Infrared Spectra of Jute Stick Bleached with Sodium Chlorite and Hydrogen Peroxide

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SYNOPSIS

Jute stick was bleached with sodium chlorite and alkaline hydrogen peroxide solutions. The infrared (IR) spectra of bleached samples and jute stick were analyzed and compared. The bleached samples were characterized by higher absorbance intensity ratios (A_ν/A_{2900}) of the bands attributed to hemicellulose. Among the bleached samples the chlorite-bleached sample showed higher intensity for the bands mentioned. The bands attributed to lignin are either absent or very weak in the chlorite-bleached jute stick as compared to that of peroxide-bleached jute stick, although some residual lignin was present in the substrate. The 1635 cm^{-1} band attribute to the vibration of adsorbed water molecules in the noncrystalline regions in cellulose appears as a sharp peak in chlorite-bleached jute stick and as a shoulder in peroxide-bleached jute stick. This can be attributed to the difference in the nature of the two bleaching processes.

INTRODUCTION

Bleaching of jute stick with sodium chlorite or alkaline hydrogen peroxide is mainly a process of oxidation of lignin. Being phenolic in nature, the lignin macromolecule is prone to oxidation by either homolytic or heterolytic pathway.[1] Sodium chlorite bleaching belongs to the group that oxidizes lignin by degrading the aromatic rings, whereas alkaline peroxide bleaching belongs to the group that oxidizes lignin by oxidations limited to specific groups.

Although bleaching of jute stick by chlorine dioxide and sodium chlorite has not been studied, bleaching of jute fiber by the chemicals mentioned has been well documented by a number of workers.[1]

Similarly, although no bleaching of jute stick by alkaline hydrogen peroxide has been studied, bleaching of jute fiber by these chemical has been well documented.[1]

IR spectroscopy using potassium bromide disk technique has been shown[1] to be a useful tool for investigating the fine structural characteristics of cellulose and chemically modified cellulose and lignins.[1] Slight differences in IR spectra may signal differences in the ratio of constituent units and the order in which they are linked. The study of the differences in spectra of various chemically treated jute stick and their significance to structure is probably the most valuable area of study in the field of jute stick IR spectra.

Although only IR spectra of jute stick and alkali-treated jute stick have been recently reported,[2] no study on the IR spectra of bleached jute stick is available, whereas fairly detailed work on the IR spectra of jute fiber has been done.[1]

In the present investigation results on IR spectra of defatted jute stick, chlorite-bleached jute stick, and peroxide-bleached jute stick have been analyzed and discussed.

MATERIALS AND METHODS

Jute Stick

Jute stick (*Corchorus capsularis* variety JRC 7447) was disintegrated in a Wiley mill, using different sieves. The disintegrated sample was defatted using a mixture of benzene-ethanol (2 : 1, v/v) and passed through 40- and 60-mesh sieves. The 40- to 60-mesh samples were used to study the major chemical com-

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Table I Major Chemical Constituents of Defatted Jute Stick and Bleached Jute Sticks, Calculated on the Basis of 100 g OD Sample

Chemical Constituents	Defatted Jute Stick JRC 7447 (%)	Chlorite-Bleached Jute Stick (%)	Peroxide-Bleached Jute Stick (%)
Yield	Not applicable	83.35	91.16
Ash	0.92	0.19	1.70
Pentosans	22.28	26.2	24.1
α-Cellulose	41.4	47.4	43.95
Lignin	23.8	18.2	24.3

positions. The ($1 \times 1 \times 3$ mm) jute stick sample was used for sodium chlorite and alkaline hydrogen peroxide bleaching. The 100-mesh bleached samples were used for IR spectroscopic study.

The terms "defatted jute stick" and "jute stick" have been used synonymously.

Sodium Chlorite Bleaching

An aqueous solution of sodium chlorite (1% w/v, 500 mL) was heated (70°C) in a 1-liter spoutless beaker and acidified (~pH 4) with acetic acid. Then jute stick (16 g) was added and the mixture stirred occasionally under cover for 2 h. The residue was washed thoroughly with distilled water, soaked for 10 min in aqueous sulfur dioxide (50%), again washed several times with distilled water, and finally dried in air. Yield of the bleached sample was 83.35%.

Hydrogen Peroxide Bleaching

A mixture of hydrogen peroxide (30% w/v, 5 mL), sodium silicate (5 g) and disodium hydrogen phosphate (2.5 g) in 450 mL distilled water was heated (70–80°C, water bath) in a 1-liter spoutless beaker covered with watch glass. Jute stick (15 g) was added to it and the content heated and stirred occasionally for 2 h. The reaction mixture was filtered and the residue washed thoroughly with distilled water. The resulting mass was soaked for 10 min in aqueous sulfur dioxide (50%), again washed several times with distilled water, and finally dried in air. Yield of the peroxide-bleached jute stick was 91.16%.

Analysis of Jute Stick Samples

Ash content and lignin content were estimated following TAPPI methods.[3] α-Cellulose was estimated by the modified method of Chattopadhyay et al.[4] Pentosans were estimated using Krober's tables following the procedure of Schorger.[5]

Infrared Spectroscopy

The samples were mixed thoroughly in a mortar with 200 mg of KBr, which was previously dried at 120–150°C for 16 h. KBr pellets were made in a hydraulic press at a working pressure of 8 tons for 10 min pressing time, under vacuum. The spectra were recorded in a Shimadzu double-beam spectrophotometer, IR-440 under normal slit program and scanning speed of nearly 19 s/100 cm^{-1}. A blank KBr pellet was used in the reference beam.

RESULTS AND DISCUSSION

The major chemical constituents of jute stick, $NaClO_2$-bleached and H_2O_2-bleached jute sticks, calculated on the basis of 100-g oven dry (OD) samples are shown in Table I. The major chemical constituents of the bleached samples, calculated on the basis of 100 g original OD jute stick are shown in Table II. The percent losses (with respect to original content) of lignin, pentosans, and α-cellulose are shown in Table III. From the figures in Table III it can be stated that, under the conditions of bleaching, the loss of lignin in the case of chlorite-bleached jute stick is 36.2% as compared to 5.6% in the case of hydrogen-peroxide bleached jute stick.

Table II Major Chemical Constituents of Bleached Jute Sticks, Calculated on the Basis of 100 g OD Original Defatted Jute Stick

Chemical Constituents	Chlorite-Bleached Jute Stick (%)	Peroxide-Bleached Jute Stick (%)
Pentosans	21.68	21.96
α-Cellulose	39.5	40.96
Lignin	15.17	22.15

Table III Percent Loss of Lignin, Pentosans, and α-Cellulose of Bleached Jute Sticks[a]

	Loss of Lignin (%)	Loss of Pentosans (%)	Loss of α-Cellulose (%)
Chlorite-bleached jute stick	36.2	2.69	3.2
Peroxide-bleached jute stick	5.6	1.43	4.5

[a] Calculated on the basis of original contents: Lignin = 23.8%, pentosans = 22.28%, and α-cellulose = 41.4% (see Table I).

IR spectra of jute stick, $NaClO_2$-bleached and H_2O_2-bleached jute sticks, are shown in Figure 1. The summary of the results, including the significance of bands, the ratios of absorbance maxima of individual bands, and the 2900 cm^{-1} band (A_ν/A_{2900}) has been recorded in Table IV, following the baseline correction method.[6] The 2900-cm^{-1} band has been chosen as an internal standard, as it is present as a prominent peak in the IR spectra of isolated lignin, hemicellulose, and α-cellulose of jute stick.[2] The internal standard, though not fully established, has been adopted for making a comparative study of the spectra.

The 3350-cm^{-1} band ascribed to H-bonded H–O stretching[7] has higher absorbance intensity ratio for the bleached jute stick samples as compared to that of defatted jute stick. This finding is in concurrence with the higher α-cellulose contents of the bleached samples (see Table I). The 2900-cm^{-1} band is assigned to C–H stretching in methyl and methylene groups.[7] The band near 1735 cm^{-1}, assigned to C–O stretching of the carbonyl and acetyl groups in hemicellulose of jute stick,[1,8,9] shows a weaker band in the case of peroxide-bleached jute stick, as compared to that of chlorite-bleached jute stick. This

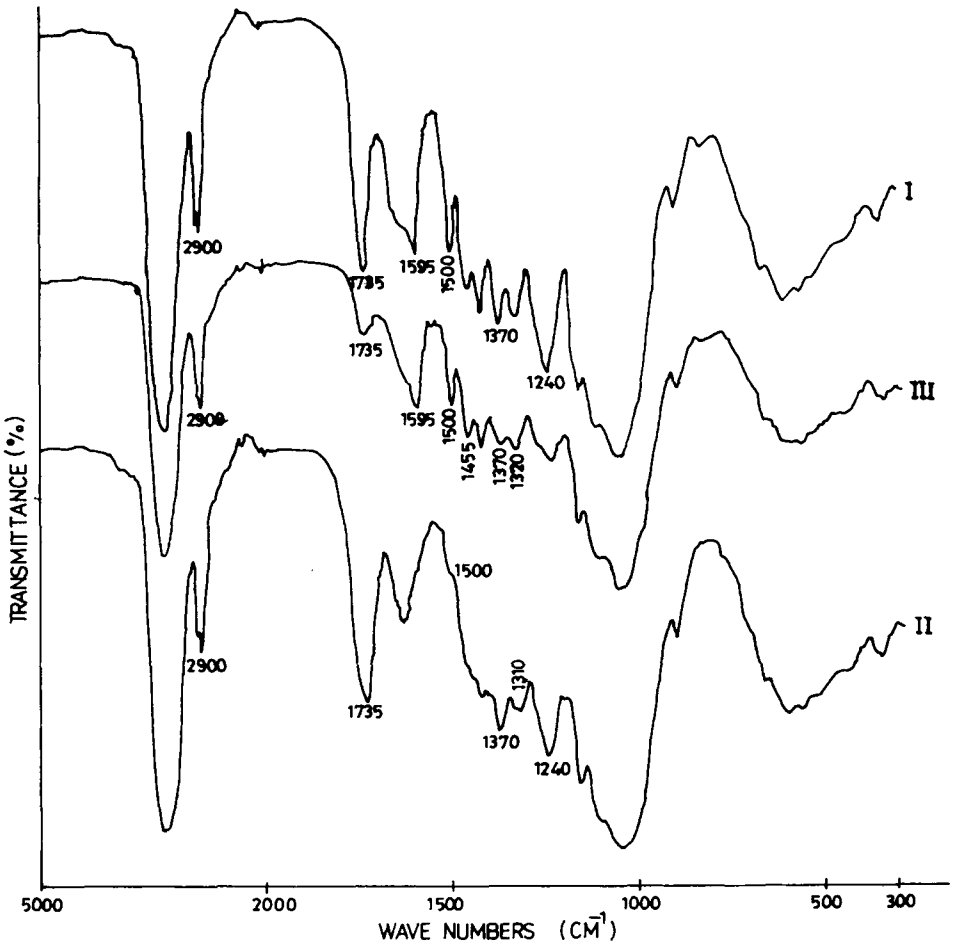

Figure 1 IR spectra of (I) defatted jute stick, (II) $NaClO_2$-bleached jute stick, and (III) H_2O_2-bleached jute stick.

Table IV Absorbance Intensity Ratios of IR Spectra of Jute Stick and Bleached Jute Sticks[a]

Position of Bands (cm^{-1})	Assignments	Jute Stick (A_ν/A_{2900})	Chlorite-Bleached Jute Stick (A_ν/A_{2900})	Peroxide-Bleached Jute Stick (A_ν/A_{2900})
3350	HO stretching (H bonded)	0.2435	0.3163	0.4778
2900	CH stretching in methyl and methylene	1.0 (0.4089)	1.0 (0.3768)	1.0 (0.5682)
1735	CO stretching in carboxyl and unconjugated β-ketone	0.9214	0.9861	1.7599
1630–1635	H_2O molecules in noncystalline cellulose	shoulder	1.7192	shoulder
1595	Aromatic skeleton ring vibration	1.4724	nil	1.3105
1500	Aromatic skeleton ring vibration	1.5157	shoulder	1.5306
1455	C–H deformation and CH_2 bending	1.3905	shoulder	1.3544
1420	C–H deformation and CH_2 bending	1.3147	1.7460	1.3544
1370	C–H deformation (symmetric)	1.4514	1.6449	1.5593
1310–1325	Syringyl ring breathing with CO stretching and HO in-plane bending	1.7094	2.1865	1.6530
1230–1240	CO stretching in acetyl group	1.5157	2.0766	2.1502
1190–1200	Phenolic HO deformation	shoulder	shoulder	shoulder
1155–1160	C–O–C stretching (antisymmetric)	1.4306	1.8574	1.2691
1105	H bonding on skeletal vibration, involving C–O bond stretching	1.0560	1.3134	0.9728
1050	Due to partially acetylated xylan polyuronide	0.8246	1.0276	0.7496
1030	Aromatic C–H in-plane deformation	0.7796	1.0	0.7195
990	C–H out-of-plane deformation	shoulder	1.1151	shoulder
895	C–H bending in β-linkage	2.3736	2.3081	1.7677
830	Aromatic C–H out-of-plane vibration	6.6864	nil	1.5306

[a] Values in parentheses indicate absorbance intensities at 2900 cm^{-1} band.

can be explained on the basis of removal of acetyl group by alkali[1,10] used in alkaline peroxide.

The absorption band 1635 cm^{-1} attributed to the vibration of adsorbed water molecules in the noncrystalline regions in cellulose[7,11] gives a sharp peak in the case of chlorite-bleached jute stick and a shoulder in the case of peroxide-bleached sample. This can be related to the fact that due to the removal of lignin by $NaClO_2$ and H_2O_2 the fibrillar structures of jute stick are exposed resulting in the exposure of the noncrystalline regions of cellulose, which in turn causes adsorption of water molecules. In the case of hydrogen peroxide bleaching removal of lignin is very small, thus only a shoulder is observed.

The aromatic skeleton ring vibration[6] at 1595 and 1500 cm^{-1} show prominent peaks in the case of peroxide-bleached jute stick, whereas chlorite-bleached jute stick shows no peak at 1595 cm^{-1} and a shoulder at 1500 cm^{-1}. This can be explained by the fact that because of the substantial loss of lignin involving oxidations degrading aromatic rings in chlorite bleaching, the bands attributed to aromatic skeleton ring vibration are almost obliterated, whereas in peroxide bleaching small loss of lignin involving oxidations limited to specific groups takes place.

The absorbance of 1455 and 1420 cm^{-1} are attributed to CH_3 deformation (asymmetric) in lignin, as well as to CH_2 bending in xylan.[11] The chlorite-bleached jute stick sample gives only a shoulder at 1455 cm^{-1}, whereas prominent peak is obtained in the case of peroxide-bleached sample, and this indicates that the band is affected mainly by the lignin component in the peroxide- and chlorite-bleached samples. The absorbance intensity ratio of 1420 cm^{-1} band of chlorite-bleached sample is higher than the peroxide-bleached sample, in concurrence with the higher pentosans content of chlorite-bleached sample as compared to that of peroxide-bleached sample (see Table I). This observation can be rationalized by the fact that the 1420-cm^{-1} band, which is weak in the chlorite-bleached sample, is also affected by the hemicellulose component of the bleached samples.

The 1370-cm^{-1} band ascribed to C–H deformation (symmetric), which may be attributed to lignin, α-cellulose, or xylan,[1,8] shows higher absorbance intensity ratios for the two bleached samples as compared to that of defatted jute stick; among the bleached samples the chlorite-bleached jute stick has higher absorbance ratio. This observation is in concurrence with the higher pentosan and α-cellulose contents of the bleached samples (see Table I). The 1310- to 1325-cm^{-1} band ascribed to syringyl ring breathing with C–O stretching in lignin[1] and H–O in-plane bending in cellulose and xylan[8,12] show an increase in absorbance intensity ratios for the bleached samples, as compared to that of jute stick. Among the bleached samples chlorite-bleached jute stick has a higher absorbance intensity ratio, in concurrence with the higher pentosan and α-cellulose contents of the bleached sample (see Table I). These two bands, although ascribed to all the three major constituents of jute stick, α-cellulose, and pentosans, appear to have greater influence on the absorbance intensity ratios of the bands under discussion.

The medium band at 1240 cm^{-1} ascribed to C–O stretching in the acetyl group in xylan[9,12,13] for the chlorite-bleached sample is stronger as compared to the corresponding band in the peroxide-bleached sample appearing at 1230 cm^{-1}, along with a shoulder at 1260 cm^{-1}. This can be explained on the basis of removal of acetyl group by alkali[1,10] used in alkaline peroxide bleaching, and the trend is similar to that in the case of alkali treated jute stick samples.[2]

The 1155- to 1160-cm^{-1} band attributed to both α-cellulose and hemicellulose[1,8,11] shows highest absorbance intensity ratio for the chlorite-bleached jute stick as compared to that of peroxide-bleached and defatted jute stick in concurrence with the highest α-cellulose and pentosan contents of the chlorite-bleached sample (see Table I). The 1105-cm^{-1} band assigned to H bonding on the skeletal vibrations involving stretching of the C–O bond and attributed to both α-cellulose and hemicellulose[8,9,12,14] again shows highest absorbance intensity ratio for chlorite-bleached jute stick as compared to that of peroxide-bleached and defatted jute stick in concurrence with the highest α-cellulose and pentosan contents of the chlorite-bleached sample (see Table I).

The 1050-cm^{-1} band assigned to skeletal vibration involving C–O stretching in hemicellulose[8] shows highest absorbance intensity ratio for chlorite-bleached jute stick in accordance with the highest pentosan content of the chlorite-bleached sample (see Table I). The 1030-cm^{-1} band assigned to aromatic C–H in-plane deformation, guaiacyl-type and C–O deformation for primary alcohol in lignin[1] and to skeletal vibration involving C–O stretching in hemicellulose and cellulose[8] again shows highest absorbance intensity ratio for the chlorite-bleached jute stick in concurrence with the highest pentosan and α-cellulose contents of the chlorite-bleached sample (see Table I).

The 990-cm^{-1} band, which appears as a shoulder in the peroxide-bleached jute stick and as a small band in the chlorite-bleached sample, is assigned to C–H out-of-plane deformation in xylan.[8] The 895-cm^{-1} band assigned to hemicellulose,[8] shows higher absorbance intensity ratio in the case of chlorite-bleached sample as compared to that of peroxide-bleached jute stick. This observation may be ascribed to the presence of higher pentosan content in the chlorite-bleached jute stick (see Table I). The 830-cm^{-1} band assigned to aromatic C–H out-of-plane vibration in lignin[1] shows a clear peak in the peroxide-bleached jute stick only; this finding may be attributed to the higher lignin content of the peroxide-bleached jute stick and higher loss of lignin in the chlorite-bleached jute stick involving oxidations degrading aromatic rings.

CONCLUSION

The bands 1735, 1370, 1310–1325, 1230–1240, 1155–1160, 1105, 1050, 1030, and 895 cm^{-1} ascribed mainly to hemicellulose show higher absorbance intensity ratios for the bleached samples as compared to that of defatted jute stick. Among the bleached samples, stronger bands are observed in chlorite-bleached jute stick with higher absorbance intensity ratios for these bands, in concurrence with the higher pentosan content of the chlorite-bleached sample. The 1735- and 1240-cm^{-1} bands in chlorite-bleached and defatted jute stick appear as small peaks in the case of peroxide-bleached jute stick. The 1240-cm^{-1} band appears at 1230 cm^{-1} along with a shoulder at 1260 cm^{-1} in peroxide-bleached jute stick. This finding is similar to that of alkali-treated jute stick samples and is probably due to the effect of alkali used in alkaline peroxide bleaching. The bands 1595, 1500, 1455, and 830 cm^{-1} assigned to lignin are either absent or very weak in the chlorite-bleached jute stick. This finding can be attributed to the higher loss of lignin in the chlorite-bleached sample involving oxidative degradation of aromatic rings, whereas in

the case of peroxide-bleached sample, such losses are small due to oxidations limited to specific chromophoric groups.

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