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Synthesis and characterization of cellulose acetate from rice husk: Eco-friendly condition

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ABSTRACT

Cellulose acetate was synthesized from rice husk by using a simple, efficient, cost-effective and solvent-free method. Cellulose was isolated from rice husk (RH) using standard pretreatment method with dilute alkaline and acid solutions and bleaching with 2% H_2O_2. Cellulose acetate (CA) was synthesized successfully with the yield of 66% in presence of acetic anhydride and iodine as a catalyst in eco-friendly solvent-free conditions. The reaction parameters were standardized at 80 °C for 300 min and the optimum results were taken for further study. The extent of acetylation was evaluated from % yield and the degree of substitution (DS), which was determined by ^{1}H NMR and titrimetrically. The synthesized products were characterized with the help modern analytical techniques like FT-IR, ^{1}H NMR, XRD, etc. and the thermal behavior was evaluated by TGA and DSC thermograms.

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1. Introduction

Lignocellulosic biomass is the most abundant renewable biomass on the earth with a worldwide yearly supply of approximately 200 billion tones (Ragauskas et al., 2006; Sánchez & Cardona, 2008; Zhang, 2008). Lignocellulosic biomass comprising forestry, agricultural and agro-industrial wastes are inexpensive, relatively carbon-neutral source of energy sources (McKendry, 2002). An intense research scrutiny was currently undertaken worldwide to identify attractive chemical transformations to convert biomass into organic chemicals and to develop economically feasible processes for these transformations on a commercial scale (Naik, Goud, Rout, & Dalai, 2010). Lignocellulosic biomass is composed of cellulose, hemicelluloses and lignin as well as other minor components. Among them cellulose is the most abundant renewable organic material produced in the biosphere and widely distributed in higher plants, in several marine animals, and to a lesser degree in algae, fungi, bacteria, invertebrates, and even amoeba (Habibi, Lucia, & Rojas, 2010). Cellulose is a polysaccharide made of D-glucose connected together via β-1,4-glycosidic bonds and is a promising raw material for producing important chemicals, including cellulosic-ethanol, hydrocarbons, and starting materials for the production of polymers (Hahn-Häegerdal, Galbe, Gorwa-Grauslund, Lidén, & Zacchi, 2006; Mosier, Sarikaya, Ladisch, & Ladisch, 2001; Ragauskas et al., 2006).

The production of cellulose derivatives has extensive interest worldwide, mainly because of its abundance in nature, its biodegradability and its lower environmental impact in comparison with polymers obtained from fossil sources (Zhang, 2007). Nowadays derivatives of cellulose have been widely used in waste treatment, oil recovery, paper manufacturing, textile finishing, food additives and pharmaceutical application (Yan, Li, Qi, & Liu, 2006). Cellulose acetate, one of the important derivatives of cellulose which are industrially more important and it is estimated that annually 1.5 billion pounds are manufactured globally (Biswas, Shogren, & Willett, 2005). Cellulose acetate has vast industrial applications such as coatings, cigarette filters, textile fibers, consumer products, filtration membranes, composites, laminates, and medical and pharmaceutical products (Yu et al., 2013; Li et al., 2009; Yu, Yu, Chen, Williams, & Wang, 2012).

Traditionally, cellulose acetate is produced from native cellulose like sugarcane bagasse by Cerqueira and his co-workers, polysaccharide by Edgar and his co-workers and valonia cell by Sassi and his co-workers using acetic acid and acetic anhydride in the presence of a sulfuric acid as a catalyst (Cerqueira, Filho, & Meireles, 2007; Edgar et al., 2001; Sassi & Chanzy, 1995). But in the recent time, synthesis of cellulose acetate includes the use of ionic liquids in room temperature using any catalyst (Wu et al., 2004), superacids like SO_4^{2-}/ZrO_2 in a solvent free ball milling reactor (Yan et al., 2006), dialkylcarbodiimide, N,N-carbonyldiimidazole, iminium chlorides (Heinze, Liebert, & Koschella, 2006) and iodine as a catalyst for

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esterification of cellulose and corn starch (Biswas et al., 2005) cellulose and starch (Biswas et al., 2007) and polysaccharide (Biswas et al., 2009) in the presence of acetic anhydride. The catalysts used by the researchers were eco-friendly and have no pollution effect to the environment. Only sulfuric acid has some effect to the environment, so researchers tried to solve the problem and have great success with high yield of the product, cellulose acetate.

The present paper focused on the preparation of cellulose acetate in heterogeneous medium using iodine as catalyst. Being as cheap, convenient, commercially available and environment friendly reagent, iodine is currently being extensively explored regarding its catalytic properties on various substrates in various organic synthesis (Behmadi, Roshani, & Saadati, 2009; Biswas, Saha, Lawton, Shogren, & Willett, 2006; Phukan, 2004; Yadav, Reddy, Rao, & Reddy, 2003; Yadav et al., 2008). So, we have selected the catalyst as iodine in presence of acetic anhydride and also till this time no work had been reported on preparation of cellulose acetate from rice husk using eco-friendly solvent free condition with good yield 66%.

2. Materials and methods

2.1. Materials and chemicals

Rice Husk used in the experiments was supplied by local rice milling industry, Bhatemora Rice Mill Pvt. Ltd., Jorhat, Assam (North-East part of Assam). RH was extensively washed with distilled water in order to remove impurities (mainly dust). The materials were first dried in sunlight and cut into smaller pieces and milled to pass through a 1–2 mm mesh. The milled samples were then stored at room temperature. The reagents and chemicals using in our study were of standard analytical grades such as acetic anhydride, iodine, sodium thiosulfate, ethanol, sodium hydroxide, hydrochloric acid, methylene chloride and other chemicals. All reagents were used without further purification.

2.2. Isolation of cellulose from rice husk

Dry powdered RH sample was extracted with mixture of organic solvent (hexane–methanol) (2:1, v/v) using Soxhlet apparatus for 10 h for removal of the oil/wax etc. After that the delignification was undergoing follow-up with two-step processes. At first the extractive free rice husk (10 g) was soaked in 300 ml different types of alkali (5%, w/v) with ratio of liquor to material 30:1 and heated to 80 °C for 5 h. After alkali treatment, slurry was allowed to cool and treated with 10% H_2SO_4 acid to neutralize the solution with 3–4 of pH value at 50 °C. After that the biomass was separated by filtration through Buchner funnel using vacuum pump. The residual biomass was then undertaking for bleaching treatment using 2% H_2O_2 solution with pH value 9 and ratio of liquor to material 30:1 and stirring for 5 h at room temperature. The chemical modification of lignocellulosic biomass was achieved by using oxidizing agents, such as H_2O_2 to improve their properties and make them suitable for different uses (Salam, Reddy, & Yang, 2007; Wójciak et al., 2007). After bleaching, the biomass was washed with distilled water for several times. After filtration samples were oven dried (Fig. 1) and the content of alpha-cellulose was then determined according to TAPPI standard method T203 (Amal, Moustafa, Khodair, & Hammouda, 2007; Guozhi et al., 2013).

2.3. Acetylation of cellulose

For the preparation of cellulose acetate, 0.2 g of RH cellulose was taken in to a 100 ml round bottomed flask fitted with a mechanical stirrer. 10 ml acetic anhydride was added in to the material

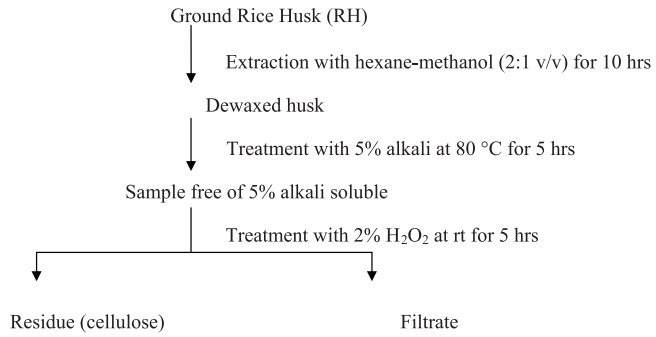

Fig. 1. Flowchart for extraction of cellulose from RH.

and required amount of iodine was added for different concentrations (0.1, 0.15, 0.2, 0.25 and 0.3 g) accordingly. The mixture was heated to 50, 60, 70, 80, 90 and 100 °C and left for 60, 120, 180, 240, 300 min at 80 °C. At the end of every experiment, the reaction mixture was allowed to cool at room temperature and treated with 5 ml saturated solution of sodium thiosulphate with stirring. The colour of the mixture was changed from dark brown to colorless, indicating the transformation of iodine to iodide. The mixture was then transferred to a beaker containing ethanol (30 ml), stirred for 60 min. The product was filtered and thoroughly washed with 75% (v/v) ethanol and distilled water to remove the unreacted acetic acid and byproducts. The solid material was then dried at 60 °C in an oven. The oven-dry materials was dissolved in methylene chloride and filtered. Cellulose acetate was formed as a film in-side the flask after evaporating the filtrate. Ethanol was used to remove the film from the flask and filtered through a filter paper. The cellulose acetate collected on the filter paper was dried at 60 °C in oven for 24 h.

2.4. Determination of degree of substitution (DS)

The average value of acetate groups (—CH_3COO) groups that replace hydroxyls in every glucose cycle gives the degree of substitution (DS) (Cai et al., 2013) and the values were determined by ^1H NMR spectroscopy and by titration with aqueous sodium hydroxide solution (Mullen & Pacsu, 1942).

2.5. Characterization of the acetylated cellulose

The functional group and chemical structure were evaluated by FT-IR spectroscopy using a Perkin–Elmer FT-IR-2000 spectrometer. Thirty-two scans were accumulated for each spectrum at a resolution of 4 cm^{-1} in the region from 4000 to 400 cm^{-1}, using KBr pellets. NMR spectra were recorded on Advance DPX 300 MHz FT-NMR spectrometer using tetramethylsilane (TMS) as an internal standard. Thermogravimetic analysis was performed with Universal V4.7A equipment from TA-Instrument at a heating rate of 10 °C/min from 30 °C to 600 °C under argon atmosphere. Powder X-ray (XRD) measurement was performed on a Rigaku Ultima IV diffractometer with Cu Kα radiation at 40 kV and 40 mA in the range of $2\theta = 5–60^\circ$, and the scanning rate is 5°/min.

3. Results and discussion

3.1. Isolation of cellulose from RH

3.1.1. Pretreatment of RH

Alkali pretreatment was carried out to remove lignin and the hemicelluloses from RH. We have taking five different common alkalis and the mixture of alkali for our investigations. In the first step of alkaline pretreatment and acid treatment, solubilize the

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