

Infrared Spectra of Alkali Treated Jute Stick

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Synopsis

The infrared spectra of alkaline jute stick have been discussed and compared to that of untreated and control sample. A higher shift in the O—H and lower shift in the C—H stretching frequencies were observed in alkaline sample. The presence of a strong band at 1440–1430 cm^{-1} may be due to the coupling of COO^- frequency with CH_2 deformation frequency. The C—O stretching mode at 1240 cm^{-1} disappears on alkaline treatment with the formation of new peaks at 1265 and 1225 cm^{-1} . The β -glucosidic band at 895 cm^{-1} is shifted to 880 cm^{-1} with doubled intensity in alkaline jute stick.

INTRODUCTION

Jute stick, an agrowaste of jute cultivation, can be used as raw material for making paper,¹ particle board,² and can be processed for rayon.³ Work is in progress in this laboratory on the conversion of jute stick as energy source for alcohol and biogas. The chemical composition (Table I) shows that it is hard wood in nature and is a heterogeneous polymer of cellulose, hemicellulose, and lignin which are associated with each other in a manner not clearly known. During alkali treatment it loses some of its hemicellulose and lignin and its lattice structure changes from cellulose I to cellulose II. The i.r. study has been found to be a useful tool for investigating the structural changes in cellulose. Nelson and O'Connor⁴ pointed out that the CH_2 bending frequency at 1420 cm^{-1} decreases while the β -glucosidic band at 895 cm^{-1} increases in intensity during mercerisation. They also noted that the broadening of bands in the region 1400–1200 cm^{-1} in amorphous cellulose. Sao et al.⁵ observed two distinct bands near 1260 and 1275 cm^{-1} in the spectra of mercerised ultimate cells of jute fiber. Though considerable work has been done on i.r. of cellulose, a small amount of literature is available on i.r. of lignocellulosic wood materials. The present paper deals with our effort to use i.r. in the investigation of structural changes in jute stick due to alkali treatment.

EXPERIMENTAL

Jute stick was crushed into 80–100 mesh size and extracted with ethanol-benzene (1 : 2) for 12 h. The chemical constituents of the defatted material viz., ash, lignin, cellulose, pentosans, etc., were estimated by Tappi standard methods.⁶

TABLE I
The Chemical Composition of Jute Stick (Raw)

Composition	%
Ash	1.28
α -cellulose	41.10
Pentosans	24.60
Lignin	22.85
Acetyl value	4.51
Uronicanhydride	5.40
Fat and Wax	1.82

Alkaline Treatment

Alkalisiation of jute stick was carried out with different concentrations of alkali by immersing the material into an emulsion of NaOH-benzene (1 : 1) solution. Vigorous stirring was continued for 1 h at room temperature and then centrifuged off. The benzene present in the cake was allowed to evaporate. The alkaline jute stick powder thus obtained was air dried for several days for further study.

Control Samples

Control samples were prepared by washing the alkaline jute stick powder with 5% acetic acid followed by water several times until it is free from alkali and acid.

Infrared Spectra

The infrared spectra of the samples were taken on Shimadzu IR-440 spectrophotometer using KBr pellet technique.

RESULTS AND DISCUSSION

The different assignments of the infrared spectra of treated and untreated jute stick are given in Table II. From Figure 1 we can see the spectra of alkaline jute stick have no clearly resolved bands and the number of peaks are less compared to that of untreated and control samples. When jute stick is treated with sodium hydroxide solution the Na^+ ions replace the hydroxyl protons of cellulose and hemicellulose and occupy the holes of the crystal lattice. Replacement of all hydroxyl protons by sodium ions depends on the strength of alkali used, swelling time, and temperature. In our experiments we used an emulsion of NaOH-benzene for swelling in order to get homogeneous product. Without an organic solvent, swelling of jute stick would not be homogeneous and there may be a possibility for an uneven degree of substitution in the final product.⁷

The important bands affected during alkali treatment are 3350, 2925, 1425, 1240, and 895 cm^{-1} . The appearance of a strong band at 1440–1430 cm^{-1} is due to alkali treatment and its disappearance on water washings shows the regeneration of cellulose from alkaline cellulose.

TABLE II
Interpretation of the Infrared Spectra of Treated and Untreated Jute Stick

Favoured environment	Approximate position of absorption bands (cm^{-1}) in jute stick		
	Untreated	Alkaline ^a	Control ^b
	—	—	3450 (sh)
Hydrogen bonded O—H stret.	3350 (s)	3400 (s)	3350 (s)
CH ₂ antisymm. stret.	—	2940 (sh)	2930 (sh)
C—H stretching	2925 (s)	2870 (m)	2895 (m)
CH ₂ symm. stret.	—	2850 (sh)	2845 (sh)
C=O stretching	1740 (s)	—	1730 (s)
Adsorbed water	1660 (w)	—	1660 (w)
Aromatic C=C skeletal vibrations	1595 (m)	1595 (b)	1595 (m)
O—H in-plane bending	1505 (m)	—	1505 (m)
COO ⁻ /CH ₂ bend. freq.	1460 (m)	—	1465 (m)
CH ₂ bending	—	1440–30 (s, b)	—
CH ₂ bending	1425 (m)	1410 (sh)	1420 (m)
C—H bending	1372 (m)	—	1370 (m)
O—H in-plane bend.	1325 (m)	1330 (w)	1320 (m)
C—H bend./C—O—C bond	—	1265 (w)	1260 (m)
C—O stretching mode	1240 (s)	—	—
O—H deformation	—	1225 (w)	1225 (m)
Antisymm. bridge (C—O—C) stret.	1160 (m)	1155 (m)	1160 (m)
Antisymm. inphase ring stret.	1110 (m)	1120 (w)	1125 (m)
C—O stret/C—C stret.	1055 (w)	1065 (m)	1060 (w)
C—O stret/C—C stret.	1035 (w)	1020 (w)	1020 (w)
—	—	—	995 (w)
α -anomer (?)	—	900 ^c (w)	—
C ₁ group freq. (β -glucosidic linkage)	895 (w)	880 (s)	895 (m)
C ₁ group freq. (β -glucosidic linkage)	—	865 ^c (s)	—
α -anomer (?)	—	850 ^c (s)	—
Aromatic C—H out of plane bending	835 (w)	—	—
O—H out of plane bend.	665 (w)	685 (w)	—
—	610 (m)	655 (w)	—
		605 (m)	

^a Alkaline swelling was carried out in 5, 12, 18, 25, and 30% NaOH solution.

^b See experimental, ^cin 18% alkaline jute stick.

s = strong, w = weak, m = medium, sh = shoulder.

O—H and C—H Stretching Vibrations

The strong band at 3350 cm^{-1} in the spectra of untreated jute stick is due to hydrogen bonded OH absorption. This band is shifted to a higher region with reduced intensity and appeared at $3400\text{--}3450 \text{ cm}^{-1}$ as a broad band in alkaline samples. It has been reported⁸ that a number of bands in this region were caused by inter and intramolecular hydrogen bondings. In cellulose II this region is distinctly different from that of cellulose I with the appearance of two bands at 3447 and 3488 cm^{-1} due to intramolecular hydrogen bondings. Though the bands associated with inter and intramolecular hydrogen bondings could not be resolved clearly in this work, the difference in O—H and C—H stretchings can be seen in the spectra of untreated, treated, and control samples.

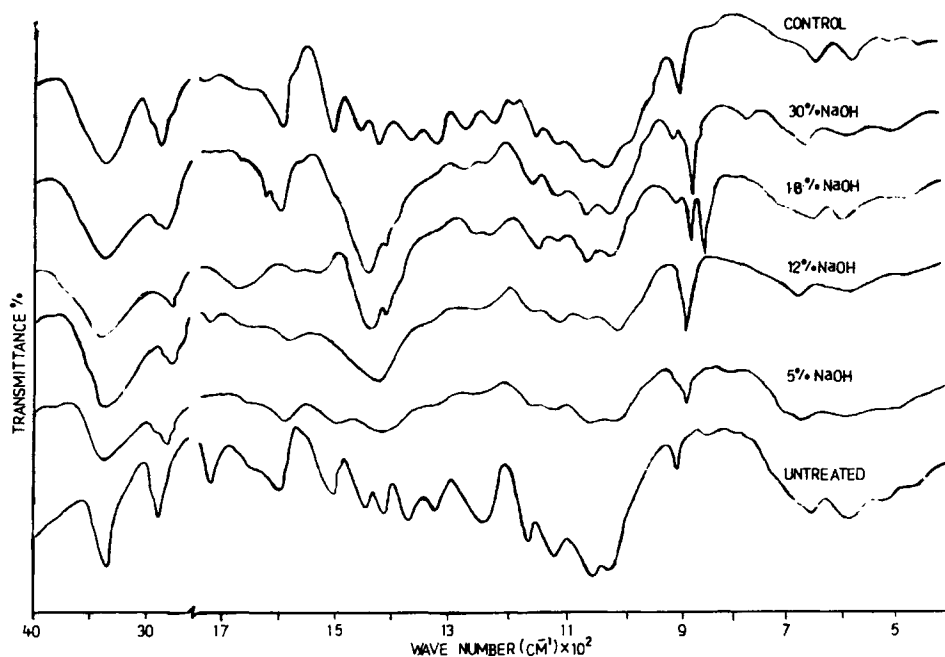


Fig. 1. IR spectra of alkaline jute stick at different treatments.

The C—H stretching frequency at 2925 cm^{-1} in untreated sample shifted to a lower region with reduced intensity and appeared at 2875 cm^{-1} in alkaline jute stick. The two shoulder peaks at 2930 and 2840 cm^{-1} in the spectra of treated samples can be ascribed for CH_2 antisymmetrical and symmetrical stretchings,⁹ respectively.

Since the alkaline treatment causes the disruption of intermolecular hydrogen bonds in cellulose lattice, it is possible for a higher shift in OH frequency. The broadening of OH bands at $3400\text{--}3450\text{ cm}^{-1}$ is due to the formation of sodium cellulose. On removal of Na^+ ions in alkaline sample by washings with acetic acid and water, the O—H stretching band again shifted to a lower region of 3350 cm^{-1} which might be due to the partial conversion of cellulose II into cellulose I. The presence of a shoulder peak at 3450 cm^{-1} in control samples is an indication of cellulose II even after water washings.

1595 and 1505 cm^{-1}

These two aromatic bands are due to lignin in jute stick and completely removed on delignification, but retained as weak bands on treatments with lower alkali concentrations. In the spectra of 12% and above alkaline samples the 1595 cm^{-1} frequency appeared as weak band and the 1505 cm^{-1} band almost disappeared due to the formation of a strong band at 1440 cm^{-1} .

The spectra of lignin shows sharp bands in this region due to stretching modes of benzene ring.¹⁰ Liang et al.¹¹ noted in the spectra of wood sections that the 1595 and 1505 cm^{-1} frequencies are associated with the stretching modes of ν_{si} and ν_{so} of benzene ring in lignin, respectively.

1500 to 1300 cm^{-1}

A group of bands in this region assigned to C—H and O—H bending frequencies and CH_2 wagging motions¹² are related to cellulose crystallinity.⁴ The C—H bending frequency at 1372 cm^{-1} in the spectra of untreated sample is completely eliminated in the spectra of alkaline sample. The CH_2 wagging frequency at 1320 cm^{-1} is shifted to 1330 cm^{-1} as a broad weak band. The CH_2 deformation band at 1425 cm^{-1} and O—H in-plane bending frequency at 1460 cm^{-1} in untreated sample are mostly affected on alkaline treatment. Instead of these two a strong deep band appeared at $1430\text{--}1440 \text{ cm}^{-1}$. The intensity of this band increases with increasing the alkali concentration during swelling (Fig. 2).

The change in intensity and position of the band at 1425 cm^{-1} is correlated with a change in the environment of C_6 group due to the replacement of hydroxyl protons by Na^+ ions. The sodium ion thus present in the lattice of cellulose as

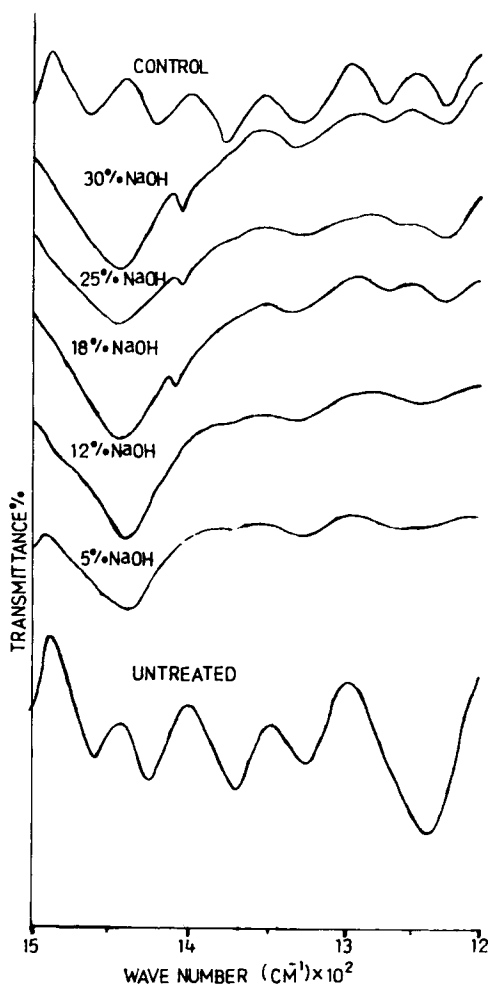


Fig. 2. Change of certain IR bands in the region $1500\text{--}1200 \text{ cm}^{-1}$ on alkali treatment.

$\text{CH}_2\text{-O}^- \text{Na}^+$ affects the CH_2 symmetrical bending frequency at 1425 cm^{-1} . Therefore it is shifted to 1420 cm^{-1} in control samples.

The broadening of this strong band at $1440\text{--}1430 \text{ cm}^{-1}$ is also associated with COO^- ion¹³ of hemicellulose portion, which is present along with cellulose and lignin in jute stick. It is reported that the intensity of CH_2 deformation band at 1425 cm^{-1} is decreased on alkaline treatment. Since both the frequencies appears in the same region it is not clear to ascribe this band either to CH_2 deformation or COO^- ion in alkaline samples. If we consider this band for COO^- ion frequency the presence of a shoulder peak at 1410 cm^{-1} in 18% and above alkaline samples may be assigned to CH_2 bending frequency since it appears with low intensity. In control sample the CH and OH bending frequencies are well resolved and appeared at 1420 and 1465 cm^{-1} , respectively.

1300 to 1200 cm^{-1}

The strong band having maxima at 1240 cm^{-1} in untreated jute stick spectra remains on delignification also. Liang et al.¹¹ assigned this similarity to that in wood corresponding to C—O stretching of acetyl group in xylan. The alkaline treatment removes the acetyl groups in xylan, but in the spectra of jute stick treated at lower alkali concentrations the intensity of this band is only reduced, indicating that cellulose and lignin might also contribute to this band.

On treatment with higher concentrations of alkali this band is replaced by two new peaks at 1265 and 1225 cm^{-1} . This is a remarkable indication of cellulosic change. Though the origin of these bands are not clearly known, it is assumed that these frequencies are due to C—O—C bond⁷ and O—H deformations (in plane bending) in cellulose II. These frequency shifts probably relate to change in hydrogen bonding system which appears to give remarkable indication of transition from cellulose I to cellulose II.

1200 to 1100 cm^{-1}

The two important bands in this region showing marked changes on alkaline treatment are those near 1160 and 1110 cm^{-1} . Liang et al.⁸ assigned the band 1160 cm^{-1} to antisymmetrical bridge C—O—C stretching mode and 1110 cm^{-1} to antisymmetrical in-phase ring stretching mode. We have observed a shift in these two frequencies with decreased intensity at 1155 and 1120 cm^{-1} in alkaline samples. These changes are due to cellulosic transition in accordance with the observations of Higgins et al.¹² They concluded that the band near 1110 cm^{-1} may be an association band analogous to those found in primary and secondary alcohols, due to the effect of hydrogen bonding on the skeletal vibration involving C—O stretching mode.

895 cm^{-1}

The sharp, weak band at 895 cm^{-1} in the spectra of raw jute stick is a characteristic of β -glucosidic linkage.^{4,12} On alkaline treatment its intensity is doubled and shifted to lower frequency at 880 cm^{-1} . O'Connor reported that the motion of the oxygen atom attached to C_1 reflects the changes in the environment due to its rotation about glucosidic linkage ($\text{C}_1\text{-O-C}_4$). These changes disrupted the intermolecular hydrogen bonds in cellulose lattice. When

cellulose I lattice is destroyed by strong swelling or grinding, it would permit the glucosidic rotation into a favorable conformation of cellulose II. The glucosidic rotation thus affects the C_1-H bending mode causing shift to lower frequency with doubled intensity and appeared at 880 cm^{-1} in the spectra of alkaline jute stick samples. In 18% and above alkali treatments this is further shifted to 865 cm^{-1} . A small band 900 cm^{-1} and a sharp peak at 850 cm^{-1} is found in 18% alkali treated sample. Barker et al.¹⁴ found similar bands in the spectra of α -glucose associated with type 2 absorptions appeared at $917 \pm 13\text{ cm}^{-1}$ and $844 \pm 8\text{ cm}^{-1}$ in α -anomer and $891 \pm 7\text{ cm}^{-1}$ in β -anomer believed to be one of the C_1-H deformation modes. However the absence of these bands in control samples shows the uncertainty of anomeric change.

Other Assignments

The band near 1740 cm^{-1} is due to $C=O$ stretching frequency of acetyl and carboxyl groups in 4-O-methylglucuronoxylan component of hemicellulose in jute stick. The intensity of this band is reduced on alkaline treatment or delignification. The weak band at 1660 cm^{-1} is due to adsorbed water. Its intensity would considerably reduced if the sample is dried severely.

The group of bands in the region $1100-950\text{ cm}^{-1}$ are mainly due to $C-O$ stretching modes in cellulose and hemicellulose. Higgins et al.¹² noted these bands might be due to coupled $C-O$ stretching mode with $C-C$ stretching frequency.

CONCLUSIONS

The following observations were made on comparing the spectra of alkaline jute stick to that of untreated and control sample.

1. The higher shift in $O-H$ stretching frequencies is due to the disruption of intermolecular hydrogen bonds in cellulose I crystal lattice on mercerisation.
2. The interaction of Na^+ ion with neighbouring atoms in cellulose II lattice brought up changes in CH_2 and $O-H$ bending frequencies in the region $1500-1300\text{ cm}^{-1}$ resulting a strong band near $1440-1430\text{ cm}^{-1}$ and broadening of the region $1400-1300\text{ cm}^{-1}$.
3. The $C-O$ stretching mode due to cellulose and lignin at 1240 cm^{-1} completely disappears on alkali treatment, instead two new peaks at 1265 and 1225 cm^{-1} appears due to $C-O$ bending and $O-H$ deformations in cellulose II and remain in control samples. This is supported to the presence of mixed lattice at 12% and above alkali treatments.
4. The shifting of β -glucosidic band from 895 cm^{-1} to 880 cm^{-1} on alkaline treatment is due to glucosidic rotation about C_1-O-C_4 linkage and thus lattice changes from cellulose I to cellulose II. Again its shift to 895 cm^{-1} on water washings might be due to partial generation of cellulose I from cellulose II.

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