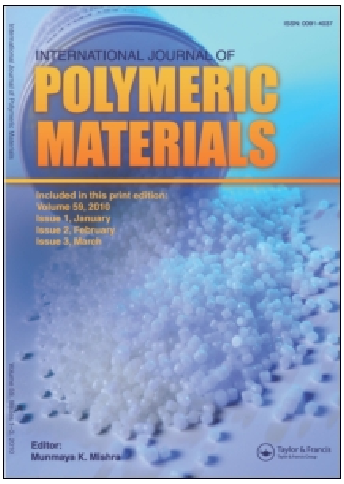

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IR and X-ray of Non Conventional Pulping Methods for Production of High Efficiency Pulp

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In X-ray diffraction analysis studies for different pulping methods in this study, it was found that the half height width (H.H.W.) do not vary much from one method of pulping to the other, but they are all lower than that of the starting bagasse. Moreover, the crystallinity indices for different bagasse pulps are in good agreement with the results of IR-spectra for these pulps where, it was found that, the higher crystallinity index is for (AO) and PA-EDTA bagasse pulps while, the lower crystallinity index is for curde bagasse. Moreover, it was found that the interplanar spacing (*d*) values of different bagasse pulps are slightly affected by the pulping methods.

In case of bleached bagasse pulps, it has been found that, the (H.H.W.) of bleached different bagasse pulps is lower than that of unbleached pulps. However, it has been also found that the crystallinity indices of bleached different bagasse pulps were higher than that of unbleached bagasse pulps. Moreover, the interplanar spacing (*d*) values for bleached different pulps are also slightly affected during bleaching process.

Keywords: Pulping; Bagasse; Bleached pulp; X-ray diffraction; IR spectra

1. INTRODUCTION

There are no absolute methods for measuring the fine structure of the pulp. However, some properties of cellulose give a clear comparative indication of the fine structure. The best common examples are the degree of swelling in water or in sodium hydroxide liquor. The fine structure also includes the ratio of crystalline to amorphous cellulose.

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In this work, the crystallinity of different pulps was investigated to give an indication to the changes in cellulose crystallinity during pulping and bleaching processes. This study was carried out by analysing a series of different bleached and unbleached bagasse pulps using X-ray diffraction and infrared (IR) spectroscopy as a tool for following of different band intensities of different groups of lignin and cellulose in the produced pulp.

Although a large number of methods have been employed to investigate the crystallinity or accessibility of pure celluloses [1], very few are suitable for investigating the crystallinity of celluloses in wood and pulp. To date, only X-ray diffraction [2,3], has been used for cellulose crystallinity determination in lignocellulosic materials and pulps. Other methods are unsuitable due to interference from hemicelluloses and lignin.

X-ray diffraction measures the fraction of molecules which are arranged in a regular repeating pattern [4]. To be seen as crystalline by X-ray, the crystallites must be of a certain minimum size [5]. Diffraction patterns of cellulose show a number of peaks superimposed on a broad background. These features are commonly attributed to the "crystalline" and "amorphous" portions of the sample. The width of the peaks in the diffractograms are inversely proportional to the lateral width of the crystallites. In X-ray diffraction, materials on the surface of the crystallites, which will be of greater mobility and a lower degree of order than the material in the interior of crystallites, will be included within the crystalline fraction if they are too small to be seen as regions of disorder.

Infrared spectroscopy has been employed to determine the degree of crystallinity and crystalline modification of pure celluloses [6,7]. The intensities of certain bands in IR spectra have been found to be sensitive to variations in cellulose crystallinity or crystalline form. Such variations may be determined using the ratio of a band which is affected by cellulose crystallinity to that of a band which is comparatively insensitive to crystallinity changes. The ratios of the peaks at 1429 to 894 cm^{-1} (A_{1429}/A_{894}) [8,9] and A_{1372}/A_{2900} [9,10] have been used to measure relative cellulose crystallinities, and A_{1370}/A_{670} [6,7] has been employed for investigating the transformation of cellulose I to cellulose II. Such determinations give only relative crystallinities, due to the lack of 100% crystalline standard and because A_{1370} is always present for totally amorphous cellulose. The region between 3500–2950 cm^{-1} which includes vibrations of the hydroxyl groups which is of greatest use, is poorly resolved, making it of little value for crystallinity determination. Recently, Fengel [11] has shown that deconvolution of cellulose FTIR spectra allowed the transformation of cellulose I to cellulose II and crystalline to amorphous cellulose to be qualitatively observed using the region of the IR spectrum attributed to vibrations of the OH groups.

X-ray diffraction and IR-spectroscopy of different non-conventional bagasse pulps is the aim of our work.

2. EXPERIMENTAL

2.1. Pulping

All pulping experiments in this work have been carried out in a 4 litre stainless steel rotating pressure reactor, immersed in a temperature controlled oil bath. In each experiment 100 g oven dry of depithed bagasse and the cooking Liquor were mixed in the reactor at ambient temperature. The cooking Liquor consisted of a mixture of 16% sodium hydroxide, 0.1% anthraquinone and different doses of hydrogen peroxide from 1 to 4% based on oven dry bagasse basis. In some experiments small quntites of chelating agent (EDTA) (ethylenediaminetetraacetic acid) were used as carbohydrate degradation inhibitor. The liquor to bagasse ratio was 6 : 1, the degree of temperature was 140 and 160°C for 30 and 60 minutes. All these data are specified for the production of peroxide-alkaline bagasse pulps. But in the case of alkali-oxygen pulping of bagasse, we used two stages. In the first stage, depithed bagasse was impregnated with different concentrations of sodium hydroxide varied from 4 to 14% based on o.d. bagasse weight at room temperature for overnight using liquor to bagasse ratio 10 : 1, in some experiment using 20 : 1 as liquor ratio for comparison. Then sequezing the soaked bagasse until the liquor become double the bagasse weight. In the second stage soaked bagasse was cooked with oxygen at pressure gauge 5 kg/cm^2 in different concentrations of sodium hydroxide. The pulping temperature used in this experiment was 130 and 140°C with time different from 30 to 90 min at maximum temperature. The liquor to soaked bagasse ratio was 6:1. The sealed reactor was then placed into the oil bath for the specified reaction time. Approximately 75 minutes were necessary before the contents of the reactor attained the final reaction temperature. This heat up time is not included in the stated reaction time. At the end of the cook, the pulp has been washed with stirred tap water, screened to remove the unreacted parts of bagasse (rejects), then centrifugated for 3 minutes in order to keep certain amount of humidity inside the fibers, weighed and then kept in a refrigerator in plastic bags. The dry weight of the solid residue is expressed as pulp yield.

2.2. Bleaching

All pulps were bleached under constant conditions by using one to three steps including chelation pretreatment (Q) by EDTA [ethylenediaminetetraacetic acid], hydrogen peroxide (P), Sodium chlorite (C), sodium chlorite with potassium permanganate (C/K), hypochlorite (H) and extraction with sodium hydroxide (E). All the stepwise bleaching experiments conditions will be discussed in the following:

2.2.1. Pretreatment by Chelating Agent (EDTA)

In polyethylene bag about 0.5% EDTA was added for each 100 g dry unbleached pulp, at consistency 5% taking into consideration the percentage of the moisture. Left the sample for one hour at 40°C in water bath, then the pulp was washed with water.

2.2.2. Chelation Acid Pretreatment (QA)

In some bleaching experiments 0.5% EDTA 1% with $NaHSO_3$ (sodium bisulfite) were added for each 100 g dry pulp for one hours at 5% consistency and temperature 90°C. The pH was adjusted with 4N H_2SO_4 to be between 2.0–70. The pulp washed with water to neutralize the acid effect.

2.2.3. Peroxide Bleaching Stage (P)

The pulp was bleached using a bleaching mixture containing 4–2% hydrogen peroxide, 0.3% EDTA, 0.5% Magnesium sulfate, 2%

sodium silicate and 2% – 1% sodium hydroxide [all of them were added based on dry weight of unbleached pulp]. The pH of this mixture was 11 – 11.5, and the pulp consistency was 10% at 80°C for 2 hours. Then the pulp was washed with water.

2.2.4. Acid Wash (A)

In some experiments of hydrogen peroxide bleaching, the pulp after being washed with water, it suspended in distilled water acidified at room temperature using 1% oxalic acid at a consistency ca- 1%. The pH was adjusted to 2.0. After 0.5 hr the pulp was washed by distilled water to neutralize the pH. In this case the bleached pulp was called (P_A).

2.2.5. Extraction by Sodium Hydroxide (E)

In well stoppered glass bottles, the sodium hydroxide is added to the pulp (for each 100 g dry pulp, about 6 g NaOH will be added) at consistency 10% taking into consideration the percentage of moisture, left the sample for 1 hour at 70°C with shaking every 10 minutes. After one hour, the sample is washed till neutral using phenolphthalene as indicator, then weighed.

2.2.6. Sodium Hypochlorite Bleaching (H)

The beated fibers were treated with an alkaline solution of sodium hypochlorite. The bleaching requirement was 4 g of chlorine per 100 g of sample at pH 7–9, consistency 5% and the flask was placed in a water bath adjusted at 80°C for 2 hr with occasional shaking then washed with water till neutrality.

2.2.7. Sodium Chlorite Bleaching (C)

The beated fibers were soaked in water overnight then treated with 5% sodium chlorite at liquor ratio 1 : 20, the pH was adjusted at 4–6 with acetic acid. The sample was placed in a water bath adjusted at 80°C for 2 hr with occasional shaking, then washed with water till free from acid.

2.2.8. Sodium Chlorite/Potassium Permanganate Bleaching (C/K)

In this method, two oxidizing agents were employed, namely, sodium chlorite and potassium permanganate. The beated fibers were heated with a solution containing 5 g/l $NaClO_2$ and 0.4 g/l. $KMnO_4$ at pH 4–6 and liquor ratio 1:50 at 90°C for 2 hr. The heated sample was then washed with water till neutrality and then treated with a solution of 1% oxalic acid for 15 min at room temperature, then washed with water until free from acid.

2.3. Physical Analysis of the Pulps

2.3.1. Infrared (IR) Spectra of the Pulp

Infrared spectra of the samples was carried out on a Beckmann Infrared Spectrophotometers Model 4220 using KBr discs technique [12].

The pulp samples were cut in a kondux mill to pass a 40 mesh screen. Exactly 2 mg of the pulp sample was then mixed thoroughly with 350 mg of potassium bromide. An intimate mixture was obtained by vibrating the sample and the potassium bromide in a vibration mill.

The mixture is transferred to a die (G251) where it is compressed under vacuum between two mirror polished optically flat surfaces to produce a transparent pellet.

In this study, infrared crystallinity indices were measured by the method of Nelson, O'Connor [10] taking the ratio of absorption band at 1372 cm^{-1} and 2900 cm^{-1} which is assigned to C—H bending and C—H streching vibration respectively. Degree of crystallinity depends upon the location of the unbonded cellulosic materials undergoing recrystallization [13].

Different bagasse pulps prepared from soda-AQ, peroxide alkaline and alkali-oxygen pulping methods were chosen for such study. Bleaching of these pulps by different bleaching methods produced different bleached pulps. Infrared investigation of these pulps were considered. The IR spectra of different unbleached and bleached bagasse pulps were measured over wavenumbers 200–4000 cm^{-1}. The IR-absorption bands and their assignments are shown in Table I.

TABLE I IR absorption bands and their assignments

Absorption wavenumber (cm^{-1})	*Assignment*
890	C—H Deformation (amorphous cellulose for cell. 1).
1110	C—O Stretching (C—OH)
1165	C—O—C Antisymmetrical stretching (glycopyranose vibration)
1205	OH in plane bending
1280	OH Deformation
1370	Crystallinity in a mixture of cellulose I and II
1425	Measurements of the degree of crystallinity (Cell. I)
1630	H—OH bond or C=C
1725	C=O stretching
2885	Unmodified measurements of crystallinity in a mixture of cellulose I and II
3450	OH stretching (H-bonded)

2.3.2. X-ray Diffraction

The different patterns of the previous samples of pulps were investigated by diffraction using X-ray technique. Samples in the form of discs were examined using phillips 1730 diffractometer operated at kr 40 and mA 25 using Ni filter as a target. Diffractometery was performed between the diffracting angles 2° to 40°C.

When a parallel beam of X-rays is incident on a crystal, diffraction occurs according to the Bragg equation:

$$n\lambda = 2d\,\mathrm{Sin}\,\theta$$

where

n = an integer referring to the order of reflection.
λ = wave length of the incident beam (= 0.154 nm).
d = interplanar spacing.
θ = angle between the incident beam and the diffraction crystal.

As n, λ and θ are known, then the equation provides a means of evaluating the interplanar spacing (d).

Besides kappa number and viscosity of different bagasse pulps, X-ray diffraction was used as an alternative method for pulp characterization. It is possible by this method to determine the crystallinity of the material through the relative peak intensities. For lignocellulosic, the peak which corresponds to the crystalline portion is at approximately 22°. The amorphous region of the pulps produces no defined peak, but produces a wide band in the region of 18°. The relative crystallinity can be calculated by Eq. (1).

$$\text{Crystallinity}\ (\%) = \frac{I(22°) - I(18°)}{I(22°)} \times 100 \qquad (1)$$

where $I(22°)$ is the height of the 22° peak in cm and $I(18°)$ is the base line [14].

In this study, the relative crystallinity, interplanar spacings (*d*) and half height widths (HHW) of different bleached bagasse pulps prepared by different bleaching methods, were measured by X-ray diffraction to elucidate the influence of these methods on the physico-chemical properties of the produced different pulps.

3. RESULTS AND DISCUSSION

3.1. X-ray Diffraction Analysis of Bleached Bagasse Pulps

The X-ray diffractograms of different bagasse pulps bleached by one-stage (sodium chlorite-potassium permanganate) bleaching method are illustrated in Figures 1-3.

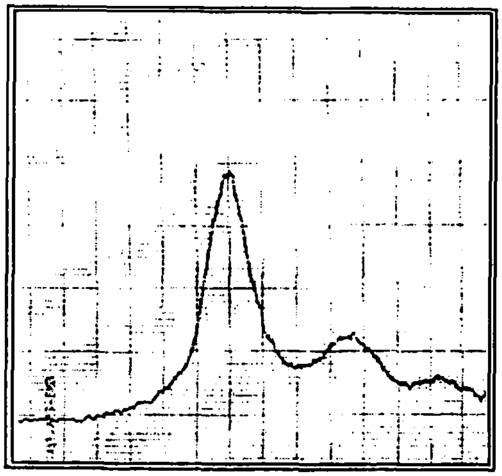

FIGURE 1 X-ray diffractogram of bleached (SAQ) pulp by using $NaClO_2/KMnO_4$.

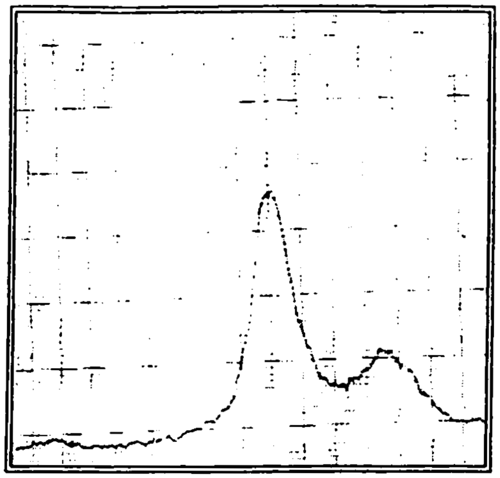

FIGURE 2 X-ray diffractogram of bleached (PA) pulp by using $NaClO_2/KMnO_4$.

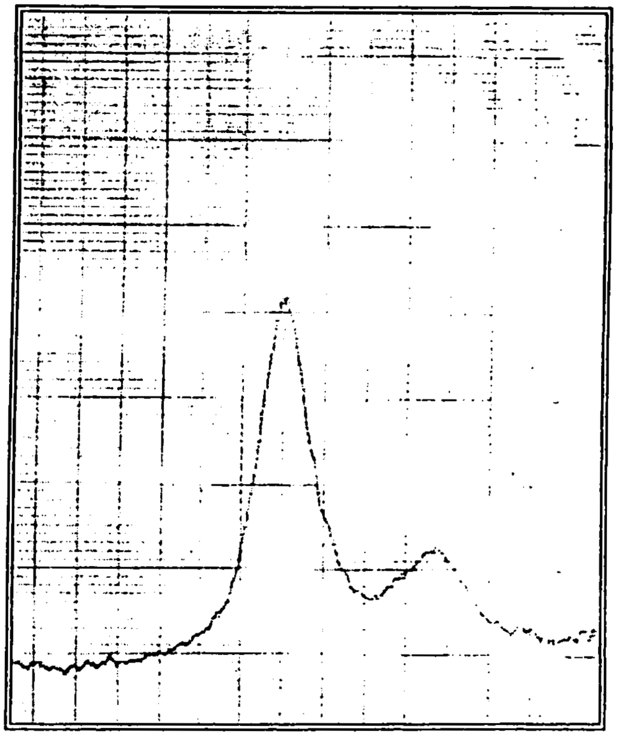

FIGURE 3 X-ray diffractogram of bleached (AO) pulp by using $NaClO_2/KMnO_4$.

The width of each peak at half maximum intensity could be regarded as a measure of the angular disperison of the crystallites within the fiberils, which may be an indication of the crystallite size (extent of order). It is known that as the half height width increases the disordered region increase as well.

The changes in the half height widths of the intensity peaks for the different bagasse pulps bleached by one stage bleaching method were obtained and the results are reported in Table II.

By comparing the values of half height widths of bleached different bagasse pulps (Tab. II) with that of unbleached pulps [15], it can be noticed that the half height widths of bleached different bagasse pulps are lower than that of unbleached pulps. Moreover, the half height widths of bleached bagasse pulps can be arranged in the following descending order: I > II > III respectively, as demonstrated in Table II.

The crystallinity index, which is an indication of the degree of order, is calculated for all bleached different bagasse pulps by the same method mentioned before, and the results are represented in Table II. It is clear from the forementioned Table II that the lower crystallinity index is for the bleached bagasse pulp prepared from soda-AQ pulping method. Meanwhile, the higher crystallinity index is for alkali-oxygen bagasse pulp bleached by one-stage bleaching method (pulp. III). Therefore, the increase in the crystallinity indices for these pulps is in the following order: I < II < III respectively. The normalized *d*-spacing (interplanar spacings) for different pulps bleached by one-stage bleaching method was calculated from the Bragg equation as mentioned before and the results are demonstrated in Table II. If no changes in the interplanar spacings (*d*) occur due to bleaching then all reflections will occur at the same values of 2θ as found for unbleached pulps [15]. However, from Table II it was found

TABLE II Half height width, peaks intensities, crystallinity indices and interplanar spacings of different bagasse pulps bleached with one stage $NaClO_2$, $KMnO_4$

Pulp no.	*Pulping methods*	*Half height width*	*Intensity (22°)*	*Intensity (18°)*	2θ	*Crystallinity index*	*Interplanar spacing (d)*
I	Soda-AQ	1.8	7.8	3.0	26.0	61.5	0.3422
II	Peroxide-alkaline	1.6	8.6	2.8	26.2	67.4	0.3397
III	Two stage-alkali oxygen	1.5	9.2	2.8	26.1	69.6	0.3410

that the lattice spacings (*d*) of bleached different bagasse pulps are slightly affected by this method.

3.2. Infrared Spectra of Bagasse

Depithed sugar-cane bagasse was extracted by a mixture of methanol and benzene (in ratio 1 : 1) for 8 hours, then investigated by IR-spectroscopy. The results are reported in Table III and Figure 4. It is well known that, IR-spectra of bagasse is influenced by the spectra of its three main biopolymers, namely, lignin, hemicellulose and α-cellulose.

TABLE III Crystallinity and asymmetry indices and mean hydrogen bonding of bagasse raw material

Crystallinity index	*Asymmetry index*	*Mean hydrogen bonding* (A_{OH}/A_{CH})	ν_{OH} (cm^{-1})
0.675	2.200	2.200	3446

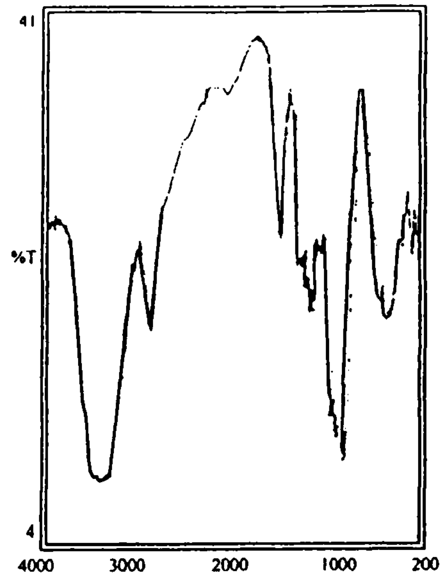

FIGURE 4 IR-spectra of bleached (SAQ) pulp by using QPP' sequence.

3.3. IR-spectra Analysis of Bleached (SAQ) Bagasse Pulp

Different bleached soda-anthraquinone bagasse pulps prepared by different bleaching methods were investigated by IR-spectra. Crystallinity indices, hydrogen bonding and asymmetry indices of these pulps were measured from the charts of Infrared. IR-spectra and intensities of absorbance of different bands are demonstrated in Tables IV and V and Figures 5–10 respectively.

3.3.1. Crystallinity Indices, Mean Hydrogen Bonding and Asymmetry Indices of Bleached (SAQ) Bagasse Pulp

From Table IV it can be said that, the crystallinity indices of different bleached pulps are higher than crystallinity index of unbleached SAQ

TABLE IV Crystallinity and asymmetry indices and mean hydrogen bonding of bleached Soda-AQ bagasse pulps

Pulp no.	*Bleaching sequence*	*Crystallinity index*	*Asymmetry index*	*Mean hydrogen bonding* (A_{OH}/A_{CH})	ν_{OH} (cm^{-1})
1	Unbleached*	0.947	0.843	1.376	3421
2	QPP′	0.669	0.817	1.528	3419
3	QPH	0.996	0.874	1.256	3417
4	C/K	0.959	0.787	1.635	3421
5	EC	1.015	1.031	1.289	3421
6	EHH′	0.967	0.893	1.376	3417
7	EHP	1.014	1.023	1.286	3421

* Blank experiment prepared by 16% NaOH, 0.1% AQ, with liquor ratio 6:1, at 160°C for 1 hr.

TABLE V Absorbance bands of IR-spectra of bleached soda (AQ) bagasse pulps

Pulp no.	*A*900 (cm^{-1})	*A*1110 (cm^{-1})	*A*1160 (cm^{-1})	*A*1370 (cm^{-1})	*A*1425 (cm^{-1})	*A*1625 (cm^{-1})	*A*1725 (cm^{-1})	*A*2900 (cm^{-1})	*A*3450 (cm^{-1})
1 Unbleached*	0.465	0.663	0.612	0.538	0.509	0.488	0.387	0.569	0.783
2	0.585	0.921	0.854	0.694	0.658	0.602	0.432	0.721	1.097
3	0.643	0.854	0.796	0.721	0.688	0.619	0.515	0.727	0.903
4	0.498	0.839	0.769	0.606	0.581	0.509	0.372	0.738	0.989
5	0.733	0.959	0.921	0.796	0.769	0.699	0.577	0.789	1.023
6	0.796	1.155	1.097	0.886	0.878	0.721	0.553	0.921	1.204
7	0.585	0.769	0.745	0.698	0.629	0.568	0.481	0.648	0.831

*Blank experiment prepared by 16% NaOH, 0.1% AQ, with liquor ratio 6:1, at 160°C for 1 hr.

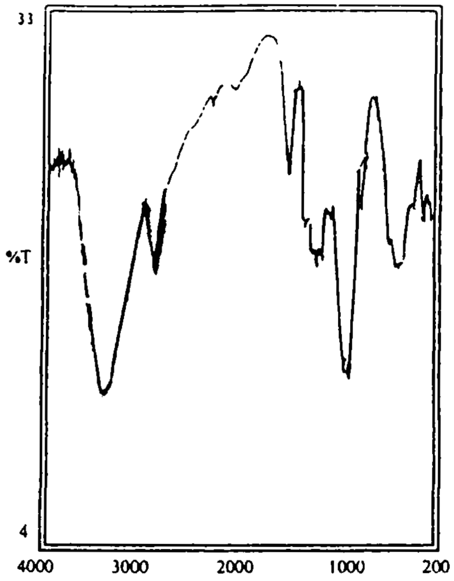

FIGURE 5 IR-spectra of bleached (SAQ) pulp by using OPH sequence.

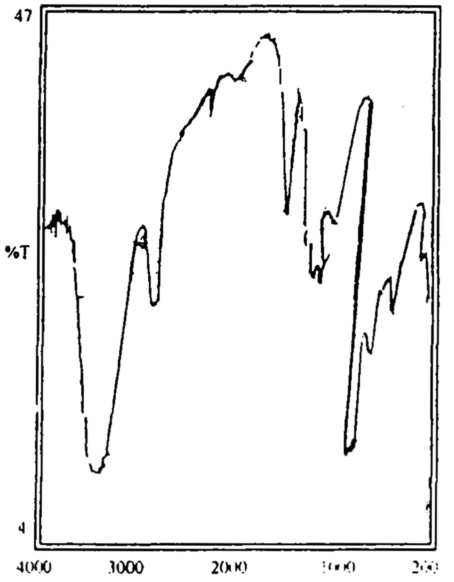

FIGURE 6 IR-spectra of bleached (SAQ) pulp by using C/K sequence.

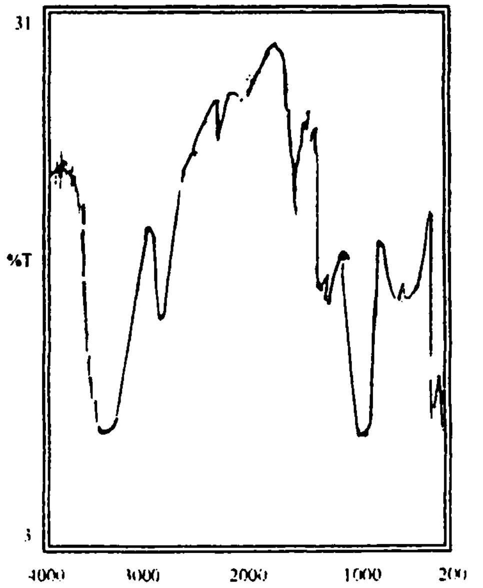

FIGURE 7 IR-spectra of bleached (SAQ) pulp by using EC sequence.

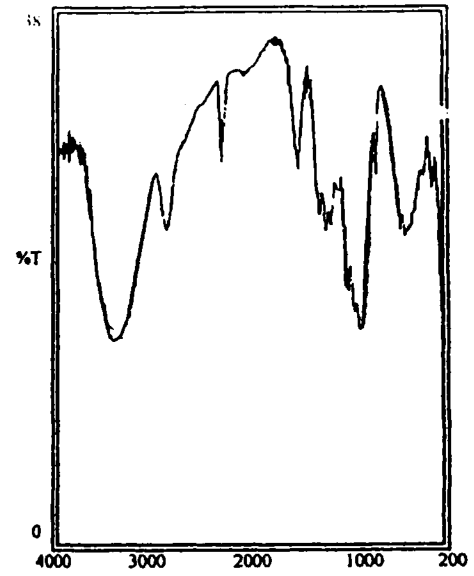

FIGURE 8 IR-spectra of bleached (SAQ) pulp by using EHH' sequence.

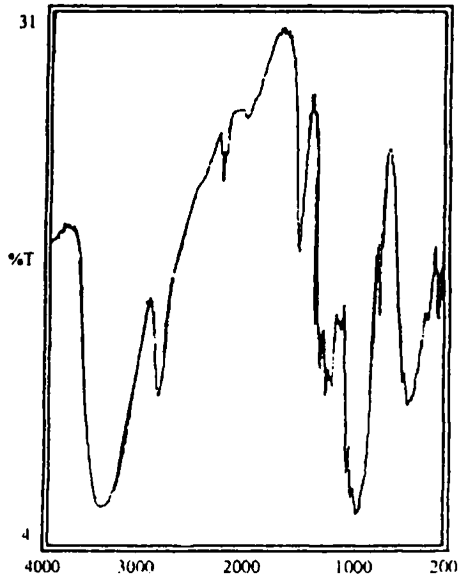

FIGURE 9 IR-spectra of bleached (SAQ) pulp by using EHP sequence.

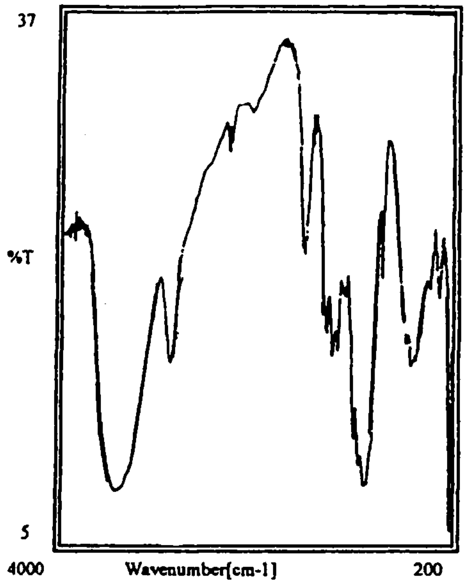

FIGURE 10 IR-spectra of bleached (PA) pulp by using QPP′ sequence.

bagasse pulp. However, the crystallinity indices of bleached pulps were low as compared with the original raw material Table III.

Generally, from the values of crystallinity indices mentioned in Table IV it is seen that, the maximum crystallinity index was achieved at pulp bleached by EC sequence, while the minimum crystallinity index was obtained for pulp bleached by sod. chlorite/pot. permanganate (C/K). It is also evident from the same table that the crystallinity index of bleached pulp by QPH sequence is more than that of pulp bleached by QPP′ sequence. Otherwise, the crystallinity index of bleached pulp by EHP sequence is higher than that of bleached pulp by EHH′ sequence.

From all the values of crystallinity indices (Cry. I) in Table IV it can be concluded that, the increased in crystallinity indices for different bleached pulps are in the following order: unbleached SAQ pulp < C/K < QPP′ < EHH′ < QPH < EHP < EC-bleached pulps.

From the same table, it can be obvious that, the positions of maximum hydroxyl band of the different bleached pulps are approximately constant and in the same time are lower than the position of maximum hydroxyl band of raw material.

However, band asymmetry increased or decreased depending on the type of bleaching method used. Broadening hydroxyl band towards lower frequency sides Figures 5–10 resulted in a general increase in asymmetry indices.

From the values of asymmetry indices of different bleached pulps mentioned in the same table, it can be noticed that, the maximum asymmetry index was achieved at bleached pulp of EC sequence, while the minimum asymmetry index was obtained at pulp bleached by QPH sequence. Moreover, it can be concluded that, the asymmetry indices were increased in the following order: C/K < QPP′ bleached pulp < unbleached (SAQ) pulp < QPH bleached pulp < EHH < EHP < EC bleached pulps.

On the other hand, it can be said that the mean hydrogen bond strengths (A_{OH}/A_{CH}) of the different bleached pulps increased or decreased depending on the type of bleaching methods used.

It is evident from the same Table IV that, in some cases of bleaching processes such as QPP′ and C/K, the A_{OH}/A_{CH} of the produced pulps was increased, while in some other cases, the A_{OH}/A_{CH} decreased or remain unchanged, according to the type of bleaching method used.

3.3.2. Absorbance Intensity of Different Bands of IR Spectra of Bleached (SAQ) Bagasse Pulp

From the spectrum of different bleached soda-AQ bagasse pulps illustrated in Figures 5–10 and from the absorption band intensity of these spectra demonstrated in Table V it can be noticed that, the broadening of the band of —OH groups in the region 3700–3100 cm^{-1} is characteristic of the spectra of different bleached pulps. But the —OH group are not free and connected to other modes of hydrogen bonding and shifted to longer wavenumber about 3420 cm^{-1}. Moreover the absorption of the —OH group for different bleached pulps is much higher as compared to that of unbleached pulp. Another intense and sharp band appears for all different pulps at 2900 cm^{-1} which reveals the —OH stretching frequency. There is no significant shifting observed for different pulps. The absorption intensity of this band for these pulps was higher than that of unbleached pulps. In the region 1700–1600 cm^{-1} which characteristic of the carbonyl group band as mentioned before, there are very weak bands appearing in this region, and there is no significant shifting due to the different bleaching methods. Moreover, this band either overlaps the neighbouring one or it is present as a shoulder. A sharp band which is characteristic of $—CH_2$ bending frequency at 1430 cm^{-1}, possesses no significant shifting in wavenumber for all different bleached pulps. The values of the absorbance of these pulps are higher than that of unbleached pulp as shown in Table V and from the spectrum of these pulps, as illustrated in Figures 5–10, it is seen in different bleached pulps. The sharp and intense band at 1370 cm^{-1} which is assigned to $—CH_3$ bending frequency is due to the presence in lignin ($—OCH_3$ group).

Moreover, it is obvious that the absorption intensity values of this band for these pulps were higher as compared to that of unbleached pulp.

It is also obvious that the presence of two band in the region 1200–1000 cm^{-1} which is characteristic of C—O—C stretching in cellulose and —CH banding in skeletal vibration of aromatic is due to the presence of glucosidic linkage between glucose rings and due to the occurrence of —CO forming the pyranose rings. A sharp and intense band at this region is noticeable for different pulps. The absorbance intensity ratios of these pulps at this band do not vary much from one method of bleaching to the other, but they are all higher than that of unbleached soda-AQ bagasse pulp. Also, from the spectrum of these pulps as shown in Figures 5 – 10 and from the values of absorbance of these spectrum from these pulps, it is seen that a sharp and intense band at 900 cm^{-1} was characterized for all different bleached pulps which are assigned to β-linkage in cellulose and hemicellulose. A pronounced shifting from 890 to 900 cm^{-1} was observed for all different pulps. And the values of absorbance of this band vary from one bleaching method to the other, while the values of the absorbance intensity in this band for different bleached pulp were higher as compared to that of unbleached pulp, generally.

3.4. IR-spectra Analysis of Bleached (PA) Bagasse Pulp

Different bleached peroxide alkaline bagasse pulps prepared by different bleaching methods were investigated by IR-spectra. The absorbance bands and IR-spectra of these pulps are shown in Table VI and are illustrated in Figures 11 – 16 respectively. The crystallinity indices, hydrogen bonding and the asymmetry indices were calculated from the charts of IR for these pulps. The results obtained and the different bleaching sequences chosen for this study are demonstrated in Table VI. The different bleached samples were chosen in this study because they gave the best results as mentioned in previous work [15].

TABLE VI Crystallinity and asymmetry indices and mean hydrogen bonding of bleached (PA) bagasse pulps

Pulp no.	*Bleaching sequence*	*Crystallinity index*	*Asymmetry index*	*Mean hydrogen bonding* (A_{OH}/A_{CH})	ν_{OH} (cm^{-1})
1	Unbleached*	0.975	0.773	1.564	3421
2	QPP′	1.027	0.767	1.407	3421
3	QPH	1.003	0.893	1.404	3421
4	C/K	1.049	0.894	1.325	3421
5	EC	1.018	0.836	1.236	3421
6	EHH′	0.978	0.875	1.334	3417
7	EHP	1.024	0.856	1.543	3383

*Blank experiment prepared by 16% NaOH, 2% H_2O_2 and 0.1% AQ, with liquor ratio 6 : 1, at 160°C for 1 hr.

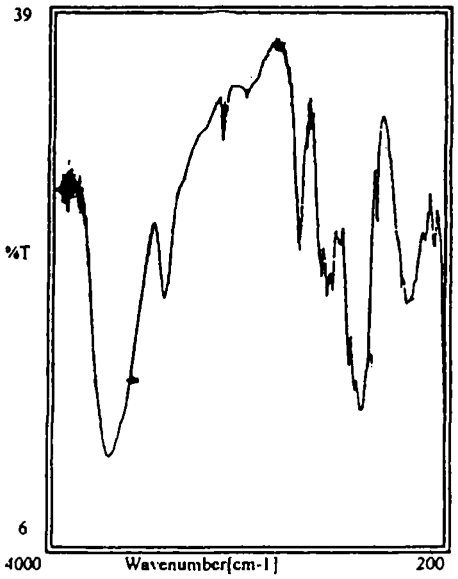

FIGURE 11 IR-spectra of bleached (PA) pulp by using QPA sequence.

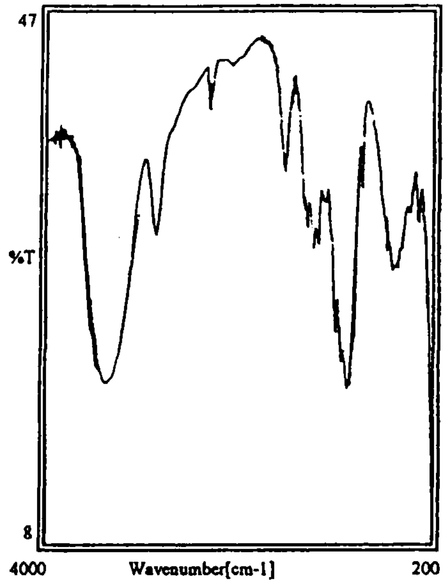

FIGURE 12 IR-spectra of bleached (PA) pulp by using C/K sequence.

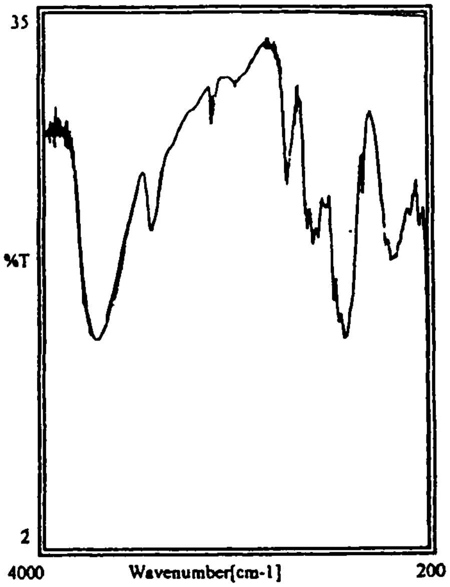

FIGURE 13 IR-spectra of bleached (PA) pulp by using EC sequence.

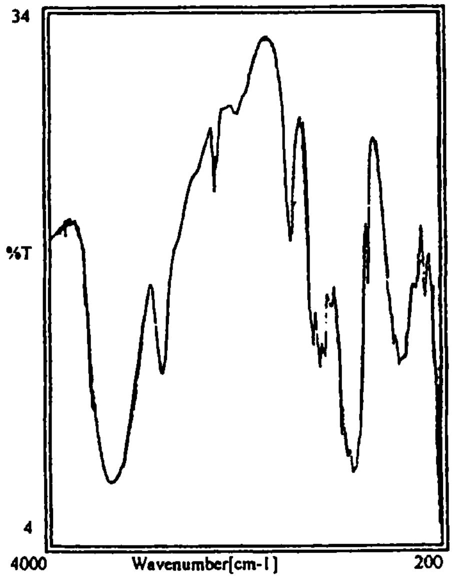

FIGURE 14 IR-spectra of bleached (PA) pulp by using EHH sequence.

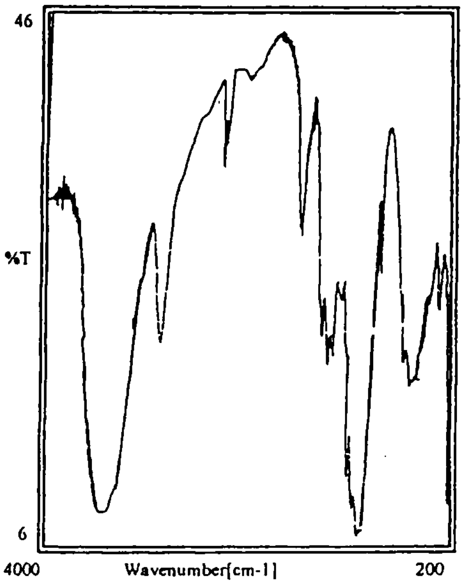

FIGURE 15 IR-spectra of bleached (PA) pulp by using QPP′ sequence.

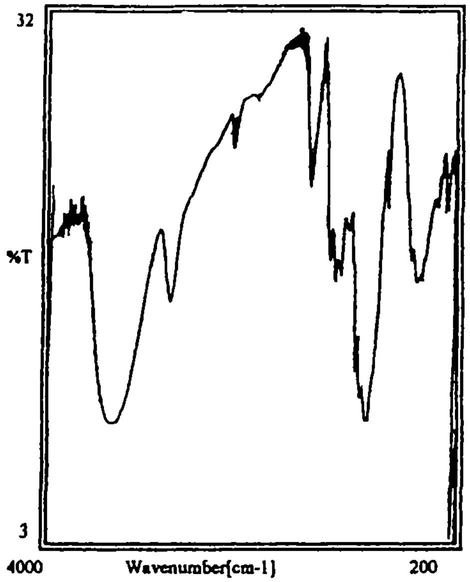

FIGURE 16 IR-spectra of bleached (AO) pulp by using QAP sequence.

3.4.1. Crystallinity Indices, Hydrogen Bonding and Asymmetry Indices

In general, and as obvious in Table VI the crystallinity indices of different bleached pulps were higher than the crystallinity index of unbleached peroxide alkaline pulp, while they were lower than the crystallinity index of curde bagasse (Tab. III).

From Table VI it is seen that the crystallinity index of bleached pulp by QPP′ bleaching sequence is higher than the crystallinity index of bleached pulp by QPH sequence. Other wise, the crystallinity index of bleached pulp by EHP sequence is higher than the bleached pulp by EHH′ sequence. In general, the maximum crystallinity index was obtained in pulps prepared from bleaching of unbleached pulps by sodium chlorite and potassium permanganate, while minimum crystallinity index was obtained for pulps prepared by EHH′ sequence. So, it can be concluded from the values of crystallinity indices for different bleached pulps mentioned in Table VI that the crystallinity indices increased in the following order: unbleached (PA) pulp < EHH′ bleached pulp < QPH pulp < EC < EHP < QPP′ < CK bleached pulp.

In the same table, it can be noticed that the positions of the maximum hydroxyl band of the different bleached peroxide alkaline pulps are approximately constant, while they were low compared with that of raw material (Tab. III). However, band asymmetry as indicated by the increased broading towards lower frequency sides Figures 11–16 respectively, depends mainly on the type of bleaching methods. Broadening towards lower frequency side results in an increase in the asymmetry index. The Asymmetry indices of different bleached pulps were increased in the following order: unbleached (PA) pulp < QPP′ < EC < EHP < EHH′ < QPH = CK bleached pulp.

On the other hand, mean hydrogen bond strengths A_{OH}/A_{CH} of the different bleached pulps are lower than that of unbleached peroxide alkaline bagasse pulps. From the same Table VI, it is evident that, replacement of hypochlorite to the peroxide in the second stage of QPP′ sequence resulted in similar value of hydrogen bond strength A_{OH}/A_{CH} for QPP′ bleached pulp. Meanwhile, replacing the peroxide in the second stage of EHH′ sequence, produces pulp with higher A_{OH}/A_{CH} than of EHH′ bleached pulp.

Thus, it can be concluded that, the A_{OH}/A_{CH} of different bleached pulps were increased in the following order: EC bleached pulp < C/K < EHH′ < QPH < QPP′ < EHP bleached pulp < unbleached (PA) pulp.

3.4.2. Absorbance Bands Intensity of Infrared Spectra of Bleached Peroxide Alkaline Bagasse Pulps

From the absorption bands values of infrared spectra of different bleached pulps in Table VII and from the spectrum of these pulps demonstrated in Figures 11–16, it is clear that all spectrum of the different pulps are characterized by a broad and intense band in the region 3500–3300 cm^{-1} which reveals the hydroxyl groups and the bonded HO-stretching vibration as expected in the cellulose polymer. It is also obvious that, the hydroxyl groups are not free but linked to different modes of hydrogen bonding as expected [16], since the bands are shifted to somewhat longer wave number, namely to about 3421 cm^{-1}. Moreover, the values of the absorbance intensity vary according to the type of bleaching method in the range 1.12–0.699.

In the absorption at 3000–2800 cm^{-1} the appearance of intense band at 2900 cm^{-1} indicated a —CH stretching, that no significant shifting was observed for different bleaching methods, but the values of absorbance of this band are varied from one bleaching method to the other. Also, in the region 1700–1600 cm^{-1}, there are very weak bands that appear as a shoulder due to the shift of CO-group which characterized in this region to carboxylic acid or other carbonyls.

TABLE VII Absorbance bands of IR spectra of bleached (PA) bagasse pulps

Pulp no.	*A*900 (*cm*$^{-1}$)	*A*1110 (*cm*$^{-1}$)	*A*1160 (*cm*$^{-1}$)	*A*1370 (*cm*$^{-1}$)	*A*1425 (*cm*$^{-1}$)	*A*1625 (*cm*$^{-1}$)	*A*1725 (*cm*$^{-1}$)	*A*2900 (*cm*$^{-1}$)	*A*3450 (*cm*$^{-1}$)
1 Unbleached*	0.426	0.643	0.594	0.523	0.507	0.475	0.376	0.569	0.903
2	0.668	1.002	0.869	0.775	0.745	0.638	0.482	0.769	1.081
3	0.573	0.769	0.745	0.658	0.638	0.566	0.458	0.658	0.921
4	0.469	0.668	0.629	0.530	0.595	0.449	0.366	0.599	0.696
5	0.615	0.769	0.757	0.668	0.658	0.602	0.502	0.663	0.824
6	0.733	1.071	1.012	0.846	0.809	0.668	0.505	0.869	1.125
7	0.568	1.010	0.921	0.699	0.653	0.523	0.382	0.668	1.071

*Blank experiment prepared by 16% NaOH, 2% H_2O_2, 0.1% AQ, with liquor ratio 6 : 1, at 160°C for 1 hr.

Deformation vibrations of C—H either in methoxyl group of lignin or in the —CH_2 bending in the hemicellulose appears at 1425 cm^{-1} band for all different bleached pulps. It is seen from the values of absorbance in this band in Table VII that the values of absorbance band of different bleached pulps are higher than that of unbleached pulp.

The band at 1370 cm^{-1} of —CH_3 bending frequency, which may be caused by lignin and α-cellulose, appears in all different bleached pulps.

The values of absorbance intensity of this band do not vary much from one method of bleaching to the other, but they are all higher than that of unbleached bagasse pulp. From the spectrum of different bleached pulps illustrated in Figures 11 – 16 and the values of the different absorbance bands demonstrated in Table VII, it is evident that the band at 1165 cm^{-1} which characterized to aromatic skeletal vibration, appears in all spectrum of different bleached pulps, as sharp and intense band. The absorbance values of this band for different bleached pulps are higher as compared to that of unbleached peroxide alkaline bagasse pulp.

Also, the band at 1000 – 1110 cm^{-1} is ascribed to the H-bonding on the skeletal vibration involving stretching of the —CO bond in the hemicellulose and cellulose. The absorption intensity values of this band for all different bleached pulps were much higher than that of unbleached bagasse pulp. Also, no significant shifting was observed in this band frequency. For the different bleached peroxide-alkaline pulps, there is a sharp and intense bands that appears at 900 cm^{-1} which is characterized to anti-symmetric out-of plane stretching due to β-linkage in cellulose and hemicellulose. No significant shifting was observed for this spectra for all these pulps. The absorbance of this band ratios decreased or increased according to the type of bleaching methods, but generally, the values of these absorbances are higher than that of unbleached bagasse pulps.

3.5. IR-spectra Analysis of Bleached Alkali-oxygen (AO) Bagasse Pulps

Different bleached alkali-oxygen bagasse pulps prepared by different bleaching methods were investigated by IR-spectroscopy. Different bleached pulps have been chosen for this study because they gave the best results in the previous work [15]. The IR-spectra and different absorbance band intensity for different bleached pulps are shown in Tables VIII and IX and Figures 17–21.

The crystallinity indices (Cry. I), asymmetry indices and hydrogen bonding were determined from the charts of the IR for these pulps. The different bleached pulps conditions chosen for this study and the results obtained are indicated in Table VIII.

3.5.1. *Crystallinity Indices, Hydrogen Bonding and Asymmetry Indices of Bleached Alkali-oxygen Pulps*

In comparing the crystallinity index of unbleached pulp with different bleached alkali-oxygen pulps Table VIII, it is seen that bleaching

TABLE VIII Crystallinity indices, asymmetry indices and mean hydrogen bonding of bleached two-stage alkali-oxygen bagasse pulps

Pulp no.	*Bleaching sequence*	*Crystallinity index*	*Asymmetry index*	*Mean hydrogen bonding* (A_{OH}/A_{CH})	ν_{OH} (cm^{-1})
1	Unbleached*	0.974	0.823	1.15	3417
2	QPP′	0.974	1.125	1.32	3405
3	QPH	0.897	1.105	1.32	3423
4	C/K	0.996	1.143	1.16	3423
5	EHH′	1.020	1.132	1.34	3405
6	EHP	1.057	1.123	1.13	3409

*Blank experiment prepared by soaking 4% NaOH, and cooking with 14% NaOH, 5 kg/cm^2 oxygen pressure 0.1% AQ, with liquor ratio 6 : 1, at 160°C for 1 hr.

TABLE IX Absorbance bands of IR spectra of bleached two-stage alkali-oxygen bagasse pulps

Sample no.	*A*900 (cm^{-1})	*A*1110 (cm^{-1})	*A*1160 (cm^{-1})	*A*1370 (cm^{-1})	*A*1425 (cm^{-1})	*A*1625 (cm^{-1})	*A*1725 (cm^{-1})	*A*2900 (cm^{-1})	*A*3450 (cm^{-1})
1 Unbleached*	0.939	1.155	1.097	1.034	1.023	0.939	0.796	1.071	1.182
2	0.657	0.921	0.886	0.758	0.725	0.638	0.535	0.783	1.021
3	0.624	0.774	0.769	0.699	0.682	0.653	0.593	0.783	0.921
4	0.399	0.458	0.453	0.426	–	–	–	0.432	0.491
5	0.569	0.886	0.809	0.661	–	0.516	–	0.673	0.886
6	0.678	0.510	0.796	0.733	–	0.658	–	0.699	0.809

*Blank experiment prepared by soaking 4% NaOH, and cooking with 14% NaOH, 5 kg/cm^2 oxygen pressure 0.1% AQ with liquor ratio 6 : 1, at 160°C for 1 h – Noise (not sharp bands).

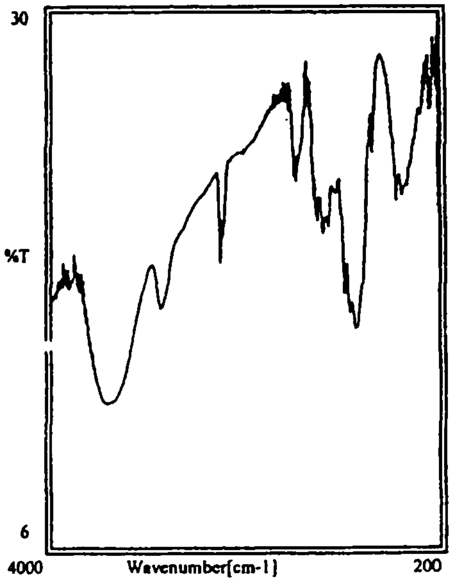

FIGURE 17 IR-spectra of bleached (AO) pulp by using QPP' sequence.

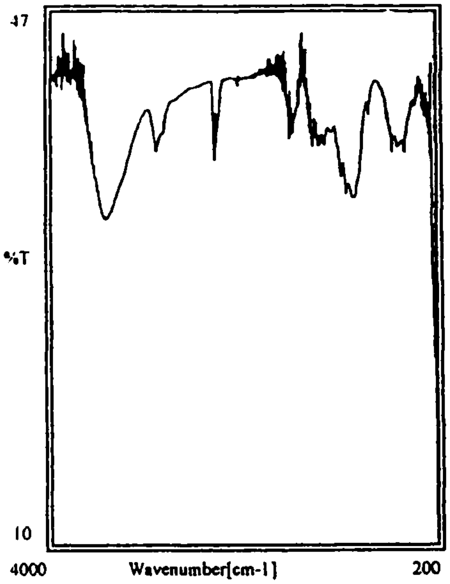

FIGURE 18 IR-spectra of bleached (AO) pulp by using QPH sequence.

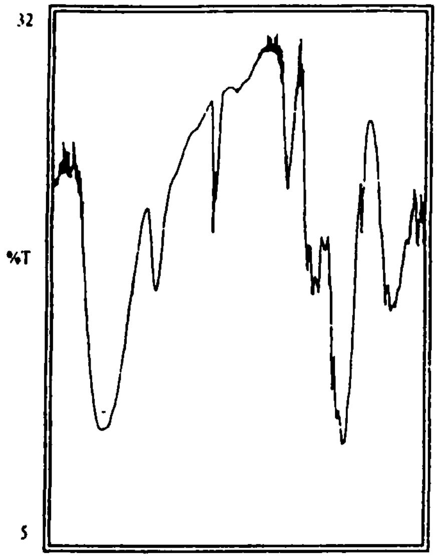

FIGURE 19 IR-spectra of bleached (AO) pulp by using C/K sequence.

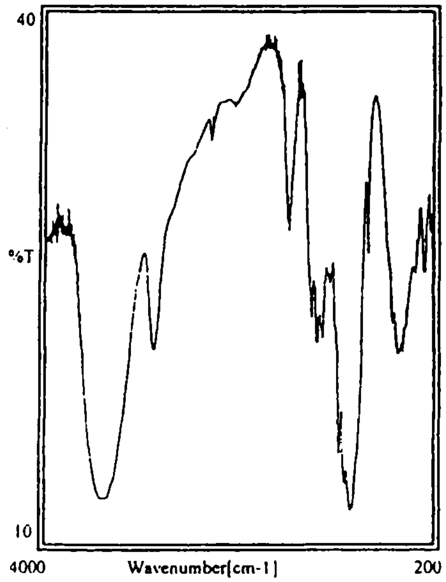

FIGURE 20 IR-spectra of bleached (AO) pulp by using EHH' sequence.

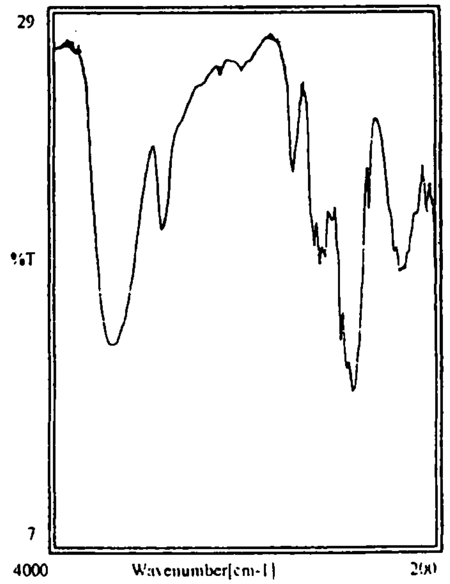

FIGURE 21 IR-spectra of bleached (AO) pulp by using EHP sequence.

of alkali-oxygen pulps by different bleaching method may increase, decrease or unchange the crystallinity index of the produced pulps as following: the crystallinity index of bleached pulp by QPP′ sequence is lower than Cry. I. of unbleached pulp. Otherwise, the Cry. I. of bleached pulp by either QPH, EHH′ or EHP sequences is higher than that of unbleached pulp. Bleaching of alkali-oxygen pulp by Q_AP sequence is not accompanied by change in Cry. I.

From Table VIII it can be noticed that the crystallinity index of bleached pulp by EHP sequence is larger than the crystallinity index of bleached pulp by EHH′ sequence. Meanwhile the Cry. I. of bleached pulp by QPP′ sequence is lower than that of QPH bleached pulp.

It can be concluded that the crystallinity indices of different bleached pulps were increased in the following order: QPP′ bleached pulp < unbleached = bleached Q_AP pulp < QPH < CK pulp < EHH′ < EHP bleached pulp.

Moreover, in the same table, it is evident that the positions of maximum hydroxyl band of different bleached pulps are approximately constant. However, band asymmetry increased or decreased depending on the type of bleaching methods used. Broadening towards lower frequency sides as shown in Figures 17–21 respectively, resulted in an increase in the asymmetry index. The increase in the asymmetry indices as reported in Table VIII is in the following order: unbleached pulp < QPP′ bleached pulp < EHP < Q_AP bleached pulp < EHH′ < CK bleached pulp < QPH bleached pulp.

On the other hand, mean hydrogen bond strengths A_{OH}/A_{CH} of different bleached pulps are decreased or increased, mainly depending on the type of bleaching process as shown in Table VIII. It is obvious that the mean hydrogen bond strengths of different bleached pulps are higher than that of unbleached pulp except in case of bleached pulp by EHP′ sequence. In the same table, it is evident that the A_{OH}/A_{CH} of bleached pulp by EHP sequence is lower than that of bleached by EHH′ sequence. Otherwise, the A_{OH}/A_{CH} bleached pulp by QPP′ sequence is more than the A_{OH}/A_{CH} of bleached pulp by QPH sequence. Generally, the hydrogen bond strengths (A_{OH}/A_{CH}) of different pulps were increased in the following order: EHP bleached pulp < unbleached pulp < QPH < bleached pulp < Q_AP = QPP′ < EHH′ bleached pulp.

3.5.2. Absorbance Bands Intensity of Infrared Spectra of Bleached Two-stage Alkali-oxygen (AO) Bagasse Pulps

From the spectra of the different bleached pulps of two-stage alkali oxygen pulps illustrated in Figures 17–21 and from the values of absorbance bands of these pulps demonstrated in Table IX it can be noticed that all spectra of different bleached pulps were characterized by the presence of a broad and intense band in the range of region 3700–3000 cm^{-1} which is assigned to the polymeric association of the hydroxyl groups and the bonded —OH stretching vibration as expected in the cellulose polymer. A slight shifting to lower or higher wavenumber was observed for different bleached pulps due to the bleaching methods used. So, the values of absorbance bands at this band were lower than that of unbleached pulp.

A sharp and intense band present in the range 3000–2900 cm^{-1} was assigned to —CH stretching frequency which showed no significant shifting due to the previous bleaching methods. Also, the absorption band ratios of these pulps are lower than that of unbleached pulp. Two very weak bands present in the region 1700 – 1600 cm^{-1} are assigned to —CO and —C=C— stretching frequency which may be related to the presence of aromatic ring in lignin within the cellulosic fibers. No significant shifting in the wavenumber was observed, but this band either overlaps the neighbouring one or it is present as a shoulder as shown in Figures 17 – 21. A sharp band which is characteristic of —CH_2 bending frequency, at 1425 cm^{-1}, possesses no significant shifting in the wavenumber, but there is a noticeable decrease in the intensity of absorbance ratios of the bands of different bleached pulps compared to that of unbleached pulp. A relatively broad band was present at 1376 cm^{-1} assigned to —CH_3 bending frequency due to the presence of lignin which contain —OCH_3 groups as mentioned before. No pronounced shifting was observed in the wave number for different pulps.

It is clear that the presence of sharp and intense three bands in the range 1200 – 900 cm^{-1} attributed to —CO stretching frequency, —C=C— stretching and H-bonding respectively, which is due to the presence of glucosidic linkage between the glucose rings and is also due to the occurrence of —CO forming the pyranose rings. Also, no significant shifting was observed in the wavenumber for the different bleached pulps. Otherwise, from the values of intensity of absorption for these bands demonstrated in Table IX, it is obvious that the absorbance intensity values of these bands were not varied from one method of bleaching to the other, but they are all lower than that of the unbleached two-stage alkali-oxygen (AO) pulp.

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