**Studies on the effect of bleaching agents on CAN retted & alkali pretreated bamboo fibres**

**Abstract:**

CAN retted Bamboo fibre bundles were pretreated with alkali followed by peracetic acid and hydrogen peroxide bleaching to obtain high quality fibres for textile application. The experimental results indicated that alkali pretreatment prior to bleaching with peracetic acid or hydrogen peroxide could significantly improve the appearance of the treated fibres. An optimum condition for this combined method of delignification and bleaching was obtained for extraction of fibres having good physical properties and appearance of the pretreated fibre bundles. The fibres were further characterized by calculating weight loss, whiteness & yellowness indices, lignin content measurement, tensile strength using Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). However, further analysis indicated that the pretreated fibres with higher concentration of sodium hydroxide i.e., 0.3 N followed by PAA bleaching step (NaOH→PAA) produced reasonable reduction in lignin content and weight loss with acceptable whiteness and tensile strength.
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4.1. Introduction

Numerous new dimensions in the manufacture and the use of textiles have created awareness and general consciousness about environmental aspects to all the researchers in the textile sector that indirectly resulted in fetching the efficiency, excellence and environmental friendliness of both process and product. Bamboo is lignocellulosic fibre composed mainly of cellulose (45-55%), hemicellulose (20-25%) & lignin (20-30%) and can be bleached with various chemicals. Bamboo fibres can also be bleached with alkaline hypochlorite or hydrogen peroxide, but it undergoes marked losses in strength. These are mainly attributed to the action of bleaching agent or alkali or alkaline reagents on the non-cellulosic constituents of bamboo i.e., hemicellulose and lignin. So, efforts were made by different scientists to develop other ecofriendly bleaching agents. In recent years, peracetic acid (PAA) is being increasingly used for bleaching of regenerated fibres, natural & bast fibres and pH sensitive fibres (regenerated & manmade fibres). PAA or peroxy acetic acid is a powerful oxidizing and acid stabilizing agent. PAA has a high oxidation potential and reactivity but with increase in pH they start decomposing. Due to stringent environment regulations, PAA is being popularized as a substitute agent for the usual sodium hypochlorite bleaching which was one of the oldest industrially used bleaching chemicals either individually or in combination with hydrogen peroxide. The popularity of hypochlorite bleaching was because of its low cost and bleaching at low temperature. But the discharge water from hypochlorite and hydrogen peroxide bleaching is a potential hazard for drinking water resources. PAA is an ecofriendly bleaching agent and provides a better white effect with very little fibre damage.

Sun et al. [1] reported that PAA breaks lignin to soluble compounds by two different reactions. These reactions increase the polarity of lignin and create water-soluble lignin fragments which can be easily washed away from the bamboo/lignocellulosic material [2].

As peracetic acid is very unstable it was synthesized in the laboratory which is termed as “In-house prepared PAA” [3]. This chapter reports the bleaching of CAN retted and alkali treated bamboo fibres with PAA (in-house prepared PAA) and comparison with bleaching with H₂O₂ in respect of some important properties.

4.2. Materials and Experiments

4.2.1. Materials

Raw culm of Bambosa vulgasis was harvested from Botanical Garden of Guru Nanak Dev University, Amritsar. All the chemicals used in this investigation were of AR grade and were purchased from Merck Ltd., Hi-media Labs, Bombay (India).
4.2.2. Methods

The fibre bundles were retted by chemical assisted natural retting (CAN) technique followed by scouring with 15 g/L Na₂CO₃ and further treated with different concentrations of sodium hydroxide. After removal from the sodium hydroxide solution, the fibres were washed, neutralized and semidrying for 1 h; the fibres were further subjected to bleaching processes for maximum separation of the fibres.

4.2.2.1. NaOH Treatment

In lignocelluloses material, alkali plays the important role for its delignification. To obtain a satisfactory maximum cellulose fibre extraction, the NaOH treatment needs a high intensity process either by using high concentration of alkali or high temperature treatment. In the last chapter 3, the effects of several methods (5 methods) on physical properties of bamboo fibres were investigated. One of them was selected as best in terms of physical appearance & strength. Some method was further optimized for sodium hydroxide concentration with the condition of the second stage being fixed as follows: (a) 10 g/L PAA loading (on the weight of fibres), temperature 70 °C, time 90 min and material to liquor ratio 1:40 & (b) 10 g/L H₂O₂ loading (on the weight of fibres), Stabilizer Clarite G (1g/L), Ultavon EL (2 g/L) & caustic soda (3 g/L), temperature 98°C, time 60 min and material to liquor ratio 1:40. The experimental results are shown in Table 4.1.

4.2.2.2. Optimization of NaOH concentration (For method B)

The retted bamboo fibres were soaked into NaOH solution with different concentration (0.05 N, 0.1 N, 0.2 N & 0.3 N) with a fibre to liquor 1:40 at 35 °C for 72 h followed by washing at 40 °C for 15 min, neutralization and drying.

4.2.2.3. Preparation of PAA (in-house prepared PAA)

Peracetic acid was prepared by reaction of anhydrous acetic acid and 30% hydrogen peroxide at room temperature for 24 h. The quantity ratio of acetic acid and 30% hydrogen peroxide was chosen as 1: 0.5 according to our earlier optimized results, 1% (V/V) sulphuric acid was added as catalyst. The strength of PAA concentration was determined in accordance with standard method described by Christiansen et al [4]. The equilibrium mixture prepared under the above conditions had PAA concentration of 10.6% and hydrogen peroxide 8.6%. This maximum yield of PAA was used for further process i.e. for the bleaching.

4.2.2.4. Sequential alkali treatment and bleaching of bamboo fibres

Two-stage delignification was carried out in a 2000 ml oil-bath glass vessel keeping it in an incubator. To keep the bath as homogenous as possible, stirring at regular intervals was employed. Bamboo fibres were first treated with 0.05- 0.3 N NaOH at 35 °C for 72 h with a fibre to liquor 1:40. The pretreated fibres were washed with water until became
neutral. The fibres were then further treated by an oxidative delignification step with PAA or H₂O₂ loadings.

(a) Bleaching with Peracetic Acid (PAA): The in-house prepared peracetic acid was used to bleach the pretreated bamboo fibres using 10 g/L of stock solution at 70 °C for 90 min using pH 7 in the presence of 5g/L sodium meta silicate as stabilizer. After bleaching samples were thoroughly washed and dried.

(b) Bleaching with hydrogen peroxide (H₂O₂): The pretreated bamboo fibres were bleached using 10 g/L hydrogen peroxide solution (30%) at 90 °C for 60 min using 2 g/L Ultavon EL and 3 g/L caustic soda in the presence of 1g/L Clarite G as stabilizer. After that the bleaching samples were thoroughly washed and dried.

4.3. Determination of Fibre Characteristics (Testing)

4.3.1. Tensile Testing

Breaking strength and breaking extension of bamboo were tested using an Instron series IX fiber breaking strength machine in a constant 27°C temperature and 65% relative humidity using ASTM Method D-5035.

4.3.2. Weight loss

Fiber weight loss was calculated using Eq. 1:

\[
\text{Weight loss (\%)} = \frac{w_i - w_f}{w_i} \times 100\%
\]

Where \(w_i\) is the initial weight of the raw bamboo fiber and \(w_f\) is the final weight of treated bamboo fiber.

4.3.3. Scanning electron microscopy observations

The deformation behavior of a single elementary retted bamboo fibre bundle was investigated by scanning electron microscopy (SEM) using Quorum Q150RES (Supra 55-CARLZEISS) equipment (EHT= 10.00 KV, Signal A= In Lens). All specimens with longitudinal-section were coated with a thin layer of gold to avoid electrical charging.

4.3.4. Chemical analysis

The chemical composition of the original bamboo culm (without outmost layer) and retted bamboo fibre bundles was analyzed for lignin contents by using TAPPI standard T250-um-85.

4.3.5. Whiteness and Yellowness Indices

The colorimetric properties [5] of the retted fibers (D₆₅ illumination, 10° observer) were determined using a Spectraflash 600 colorimeter (Datacolor International).
4.3.6. Fourier Transform Infrared Spectroscopy (FTIR)

IR spectra of the fibres were recorded by using FTIR; Make: PerkinElmer Spectrum; Model Spectrum Two 92035 using KBr disks containing 1% finely ground samples. Eight scans were taken of each sample recorded from 4000 to 450 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\) in the absorbance mode.

4.3.7. X-Ray Diffraction (XRD)

Crystallinity and crystal size of raw bamboo fibres and optimally treated bamboo fibres were determined by wide angle X-ray diffraction (XRD; 2\(\theta = 0-60^\circ\), using a Panaltical X’pert pro using Cu-Ka radiation detector (\(\lambda =1.5406\AA\) ) Bamboo fibres were ground to powder as measuring samples. The scanning velocity was 5\(^{\circ}\)/min, the voltage was 30 kV. The crystallinity expressed as the crystallinity index (Crl) was calculated as the percentage of crystalline material in fibre sample [6].

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

Where \(I_{002}\) is the maximum intensity of the (002) lattice diffraction (2\(\theta \approx 22.1^\circ\) ) and \(I_{am}\) is the intensity at 2\(\theta \approx 15.7^\circ\).

The standard size of crystallites was determined from following equation.

\[
D_{(hkl)} = \frac{K\lambda}{B_{(hkl)}\cos\theta}
\]

Where (hkl) is the lattice plane, \(D_{(hkl)}\) is the size of crystalline, \(K\) is the Scherrer constant (0.84), \(\lambda\) is the X-ray wavelength (0.94 nm), \(B_{(hkl)}\) is the FWHM (full width half maximum) of the measured hkl reflection, and 2\(\theta\) is the corresponding reflection angle [7].

4.4. Results and Discussion

In this section, the results of all these experiments and their critical analysis are presented. The major effect of alkaline pretreatment is the removal of lignin from the bamboo, thus improving the reactivity of the remaining polysaccharides. In addition, alkali pretreatments remove acetyl and the various uronic acid substitutions on hemicellulose. This alkaline hydrolysis mechanism is based on saponification of intermolecular ester bonds cross linking xylan hemicelluloses and other components such as lignin [8].

Functional groups in components of lignocellulose are aromatic ring, hydroxyl group, carbon to carbon linkage, ether (glucosidic) linkage, ester bond, and hydrogen bond. The ether bond appears to be the most interesting among the functional groups of bamboo. Therefore, the cleavage of the ether bond can lead to separation of lignin from the
polysaccharides medium and degradation of the polymers to monomer sugars and lignin fragments.

The introduction of an alkali pretreatment for partially removing lignin before PAA and H₂O₂ bleaching might reduce the PAA and H₂O₂ loading in the bleaching stage and consequently decrease the degradation of carbohydrates to obtain high quality bamboo fibre.

In sequential sodium hydroxide & peracetic acid treatment, PAA breaks lignin to soluble compounds by two different steps. In the first step, PAA decreases the molecular weight of lignin polymers by cleaving β-aryl ether bonds and both carbon–carbon and carbon–oxygen bonds linked to the aromatic rings [1] and then PAA is responsible for other reactions that increase the water solubility of lignin: dealkylation of O-methyl groups, introduction of hydroxyl groups to aromatic rings and cleavage of the aromatic rings into muconic acids [2]. Moreover, these reactions increase the polarity of lignin and create water-soluble lignin fragments which can be easily washed away from the bamboo/lignocellulosic material.

In sequential sodium hydroxide & hydrogen peroxide treatment, NaOH can make the OH⁻ concentration distribution reasonable and activate the H₂O₂, resulting in an increased bleaching efficiency. This is because the HOO⁻ that is present in H₂O₂ bleaching liquid can oxidize the carbonyl groups of lignin macromolecule side chains.

**4.4.1. Optimisation/Effect of NaOH Concentration**

In order to obtain the optimum sodium hydroxide concentration for two stage delignification of bamboo fibres, the CAN retted baboo fibres were treated with different sodium hydroxide concentration viz. 0.05 N, 0.1 N, 0.2 N & 0.3 N with a fibre to liquor 1:40 at 35 °C for 72 h followed by washing at 40 °C for 15 min, neutralization and drying. After the treatment, the lignin content, weight loss, mechanical properties, whiteness & yellowness Indices, SEM images, FTIR spectra and XRD of treated samples were observed to estimate the effect of sodium hydroxide concentration.

**4.4.2. Effect of NaOH concentration on weight loss of CAN retted, sequential sodium hydroxide & peracetic treated and sequential sodium hydroxide & hydrogen peroxide treated bamboo fiber**

Table 4.1 & Figure 4.1 show that the weight loss increased with the increase in sodium hydroxide concentration, but slowly decreased in chemical assisted natural retting (CAN) & NaOH→PAA sequence (first treated with NaOH followed by bleached with PAA) and highly decreased in case of NaOH→H₂O₂ sequence (first treated with NaOH followed by bleached with H₂O₂).
Regarding the experimental result at 0.3N NaOH that showed a different trend, it is mainly due to the fact that although NaOH at high concentration can degrade more noncellulosic substances, it can also lead to the decomposition of cellulose. The result on weight loss in Table 4.1 also showed a remarkably increase at 0.3N NaOH.

### 4.4.3. Effect of NaOH concentration on lignin content of CAN retted, sequential sodium hydroxide & peracetic treated and sequential sodium hydroxide & hydrogen peroxide treated bamboo fiber

Table 4.2 & Figure 4.2 show the changes in lignin content with the increase in concentrations of sodium hydroxide (with & without subsequent bleaching process). The maximum loss in lignin was caused by NaOH→H₂O₂ process with no acceptable weight loss in pretreated fibres with higher concentration of sodium hydroxide i.e., 0.3 N. NaOH→PAA process produced reasonable reduction in lignin content and weight loss.
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### Table 4.2: Effect of NaOH concentration on lignin content of CAN retted, NaOH→PAA treated & NaOH→H₂O₂ treated bamboo fiber

<table>
<thead>
<tr>
<th>Concentration of NaOH (Normality)</th>
<th>Lignin content (%)</th>
<th>CAN retted</th>
<th>NaOH→PAA</th>
<th>NaOH→H₂O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>9.55</td>
<td>8.13</td>
<td>6.03</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>8.36</td>
<td>7.87</td>
<td>5.08</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>7.07</td>
<td>7.09</td>
<td>3.97</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>8.17</td>
<td>7.15</td>
<td>2.80</td>
<td></td>
</tr>
</tbody>
</table>

![Figure 4.2. Effect of NaOH concentration on lignin content of CAN retted, NaOH→PAA treated & NaOH→H₂O₂ treated bamboo fiber](image)

### 4.4.4. Effect of NaOH concentration on whiteness indices of CAN retted, sequential sodium hydroxide & peracetic treated and sequential sodium hydroxide & hydrogen peroxide treated bamboo fiber

The CAN retted bamboo fibres were treated using various concentrations of stock solution of sodium hydroxide viz. 0.05 N, 0.1 N, 0.2 N, and 0.3 N at 35 °C for 72 h with a fibre to liquor 1:40. The pretreated fibres were washed with water until neutrality. The fibres were then further treated by an oxidative delignification step with PAA & H₂O₂ loadings. After that the samples were tested for improvement in whiteness. It is found that with increase in concentration of stock solution, the whiteness of the samples showed an increasing effect on whiteness in case of NaOH→PAA & NaOH→H₂O₂ sequences, but a steep fall has been observed in case of CAN retted fibres (Table 4.3 & Figure 4.3).
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4.4.5 Effect of NaOH concentration on yellowness indices of CAN retted, sequential sodium hydroxide & peracetic acid treated and sequential sodium hydroxide & hydrogen peroxide treated bamboo fiber

The yellowness indices of treated samples were measured at different concentrations of sodium hydroxide and the results are shown in Table 4.4 & Figure 4.4. From both the table and figure, it is clear that out of these three processes, pretreatment of CAN retted fibres with different concentrations of sodium hydroxide without subsequent bleaching have a major drawback of yellowing in alkaline baths.
Table 4.4: Effect of NaOH concentration on YI of CAN retted, NaOH→PAA treated & NaOH→H₂O₂ treated bamboo fiber

<table>
<thead>
<tr>
<th>Concentration of NaOH (Normality)</th>
<th>Hunter Yellowness Index (YI)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CAN retted</td>
</tr>
<tr>
<td>0.05</td>
<td>84.63</td>
</tr>
<tr>
<td>0.1</td>
<td>88.39</td>
</tr>
<tr>
<td>0.2</td>
<td>91.33</td>
</tr>
<tr>
<td>0.3</td>
<td>93.72</td>
</tr>
</tbody>
</table>

Figure 4.4. Effect of NaOH concentration on YI of CAN retted, NaOH→PAA treated & NaOH→H₂O₂ treated bamboo fiber

4.4.6. Effect of NaOH concentration on Tenacity of CAN retted, sequential sodium hydroxide & peracetic treated and sequential sodium hydroxide & hydrogen peroxide treated bamboo fiber

Table 4.5: Effect of NaOH concentration on tenacity of CAN retted, NaOH→PAA treated & NaOH→H₂O₂ treated bamboo fiber

<table>
<thead>
<tr>
<th>Concentration of NaOH (Normality)</th>
<th>Tenacity (g/den.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CAN retted</td>
</tr>
<tr>
<td>0.05</td>
<td>1.632</td>
</tr>
<tr>
<td>0.1</td>
<td>1.498</td>
</tr>
<tr>
<td>0.2</td>
<td>1.192</td>
</tr>
<tr>
<td>0.3</td>
<td>1.183</td>
</tr>
</tbody>
</table>
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The average tenacity of natural bamboo fibres after different treatments were illustrated in Table 4.5 & Figure 4.5. With the increase in the treatment intensity, it has been observed that in all the cases, the values of average tenacity initially showed a steep fall up to 0.2 N. It is caused a reduction in tenacity due to removal of non-cellulosic material. But the concentration higher than 0.2 N found to be less effective. It has been found a maximum reduction in NaOH→H2O2 treated bamboo fiber.

4.4.7. Surface morphology of bamboo fibres

Surface pictures of treated bamboo fibre with different concentrations of sodium hydroxide and further differently (individually) treated with PAA & H2O2 bleaching agents are shown in Figure 4.6. A huge amount of gum in the alkali treated bamboo fibres can be seen in Figures 4.6 (a, c & e). After treatment with PAA & H2O2, the bamboo fibres were fiberized, but it can be seen that the bamboo fibre were joined with large amount of gum on surface in case of PAA bleaching (Figures 4.6 (i, j & k)). With the bleaching with H2O2, the bamboo fibres were receiving smoother and finer surfaces (Figures 4.6 (d, f & h)). From Figures 4.6 (a, c & e) it can be observed that the fibres are still in aggregated form. These pictures show that the fibres treated with PAA & H2O2 have a more uniform geometry of fibrils arrangement than the fibres treated with different concentrations of alkali (without subsequent bleaching).
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Figure 4.6 (a): 0.05N NaOH (20µm)  

Figure 4.6 (b): 0.05 N NaOH → H₂O₂ (10µm)

Figure 4.6 (c): 0.1 N NaOH (20µm)  

Figure 4.6 (d): 0.1 N NaOH → H₂O₂ (20µm)

Figure 4.6 (e): 0.2 N NaOH (20µm)  

Figure 4.6 (f): 0.2 N NaOH → H₂O₂ (20µm & 10µm)

Figure 4.6 (g): 0.3 N NaOH (20µm)  

Figure 4.6 (h): 0.3 N NaOH → H₂O₂ (10µm)

Figure 4.6 (i): 0.1N NaOH → PAA (2µm)  

Figure 4.6 (j): 0.2N NaOH → PAA (10µm)  

Figure 4.6 (k): 0.3N NaOH → PAA (10µm)

Figure 4.6. SEM images for side-view surfaces of alkali treated and PAA & H₂O₂ bleached bamboo fibres: 4.6 (a): 0.05N NaOH, 4.6 (b): 0.05 N NaOH → H₂O₂, 4.6 (c): 0.1 N NaOH, 4.6 (d): 0.1 N NaOH → H₂O₂, 4.6 (e): 0.2 N NaOH, 4.6 (f): 0.2 N NaOH → H₂O₂, 4.6 (g): 0.3 N NaOH, 4.6 (h): 0.3 N NaOH → H₂O₂, 4.6 (i): 0.1N NaOH → PAA, 4.6 (j): 0.2N NaOH → PAA, 4.6 (k): 0.3N NaOH → PAA.
4.4.8. FTIR spectra of bamboo fibres

Fourier transform infrared spectroscopy is generally used for investigating the arrangement of constituents and the chemical changes in lignocellulosic fibres throughout bleaching/treatment on pretreated fibres with sodium hydroxide. The FTIR spectra of sodium hydroxide pretreated bamboo fibres (CAN retted), bamboo fibre treated PAA & \( \text{H}_2\text{O}_2 \) bleaching agents are shown in Figure 4.7(a), (b) & (c), respectively. Removal of residue from the bamboo fibres during the treatment with different bleaching agents was observed using FTIR (Figure 4.7b & 4.7c). A comparison was made with alkali treated CAN retted bamboo fibre bundles with treated (bleached) bamboo fibre bundles and found change in their compositions after alkali & bleaching process. In the FTIR spectra, the peaks and the absorption intensity of the bamboo fibres bleached with \( \text{NaOH} \rightarrow \text{PAA} \) process and fibres treated with \( \text{NaOH} \rightarrow \text{H}_2\text{O}_2 \) were rather week. At the range of 1700 cm\(^{-1}\) to 850 cm\(^{-1}\) in case of fibres treated with these two processes, remarkable changes were found. As discussed earlier about the absorption at 3434 cm\(^{-1}\), 3426 cm\(^{-1}\) and 3405 cm\(^{-1}\) are accredited to O-H stretch and the absorption at range 2932 - 2883 cm\(^{-1}\) along with range 2891-2850 cm\(^{-1}\) are assigned to CH stretch in CH\(_2\) and CH\(_3\) groups respectively. The skeleton stretching vibration of the aromatic rings and methoxyl C-H deformations and bending of lignin at the bands at 1615 cm\(^{-1}\), 1534 cm\(^{-1}\), 1425 cm\(^{-1}\) and 1345 cm\(^{-1}\)[9] which generally showed the presence of lignin in bamboo were almost missing in case of second stage bleaching with \( \text{NaOH} \rightarrow \text{H}_2\text{O}_2 \) & found minimal response in case of \( \text{NaOH} \rightarrow \text{PAA} \). The intensity of the bands in the alkali treated bamboo fibres (Figure 4.7a), was higher than those treated with processes \( \text{NaOH} \rightarrow \text{PAA} \) & \( \text{NaOH} \rightarrow \text{H}_2\text{O}_2 \) (Figure 4.7b & c). Though, no dominating signals were observed for alkali-treated fibres at 1506-1510 cm\(^{-1}\), showing that there was small amount of residue lignin in the fibre bundles [8] but were absent in both the cases \( \text{NaOH} \rightarrow \text{PAA} \) & \( \text{NaOH} \rightarrow \text{H}_2\text{O}_2 \).
Hence, it can be concluded that the maximum extraction or separation of fibres from fibre bundles has been possible by adopting pretreatment with alkali prior to bleaching. It has facilitated the removal of appropriate amount of noncellulosic substances.

### 4.4.9. XRD of bamboo fibres

Figure 4.8 shows the XRD pattern for CAN retted bamboo fibres (Figure 4.8 CAN), alkali pretreated bamboo fibres (Figure 4.8A, 4.8B, 4.8C & 4.8D) and subsequently bleached bamboo fibres (Figure 4.8E, 4.8F, 4.8G, 4.8H, 4.8I, 4.8J, 4.8K & 4.8L). It was found that the patterns have the similar diffraction peaks in case of simply alkali pretreated and sequential sodium hydroxide & peracetic acid (NaOH→ PAA) treated fibres with slightly different intensities. In addition to this, their crystallinity degree has been calculated by dividing the crystalline area by the total area formed by the curve in Figure 4.8.
Figure 4.8. XRD of CAN retted bamboo fibres (CAN) without treatment.

Figure 4.8A. XRD of bamboo fibres after treatment with 0.05N NaOH

Figure 4.8B. XRD of bamboo fibres after treatment with 0.1 N NaOH
Figure 4.8C. XRD of bamboo fibres after treatment with 0.2 N NaOH

Figure 4.8D. XRD of bamboo fibres after treatment with 0.3 N NaOH

Figure 4.8E. XRD of bamboo fibres after treatment A 0.05 N NaOH + H₂O₂
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Figure 4.8F. XRD of bamboo fibres after treatment with 0.1 N NaOH + H$_2$O$_2$

Figure 4.8G. XRD of bamboo fibres after treatment with 0.2 N NaOH + H$_2$O$_2$

Figure 4.8H. XRD of bamboo fibres after treatment with 0.3 N NaOH + H$_2$O$_2$
**Figure 4.8I.** XRD of bamboo fibres after treatment with 0.05 N NaOH + PAA

**Figure 4.8J.** XRD of bamboo fibres after treatment with 0.1 N NaOH + PAA

**Figure 4.8K.** XRD of bamboo fibres after treatment with 0.2 N NaOH + PAA
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In Figures 4.8 A, F, G, H & I, the typical diffraction peaks at nearby 2-theta 15.9° and 22.3° of cellulose I [10, 11], while Figures 4.8 A, B, C, D, E, J, K & L, show low intensity diffraction peaks are observed which are attributed to cellulose II. From this shifting of peaks, it is clear that a change in crystallinity of the cellulose has taken place during the alkali pretreatment and sequential sodium hydroxide & peracetic acid (NaOH→PAA, fibres were first treated with NaOH followed by bleached with PAA) treatment of fibres. During these processes, alkali and sequential bleaching steps broke the intermolecular hydrogen bonds within the bamboo structure and destroyed the original crystalline form. In Figure 4.8 G & H, the patterns of peaks observed are similar to Figure 4.8 CAN.

In addition to this, their crystallinity degree has been calculated by dividing the crystalline area by the total area formed by the curve in Figure 4.8 (A - L). The crystallinity index has been decreased in case of sequential sodium hydroxide & hydrogen peroxide (NaOH→H₂O₂ i.e. fibres were first treated with NaOH followed by bleached with H₂O₂). Being a strong oxidizing bleaching agent, it oxidized cellulose and hemicellulose along with the lignin content, thereby, reducing the tenacity. Though, hydrogen peroxide has been found as a very good bleaching agent in comparison of peracetic acid as shown in Table 4.3. The effects of several other factors like tenacity, lignin content and crystallinity were considered to select the best one in between subsequently bleached bamboo fibres with PAA & H₂O₂.

The crystalline degree has been obtained from X-ray diffraction analysis which indicated that the crystallinity of bamboo fibres improved after the pretreatments with different concentrations of sodium hydroxide (Table 4.6). The crystallinity index of bamboo fibres was found to be maximum 80.21 with NaOH 0.2 N, 69.64 with NaOH 0.05 N→H₂O₂ and 83.64 with NaOH 0.05 N→PAA.

![Figure 4.8L. XRD of bamboo fibres after treatment with 0.3 N NaOH + PAA](image-url)
The crystallinity index of bamboo fibres was strongly influenced by the composition of fibres. When the lignin and hemicellulose (both of which are amorphous) were partially removed, crystallinity index would be increased after alkali and sequential bleaching treatments. This analysis could be proved by the fact that sequential sodium hydroxide & peracetic acid (NaOH→PAA) treated fibres had higher crystallinity index than sodium hydroxide and sequential sodium hydroxide & hydrogen peroxide (NaOH→H₂O₂) treated bamboo fibres. It has been known that alkali pretreatment of lignocellulosic bamboo fibres also caused significant swelling of cellulose, resulting decrease of crystallinity with the increase in concentration of alkali. However, the crystallinity index of alkali treated fibres was higher than that of sequential sodium hydroxide & hydrogen peroxide (NaOH→H₂O₂) bamboo fibres which could be explained by the fact that lignin and hemicellulose was partially removed and the proportion of cellulose was increased. The crystallinity index of sequential sodium hydroxide & peracetic acid (NaOH→PAA) bamboo fibres was on an average more than that of NaOH treated bamboo fibres. Although acceptable weight loss and tenacity was found in case of sequential sodium hydroxide & peracetic acid (NaOH→PAA) bamboo fibres (Table 4.1 & Table 4.5). Thus for further study this sequential sodium hydroxide & peracetic acid (NaOH 0.3N→PAA) bamboo fibres has been selected.

### Table 4.6: Crystallinity analysis of pretreated and bleached bamboo fibres

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Substrate</th>
<th>Crystallinity Index (Crl)</th>
<th>Crystal Size (Ang.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaOH 0.05 N</td>
<td>70.48</td>
<td>21.48</td>
</tr>
<tr>
<td>2</td>
<td>NaOH 0.1 N</td>
<td>71.27</td>
<td>29.56</td>
</tr>
<tr>
<td>3</td>
<td>NaOH 0.2 N</td>
<td>80.21</td>
<td>20.59</td>
</tr>
<tr>
<td>4</td>
<td>NaOH 0.3 N</td>
<td>60.86</td>
<td>29.61</td>
</tr>
<tr>
<td>5</td>
<td>NaOH 0.05 N→H₂O₂</td>
<td>69.64</td>
<td>28.55</td>
</tr>
<tr>
<td>6</td>
<td>NaOH 0.1 N→H₂O₂</td>
<td>54.07</td>
<td>39.27</td>
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<td>7</td>
<td>NaOH 0.2 N→H₂O₂</td>
<td>64.60</td>
<td>23.25</td>
</tr>
<tr>
<td>8</td>
<td>NaOH 0.3 N→H₂O₂</td>
<td>45.70</td>
<td>22.0</td>
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<td>9</td>
<td>NaOH 0.05 N→PAA</td>
<td>83.64</td>
<td>30.09</td>
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<td>10</td>
<td>NaOH 0.1 N→PAA</td>
<td>79.87</td>
<td>34.14</td>
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<tr>
<td>11</td>
<td>NaOH 0.2 N→PAA</td>
<td>68.68</td>
<td>29.61</td>
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<td>12</td>
<td>NaOH 0.3 N→PAA</td>
<td>70.90</td>
<td>29.35</td>
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4.5. Conclusion

This two-stage delignification of bamboo fibres with alkali and different bleaching agents could obtain fibres with good physical appearance & properties. Alkali pretreatment prior to bleaching could significantly reduce $\text{H}_2\text{O}_2$ & PAA loading in subsequent stage by partially removing the lignin and swelling the fibres. The maximum loss in lignin was found in case of $\text{NaOH} \rightarrow \text{H}_2\text{O}_2$ process along with no acceptable weight loss. On the other hand, the pretreated fibres with higher concentration of sodium hydroxide i.e., 0.3 N followed by PAA bleaching step ($\text{NaOH} \rightarrow \text{PAA}$) produced reasonable reduction in lignin content and weight loss with acceptable whiteness and tensile strength.

4.6. References