defined in literature such as dilute acid, concentrated acid, and organosolvent pretreatment. However this study emphasizes the potential of certain ionic liquids as pretreatment solvents for lignocellulosic biomass.

Lignocellulosic biomass contains ~30–50% cellulose, a glucose polymer; 10–40% hemicelluloses, a sugar heteropolymer and ~5–30% lignin, a non-fermentable phenyl propene unit plus lesser amounts of minerals, oils, soluble sugars, and other components [4,5]. The dense network of intramolecular/intermolecular hydrogen bonds in cellulose, branched hetero polysaccharides of hemicelluloses with shorter chain lengths and three dimensional amorphous lignin provides a complex network in lignocellulosic biomass [6–8]. Because of this, new and efficient solvents and process technologies are needed to break the complex network of lignocellulosic biomass. Ionic liquid serves as a new class of designer solvents that can dissolve a large number of biomacromolecules such as cellulose, lignin, silk fibroin, and starch with high efficiency [9–11].

As an environment friendly material, the applications of ionic liquids have been extensively reported as solvent to facilitate green applications in reactions and separations due to their unique beneficial properties usually negligible vapour pressure, low flammability, high thermal stability over a wide range of temperatures and tuneable properties such as hydrophobicity, polarity and solvent power [12–16]. Due to the IL's solvent power, their use in the development of alternative methods for the extraction and processing of carbohydrates and other compounds from lignocellulosic biomass was recently explored intensively [17,18]. In this study pretreatment of lignocellulosic biomass with ionic liquid was carried out to alter the structure of lignocellulosic biomass by breaking the lignin seal and disrupting the crystalline structure of cellulose. A typical deconstruction sequence for lignocelluloses is: size reduction to chips and pretreatment that solubilises the

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hemicelluloses and alters/removes lignin and cellulose [19]. To gain a greater insight into ionic liquid pretreatment, the effect of ionic liquids with different anionic groups on the structural changes of rice straw was investigated. Various ionic liquids such as 1-methyl-3-octyl imidazolium chloride, 1-ethyl-3-methyl-imidazolium acetate, 1-butyl-3-methyl-imidazolium tetrafluoroborate have been applied as solvents in pretreatment step.

Since ionic liquids are very expensive than the conventional solvents hence recycling and reuse of the ionic liquids is a crucial factor for the economic efficiency of the extraction process. Thus in our study recovery of ionic liquids has been studied using nano filtration membrane.

2. Experimental

2.1. Materials

The lignocellulosic feedstock used in this study was rice straw (*Oryza Sativa*) collected from the Jorhat district of Assam, India. The biomass was washed, air-dried and then finely grounded with a grinder and sieved (150 μm, 300 μm, 450 μm) before use. The prepared grounded rice straw samples were then stored in plastic bags at room temperature. The ionic liquids 1-methyl-3-octylimidazolium chloride, 1-ethyl-3-methylimidazolium acetate and 1-butyl-3-methyl imidazolium tertrafluoroborate were purchased from Sigma-Aldrich (USA) and were used without further purification. The standard lignin was purchased from TCI, Japan. The commercial polyamide thin film composite membranes (FilmTec NF 270-400) viable for operation at pH 3–10 and temperature up to 45 °C were used for the recovery of ionic liquids.

2.2. Dissolution of rice straw

0.2 g of the rice straw was taken for each experiment and 5 mL ionic liquid was added to each sample and stirred using a homogenizer with a constant speed of 400 rpm at different temperatures. The samples were collected every one hour interval of time and filtered and analysed by UV visible spectrophotometer. The UV absorption peak for lignin was noted at 280 nm. After dissolution of the biomass in ionic liquid percentage of biomass dissolved was calculated according to the equation:

$$Diss = \left(1 - \frac{M_{und}}{M_o}\right) \times 100$$

where M_{und} → Mass of undissolved residue recovered.
Mo → Mass of original biomass.
Diss → Dissolution %.

2.3. Lignocellulose recovery

Once the lignocellulose has been pretreated, it needs to be recovered and further processed. The first step is to separate the three major components-cellulose, hemicelluloses and lignin. Two prominent stages appear in separating the components. Firstly cellulose is precipitated by adding an organic solvent (acetone)-water mixture (1:1). As the cellulose is precipitated the lignin remains in the solution. After evaporating off the organic solvent lignin can be recovered. Since acidification reduces the basicity of the ionic liquids which in turn lowers the lignin solubility, thus 0.1 N H_2SO_4 was added to the lignin containing IL solution to increase the amount of lignin recovery [20,11,15]. The typical process for the separation of lignocelluloses with ionic liquids is represented schematically as shown in Fig. 1.

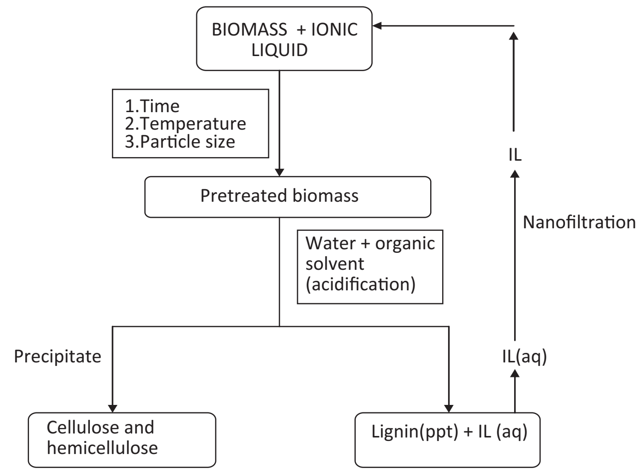

Fig. 1. Schematic representation of the pre-treatment of biomass using ILs and further regeneration and fractionation into cellulose, hemicelluloses and lignin.

2.4. Recovery and recycle of ionic liquid

Due to high cost of ionic liquid it is important to recover the used IL from its aqueous mixture after recovery of lignin. Nano filtration, a pressure driven membrane process was carried out for recovery of ionic liquid in a standard experimental set up as described in our published work [21] in which a two compartment membrane cell was used for the study. Volume of each compartment of the cell was 150 mL. The commercial polyamide thin film composite membrane was placed between the compartments with silicone-rubber packing and the cell was connected with a reservoir of 500 mL. The solution of dissolved lignocelluloses in ionic liquid was stirred continuously and circulated by peristaltic pump that was connected to the reservoir applying a pressure 5 bar and flow rate 20 mL/min. Permeate flux was calculated by using the equation given as,

$$J = \frac{V\Delta C}{A\Delta t}$$

where V is the volume of permeate at time t, ΔC is the concentration variation in the corresponding aqueous solution at the time interval Δt, A is the area of the membrane. Rejection of the membrane is given as,

$$R\% = \frac{C_f - C_p}{C_f} \times 100$$

where C_f is the concentration in feed and C_p is the concentration in permeate.

2.5. Analytical methods

Samples were analysed by UV–Visible Spectrophotometer (Thermo Scientific, EVOLUTION 201), IR (PERKIN Elmer System 2000), XRD (JDX-11P-3A, JEOL, Japan), surface morphology was studied by a scanning electron microscope (LEO 1427VP, UK), zeta potential and isoelectric point were determined by Electrokinetic Analyzer [Anton-Paar SurPASS].

3. Results and discussion

3.1. Dissolution of lignocelluloses

After ten hours of ionic liquid treatment the lignocelluloses content is high in the solution as is evident from the change in colour