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Delignification, Cellulose Crystallinity Change and Surface Modification of Coir Pith Induced by Oxidative Delignification Treatment

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Abstract: Lignocellulosic agroindustrial residue, the coir pith, poses severe pollution threats to land and water environment due to polyphenol leaching and its resistance for natural degradation. Overcoming of structural hindrances offered by coir pith has to be attained for preparing the substrate suitable for bioenergy production, and oxidative delignification has been found to be the promising option to achieve this goal. Mild hydrogen peroxide treatment was performed on coir pith to loosen the lignocellulosic binding. Treatment optimization was done based on substrate concentration and duration. Klason lignin of coir pith was estimated by chemical method. Investigations on structural modifications were carried out by FTIR, XRD and SEM analysis. Delignification efficiency of 53% was estimated and lignin loss and structural changes were analyzed by FTIR. XRD analysis led to the inference of cellulose crystallinity index reduction. SEM analysis indicated smoothening of surface and change of porous surface into pleet like structure. Thus to a greater extent optimised oxidative delignification process attained the pretreatment goals of delignification, cellulose crystallinity index reduction and surface modification.

Keywords: cellulose crystallinity index; coir pith; delignification; hydrogen peroxide treatment; structural modifications.
1. Introduction

Concept of conversion of waste to energy is of significance since it yields the twin benefits of waste management and sustainable energy production. Bio-energy, such as ethanol, methane, and hydrogen, can be generated from lignocellulosic biomass (Demirbas, 2009) using appropriate processes (Kim and Dale, 2003). Coir pith is an agroindustrial byproduct generated during the coir defibering process. Million tons of coir pith generated annually across India is heaped as waste. Resistance of coir pith to natural degradation, polyphenol leaching, and subsequent pollution of nearby receiving water bodies, etc create severe environmental problems. Various research programmes are being undertaken to convert the waste into useful products (Parab and Sudersanan, 2010). Biochar which has immense carbon sequestration potential with agricultural applications has been one among them produced from coir pith (Rojith and Bright, 2012).

Besides, cellulosic ethanol can be produced from lignocellulosic residue (Gaspar et al., 2007), and while doing so pretreatment happens to be the primary step (Galbe and Zacchi, 2007). Coir pith contains 38% lignin and therefore delignification has to be achieved to loosen the lignocellulosic binding and to expose the cellulosic component. The delignification can be done using chemical and biological methods such as solubilisation using hydrogen peroxide (Sun et al., 2000), enzymatic delignification (Sena-Martins et al., 2008) using ligninase. After effective delignification cellulose components can be enzymatically hydrolysed to glucose which can be fermented to ethanol (Sun and Cheng, 2002). Crystallinity of cellulose is an inhibitory factor for microbial and enzymatic processes and therefore, pretreatment should also serve the objective of cellulose crystallinity reduction so that enzymatic saccharification can be enhanced (Mosier et al., 2005). Pretreatment also induces surface modifications of the substrate.

Considering the economics, a combination of chemical and biological pretreatment shall be a feasible proposition to loosen the lignocellulosic binding and prepare the substrate suitable for further processing. Mild oxidative delignification treatment (Gierer, 1986) has been widely accepted as an effective chemical pretreatment method for agricultural residues. Gould (1985) reported the mechanism of alkaline peroxide delignification of agricultural residues. Oxidative delignification generates dark brown coloured filtrate termed as ‘Black Liquor’ which contains solubalized lignin and its derivatives (Mussatto et al., 2007). Lignin can be recovered from coir pith black liquor (Rojith and Bright, 2012).

Fourier transformation infrared (FTIR) spectroscopy is a commonly used tool to identify the functional groups (Kubo and Kadla, 2005) associated with the biomass (Faix, 1988). FTIR analysis helps identify the structural transformation of lignin (Cotrim et al., 1999) and cellulosic components (Telysheva et al., 2007). Degree of cellulose crystallinity can be analyzed using X-ray diffractometer.
(Segal et al., 1959). Scanning electron microscope analysis (Namasivayam and Kavitha, 2006) helps identify the morphological changes induced by the pretreatment (Kang et al., 2012).

This paper reports the effect of mild hydrogen peroxide treatment on coir pith and investigates the delignification efficiency, cellulose crystallinity changes and also analyses the structural modifications induced by the oxidative delignification.

2. Materials and Methods

2.1. Material

Coir pith was collected from a coir defibering unit at Alleppey district, Kerala, India. Collected coir pith was washed in tap water, dried and stored in air tight containers.

2.2. Methods

2.2.1. Estimation of Klason lignin

Lignin content was measured by modifying the Klason lignin method for 0.5 g of coir pith. The delignification efficiency was calculated by the following equation:

\[ \text{DE} = \frac{L_i - L_F}{L_i} \times 100 \]

where DE stands for delignification efficiency, \( L_i \) represents initial lignin content before treatment, \( L_F \) represents final lignin content after treatment.

2.2.2. Hydrogen peroxide treatment

Quantities of 1, 2, 3, 4 g of coir pith were treated with 1% \( \text{H}_2\text{O}_2 \) at pH 11.5 for varying time intervals of 8, 10, 12, 15, 20 and 24 h. The residue was filtered, washed with slightly acidified tap water until neutral pH was obtained and dried in a hot air oven at 60 °C. The experiment was repeated with 2% \( \text{H}_2\text{O}_2 \).

2.2.3. FTIR analysis

Comparison of structural changes of coir pith samples before and after oxidative delignification was achieved by Fourier transformation infrared (FTIR) analysis. FTIR spectrum of the untreated coir pith along with treated coir pith was taken with a resolution of 4 cm\(^{-1}\) and 32 scans per sample. The absorbance spectra were recorded at wave numbers from 500 – 4000 cm\(^{-1}\).

2.2.4. XRD analysis

The raw coir pith sample and the coir pith treated with hydrogen peroxide were used for analysis of cellulose crystallinity change. Rigaku X – Ray diffractometer was used to perform the
crystallinity study. The radiation used was of Cu\(\alpha\) radiation at a wavelength of 1.5418 \(\text{Å}\). The samples were scanned at a scan rate of 1° per minute with scan angle (2\(\theta\)) from 7° to 40° and the sampling rate was 0.02° (2\(\theta\)).

The cellulose crystallinity index was calculated from the equation:

\[
\text{CrI} = \frac{I_{002} - I_{\text{am}}}{I_{002}} \times 100
\]

where CrI indicates the relative degree of crystallinity, \(I_{002}\) is the maximum intensity (in arbitrary units) of the 002 lattice diffraction, and \(I_{\text{am}}\) is the intensity of diffraction in the same units at \(2\theta = 18°\).

2.2.5. SEM analysis

Scanning electron microscope analysis was performed on untreated and treated coir pith to analyze the morphological changes induced due to oxidative delignification treatment. SEM images were taken at 2, 10 and 50 \(\mu\)m range.

3. Results and Discussion

3.1. Hydrogen Peroxide Treatment

Optimum delignification efficiency was found in 10 h treatment at a ratio of 3 g substrate: 100 mL 2% \(\text{H}_2\text{O}_2\). Optimum pH for hydrogen peroxide treatment was found to be 11.5 beyond which delignification efficiency decreased. Bleaching of the substrate occurred due to the treatment and brownish coir pith turned to whitish in colour after oxidative treatment. This can be attributed to the bleaching ability of hydrogen peroxide. Klason lignin analysis of samples confirmed lignin loss due to the treatment, and delignification efficiency was found to be 53%. Oxidative delignification process leads to the solubilization of lignin and its derivative into the filtrate. Filtrate obtained was dark brown in colour and is termed as coir pith black liquor. Compositional changes of coir pith could thus be inferred due to loss of lignin content. FTIR, XRD and SEM analysis indicated structural changes induced due to the oxidative delignification treatment. Lignin structural modifications and cellulose crystallinity changes occurred during the process.

3.2. FTIR Analysis

Comparison of FTIR images of the raw and treated coir pith lead to the inference that structural changes occurred due to the pretreatment. Changes in characteristic peaks of primary components indicate compositional changes induced due to the treatment.
Aromatic skeletal vibration band around the peak 1505 cm\(^{-1}\) usually represents measure for lignin content. Vibration at 1060 cm\(^{-1}\) is associated with C–O, C–C stretching and C–OH bending in polysaccharides. 1250 cm\(^{-1}\) represents the Guaiacyl unit vibration of lignin. Weak band at 1373 cm\(^{-1}\) originates from phenolic and aliphatic methyl group of lignin. Aromatic skeletal vibrations at 1600 cm\(^{-1}\), 1443 cm\(^{-1}\) and 1513 cm\(^{-1}\) are common for lignin samples. Band at 1600 cm\(^{-1}\) may also represent the water associated with lignin. Peak near 2930 cm\(^{-1}\) arises from CH stretching in aromatic methoxyl groups. Peak around 3420 cm\(^{-1}\) results from hydroxyl groups in phenolic and aliphatic structures.

The FTIR spectra of the untreated and treated coir pith are shown in Figs. 1 and 2, respectively.

![Figure 1. FTIR graph of untreated coir pith.](image1)

![Figure 2. FTIR graph of treated coir pith.](image2)

Delignified sample analysis showed several characteristic peak shifts and peak disappearances which lead to infer that structural changes occurred due to oxidative delignification method. Lignin and carbohydrate structural alternations occurred due to the treatment. Peak shift at 1120 cm\(^{-1}\), C-H plane deformation indicates carbohydrate structural changes. Peak change at 1620 cm\(^{-1}\) and 2939 cm\(^{-1}\)
indicates lignin change. 3407 cm\(^{-1}\), 3450 cm\(^{-1}\), and 3531 cm\(^{-1}\) vibration infers structural changes in hydroxyl groups in phenolic and aliphatic structures.

3.3. XRD Analysis

A graph was plotted with XRD data of untreated and treated substrate and is shown in Fig 3. Graph values along with XRD data helps to calculate the crystallinity index values. Calculated values of crystallinity index of untreated and treated coir pith are shown in Table 1.

![XRD Graph of untreated and treated coir pith.](image)

**Table 1.** Comparison of CrI values of untreated and treated coir pith

<table>
<thead>
<tr>
<th>Sample</th>
<th>(i_{002})</th>
<th>(i_{am})</th>
<th>CrI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated Coir pith</td>
<td>622</td>
<td>379</td>
<td>39.06</td>
</tr>
<tr>
<td>Treated Coir Pith</td>
<td>515</td>
<td>348</td>
<td>32.42</td>
</tr>
</tbody>
</table>

XRD analysis leads to the inferences that decrease in cellulose crystallinity index occurred due to oxidative delignification treatment. Reduction in cellulose crystallinity makes the substrate more suitable for further bioprocessing. Enhanced microbial and enzymatic accessibility to the substrate shall be possible due to cellulose crystallinity reduction.

3.4. SEM Analysis

SEM analysis indicates surface modifications induced due to the treatment (Figs. 4-9). Morphological changes were observed. SEM image at 2 \(\mu m\) indicates smoothening of surface. Fine pores have been closed and roughness of surface has been reduced. Polished surface was formed in the case of treated sample. SEM image at 10 \(\mu m\) indicates change of porous fibrous surface into pleet like structure. This pleet like structure formation induced due to the treatment allows more surface reactions to happen. Increase in surface area was inferred due to oxidative delignification treatment which shall favor further bioprocessing. Fragmentation of surface was observed in SEM image taken at
50 µm. Fragmented surface also favors further accessibility of enzymes. Surface modifications thus make the substrate more suitable for further biochemical processing. SEM image analysis confirmed surface modifications induced due to the oxidative delignification treatment.

**Figure 4.** SEM image of untreated coir pith at 2 µm.

**Figure 5.** SEM image of treated coir pith at 2 µm.

**Figure 6.** SEM Image of untreated coir pith at 10 µm.
Figure 7. SEM image of treated coir pith at 10 µm.

Figure 8. SEM images of untreated coir pith at 50 µm.

Figure 9. SEM image of treated coir pith at 50 µm.
4. Conclusions

Oxidative delignification served to a greater extent the pretreatment goals of delignification, cellulose crystallinity reduction and surface modification. Delignification efficiency of 53% attained due to mild hydrogen peroxide treatment highlights the feasibility of adopting oxidative delignification treatment process. Reduction in cellulose crystallinity favors enhanced microbial access for further bioprocessing. Increase in surface area of substrate also favors further biochemical process. For attaining further delignification, treatment with increased hydrogen peroxide concentration can also be attempted. Enzymatic delignification followed by enzymatic saccharification shall be the next milestones for bioenergy production.

References


