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Hydrothermal and microwave assisted alkali pretreatment for fractionation of arecanut husk

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ABSTRACT

Alkaline pretreatment assisted with hydrothermal and microwave irradiation as heating mechanisms were evaluated for their efficiency to develop a lignocellulosic biorefinery from arecanut husk. Hydrothermal treatment was carried out at 121 °C for 1, 1.5 and 2 h and microwave irradiation was performed at three power levels of 900, 540 and 180 W at two time periods (1 and 3 min). Hydrothermal treatment (1 h) of biomass soaked in 20% w/v NaOH solution resulted in average recovery of 82% hemicellulose with 69.7% lignin removal. Whereas, for hydrothermal treatment (1 h) of alkali-biomass mixture (no soaking), 74.9% of hemicellulose were recovered with 64.6% lignin removal. Increasing the reaction time from 1 to 1.5 h resulted in significant increase in average hemicellulose yield (83.5%). However, prolonging hydrothermal treatment time to 2 h did not result in further increase in average hemicellulose yield (82.3%). The residue obtained after hydrothermal pretreatment (1.5 h) was concentrated in cellulose (average 69.2%). Compared to hydrothermal treatment, microwave treated biomass yielded low hemicellulose recovery and maximum yield (52%) was obtained at 900W and 3 min exposure. FTIR analysis confirmed the presence of functional groups associated with xylan of hemicellulose precipitate. Enzymatic hydrolysis of pretreated residue (unbleached and bleached) using cellulase and β- glucosidase released 75–79% reducing sugars from cellulose. The amount of glucose released from pretreated biomass was 71.5 ± 1.9% in comparison to 2.2 ± 0.1% as obtained from enzymatic hydrolysis of untreated biomass. Thus, the developed process generated cellulose rich residue, hemicellulose as precipitate and liquor rich in lignin.

1. Introduction

Biofuels are potential alternatives to fossil fuel as they overcome limitations of depleting resources, bridge gaps in supply and demand and mitigate greenhouse gas emission from petroleum resources. Countries including USA, and others in Europe have set ambitious objectives to supplement their fossil fuel demand with biofuels (Viikari et al., 2012). India, with its National Policy on Biofuels, aims to achieve 20% blending of biofuels by 2017 (NPB, 2009). In contrast to sucrose or starch based biofuel production, lignocellulosic biofuel are produced from abundantly available, non-food agricultural residues (Rass-Hansen et al., 2007). However, the high cost of bioethanol production is a major hurdle for its successful commercialization (Quintero et al., 2013).

Out of billions of tonnes for lignocellulosic biomass generated globally, in India, surplus crop residues account to 164.5 million MT (TIFAC, 2016). India is a leading producer of arecanut (53%) followed by China. The arecanut husk, which is generated as a waste byproduct, represents 60–80% of total weight of nut's total weight. In India, 0.62 MMT of arecanut was produced in 2013–14 (NHD, 2015), generating about 0.5 MMT of husk. A small portion of arecanut husk is used as solid fuel for household application and a major portion is discarded as waste. The disposal of this biomass poses a challenge for the farmers due to slow degradation rate and low bulk density of biomass and if remained unmanaged, these residues harbour diseases and attract pests. To accelerate residue removal, farmers in India commonly practice burning the residue on the farm. The presence of significant cellulose and hemicellulose content makes it a suitable substrate for valorisation to produce biofuels, biopolymers, and fine chemicals.

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Currently, bioethanol production involves the saccharification and fermentation of cellulose, while hemicellulose is generally discarded as waste (Zhang et al., 2014). Hemicellulose can be an important substrate for production of biopolymers (polyhydroxybutyrate, polybutylene succinate) and bio-based chemicals (lactic acid, succinic acid, glutamic acid) (de Jong et al., 2012). It can also be utilized for production of emerging prebiotics such as xylooligosaccharides (XOS) (Aachary and Prapulla, 2009) and xylitol (Liaw et al., 2008). As compared to cellulose and hemicellulose, lignin has highest specific energy content and used as fuel for power generation. It can also be used as substrate for aromatic compounds (via catalytic pathway), syngas and hydrogen production (via thermochemical pathway) (Azadi et al., 2013). Therefore, a biorefinery approach can provide pathway for valorisation of lignocellulosic biomass and create value added products in comparison to current biofuel production process.

To overcome the recalcitrant nature of cellulose to improve the yield of fermentable sugars, a variety of physical, chemical, and biological pretreatment approaches have been proposed (Chaturvedi and Verma, 2013; Kumar et al., 2009). Application of steam is the most commonly employed heating mechanism in most of the pretreatment approaches. Recently, microwave irradiation has gained increasing importance due to its high heating efficiency. Microwave irradiation induces structural changes in biomass thereby increasing porosity and thus accessibility to the underlying cellulose (Azuma et al., 1984; Hu and Wen, 2008). Additionally, ionic compounds such as lime or sodium hydroxide may further increase the loss tangent factor, which is a measure of the substance's heating ability in a microwave, thereby facilitating biomass reaction (Meissner and Wentz, 2004).

Steam assisted alkali pretreatment has been evaluated for recovery of hemicellulose from corn cobs (Samanta et al., 2012) and pigeon pea (Samanta et al., 2013). The authors reported 90–96% hemicellulose recovery using 16% NaOH in assistance with steam. Both chosen crops were rich in native hemicelluloses and poor in lignin content. Therefore, fractionation challenges were minimal which indicated that low lignin biomass feedstock can be easily utilized for hemicellulose recovery using the above approach. Ultrasound assisted lime pretreatment was reported for production of bioethanol from arecanut husk (Sasmal et al., 2012). Simultaneous saccharification and fermentation of pretreated arecanut husk was able to produce 73–85% bioethanol with different variety of husk. Fractionation of lignocellulosic components of sweet sorghum bagasse was studied using hydrothermal and microwave assisted treatments. A two-step process involving hydrothermal or microwave assisted autohydrolysis (121 °C, 30–120 min) was designed to recover hemicellulose first (70–73%), followed by hydrothermal/microwave assisted lime treatment for separation of cellulose and lignin (58–60%) (Kurian et al., 2015). However, a two-step process may not be economical in terms of energy input and yield recovery. If interest is in prebiotics such as XOS, controlled breakdown of xylan into XOS would be challenging. Sun et al. (2014) reported hydrothermal pretreatment of *Eucalyptus urophylla* in temperature range of 100–240 °C for recovery of hemicellulose. The pretreated biomass was then subjected to alkaline pretreatment (2% NaOH, 90 °C, 2.5 h) to obtain cellulose rich fraction for enzymatic hydrolysis.

The present work aims to develop a biorefinery approach to achieve effective fractionation of cellulose, hemicellulose (xylan rich fraction), and lignin from arecanut husk. High recovery of hemicellulose in the form of xylan following pretreatment allows for the potential to generate additional value added products. Alkaline pretreatment at different alkali concentrations with and without heat assistance (hydrothermal and microwave) was studied to develop a single step process for fractionation of lignocellulosic components which has not been reported for high lignin biomass feedstock.

2. Materials and methods

2.1. Materials

Analytical grade chemicals and reagents were procured and used as such. Sodium hydroxide pellets (low chloride) was obtained from Merck Millipore, USA. Glacial acetic acid was procured from Sigma Aldrich, USA. Double distilled water was used for preparation of reagents. Arecanut was collected from farms in Sirsi district of Karnataka, India. The nut was shredded, sieved, dried until constant moisture content and finally stored in air- tight container until further use.

2.2. Experimental design

Fig. 1 represents the experimental approaches employed in the work to achieve biomass fractionation.

2.3. Conventional alkali pretreatment

Biomass was extracted sequentially with 95% ethanol, followed by distilled water to remove extractives. To 5 g of extractive free biomass 50 ml of desired concentration (5, 10, 15 and 20% w/v) of alkaline (sodium hydroxide) solution was added and mixed to ensure complete wetting of biomass. The mixture was incubated at 35 °C for 16 h at 150 rpm. After incubation, the mixture was filtered to collect filtrate and the residue was washed with 100 ml distilled water. The washed residue was dried at 50 °C and stored in air tight container. The filtrate was centrifuged at 5000 rpm for 15 min to obtain clear supernatant. The pH of the supernatant was adjusted to pH 5 using glacial acetic acid. To this solution, 1.5 times the volume of ethanol (95%) was added to precipitate hemicellulose and allowed to stand overnight at room temperature. The precipitate was collected after centrifugation, washed twice with distilled water and pellet dried at 50 °C and stored in air tight container. The filtrate (black liquor) contains dissolved lignin. The percentage of hemicellulose recovered after alkali pretreatment was estimated by measuring the relative recovery (%) by the following formula:

$$\%\text{hemicelluloserecovery} = (\text{WEH}/\text{WH}) \times 100$$

Where,

WEH is the dry weight of extracted hemicellulose

WH is the weight of hemicellulose in dry biomass

The dried pretreated residue (cellulose rich fraction) was used for enzymatic hydrolysis experiments.

2.4. Hydrothermal assisted alkaline pretreatment

Hydrothermal assisted alkaline pretreatment was carried out at different alkali concentrations (5, 10, 15 and 20% w/v) at solid to liquid ratio of 1:10 for 1 h, 1.5 h and 2 h at 121 °C. Briefly, 5 g extractive free biomass was mixed with 50 ml of alkaline solution of desired concentration and mixed well to ensure complete wetting of biomass. The mixture was autoclaved at 121 °C for desired time period. After the desired time period, the mixture was allowed to cool to room temperature and filtered. The protocol for recovery of hemicellulose was similar to that described in Section 2.3.

2.5. Microwave assisted alkaline pretreatment

A general purpose microwave oven (Model MC3283FMPG, LG, South Korea) operating at 2450 MHz, with adjustable microwave