Bleaching of Egyptian Bagasse and Rice Straw Pulps with Hydrogen Peroxide

Part I- Specifications, Properties and Structure of Unbleached and Bleached Pulps

Magdi Z. Sefain, Mohamed H. Fadl, Fardous Mobarak, Sayed Sherif and Nesrine F. Kassem.

National Research Centre, Cellulose and Paper Dept., Dokki, Cairo, Egypt.

ABSTRACT

Bagasse and rice straw pulps were bleached with different concentrations of hydrogen peroxide for different periods and temperatures. Breaking length, tear factor and brightness were estimated. Results revealed that an improvement in brightness was obtained with a little loss in the breaking length and tear factor. The kinetic of oxidation was featured with infra-red investigations. The changes in surface were investigated by Scanning Electron Microscopy.

INTRODUCTION

Traditionally, pulp bleaching has been carried out with chlorine and hypochlorite, which constitutes a severe source of environmental pollution. Today, there are several techniques available to use chlorine-free solutions for the bleaching of chemical pulps mainly from wood materials with high brightness through the formation of hydroxyl radicals from hydrogen peroxide in alkaline medium(1). However, the application of the above technique on the pulps obtained from agricultural residues is still in study stages. The decomposition of hydrogen peroxide may generate exceedingly reactive hydroxyl radicals. Walling (2) proposed the following sequence leading to the formation of hydroxyl radicals :

$$M^{n+} + H_2O_2 \rightarrow M^{n+1} + OH + {}^{\cdot}OH \quad (a)$$

$$M^{n+1} + OOH^- \rightarrow M^{n+} + O_2^- + H^+ \quad (b)$$

$$M^{n+1} + O_2^- \rightarrow M^{n+} + O_2 \quad (c)$$

where M/M^n represents transition metal ions.

According to this, decomposition of hydrogen peroxide involves an interplay between dissociated and undissociated forms of hydrogen peroxide. The hydroxyl radical is an electrophile and one of the strongest one-electron oxidants available in a aqueous medium (3). Actually, the colouration of the pulp is due to the chromophores contained in the residual lignin (after pulping); these chemical groups with conjugated double bonds are able to absorb light at particular visible wavelength, and thus causing a visual colouration. Bleaching reagents modify the chromophores and decrease the total absorption in the visible spectrum. The bleaching action of alkaline hydrogen peroxide is due to the chemical oxidation of chromophores by perhydroxyl anion (HOO^-). It has been suggested (4) that chromophore formation as well as chromophore elimination should be considered as a reversible process.

Since the introduction of peroxide reinforced alkaline extraction, many works were carried out utilizing peroxide as bleaching agent for bagasse pulp and agro-based fibers (5, 6). It is (7) reported that transition metals catalyz the decomposition of hydrogen peroxide reducing the pulp brightness. However, sodium silicate is widely used as an efficient stabilizer for peroxide decomposition and enhances brightness response (8). Addition of magnesium sulphate to the silicate in peroxide bleaching enhances the brightness due to the absorption of the metal ions by a colloidal suspension of magnesium silicate (9). In some work (10) chelation reaction was used to wash out metals from the pulps using chelating agents such as EDTA.The present work represents part of more general study aiming to utilize nonchlorine bleaching agents suitable for both: a) producing paper from agricultural residues and b) minimizing environmental pollution.

EXPERIMENTAL

Materials

Unbleached Egyptian bagasse pulp and rice straw pulps were taken from one of the local pulp mills which possess the following properties.

	α-cellulose (%)	Pentosan (%)	Lignin (%)	Ash (%)
Bagasse	67.2	25.8	7.0	0.95
Rice Straw	56.1	24.4	6.6	9.35

Hydrogen Peroxide solution was received from "Adwic", about 30% w/v, M.W.= 34.01, Wt. per ml at 20°C ≅ 1.10g was used and diluted to appropriate concentrations.

Methods of treatment

A solution containing 0.5 g/lt magnesium sulphate, 2 g/lt sodium hydroxide and 2 g/lt sodium silicate were added to the pulp at a consistency of 10 % in plastic bags. Then 1,3 and 5% w/v H_2O_2 solution was added. The resulting solution was placed in a water bath with the pulp at 70°C for 30,60 and 90 min. at pH 11.0 with occasional shaking. Then the pulp was washed till neutrality. Parallel experiments were carried out at 80°C. Laboratory hand-made paper sheets were made from the above pulps using SCA Swedish Standard.

Physical tests of hand sheets

Sheets were subjected for breaking length measurements using Lloyd instrument, tear resistance using Elemendrof Tear Tester and % brightness using Carl Zeiss ELERPHO Tester. For each sample test, at least five experiments were carried out and the arithmatic mean of the results were calculated.

Infrared absorption spectra

Unbleached samples and those treated with 5%w/v H_2O_2 were subjected for infrared absorption spectrum between wave length 400-4000 cm^{-1} using Jaxo FTIR double beam 300 E spectophotometer.

Sample A denoted for unbleached bagasse pulp.

Sample B denoted for bleached bagasse pulp.

Sample C denoted for unbleached rice straw pulp.

Sample D denoted for bleached rice straw pulp.

A semiquantitative calculation of the relative absorption of some selective bands is made (11) taking the absorption intensities at 2885 cm^{-1} as a reference (for unchanged CH_2 groups).

Table 1. Absorption intensities of the experimental samples.

	Absorption Intensities (log 1/T)			
Wave No. (cm^{-1})	Unbleached rice straw pulp	Bleached rice straw pulp	Unbleached bagasse pulp	Bleached bagasse pulp
1110	0.57	0.59	0.40	0.97
1280	1.01	1.04	1.20	0.96
1630	1.10	1.12	1.42	1.39
1725	1.22	1.36	1.83	2.03
3450	0.52	0.44	0.26	0.92
Cr. I. (A_{1370}/A_{2885})	1.01	0.89	0.93	0.89
Asym. Index	0.86	0.78	0.73	0.75
Mean H bond strength (A_{OH}/A_{CH})	0.46	0.40	0.20	0.65

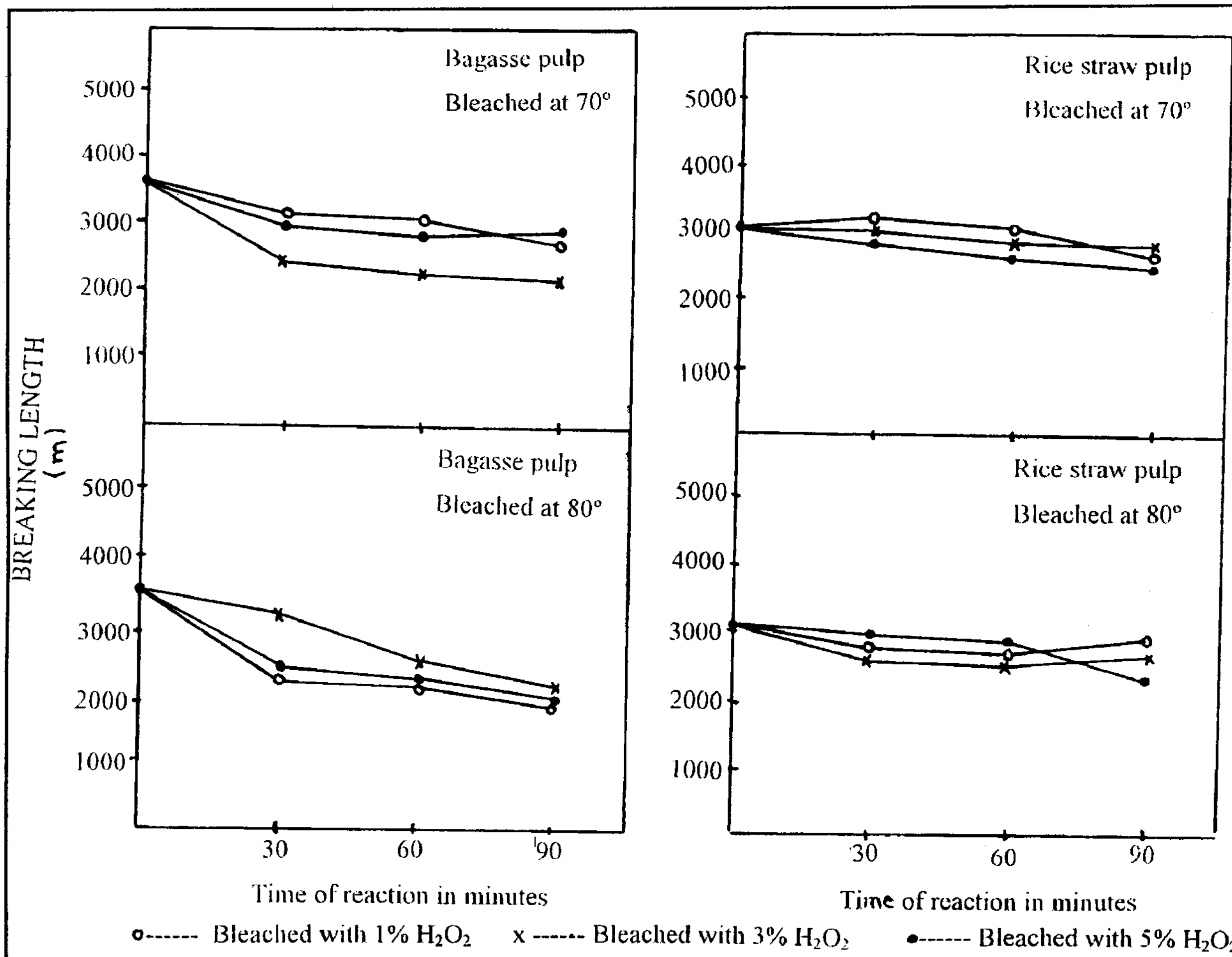


Figure 1. Effect of bleaching time and temperature on the breaking length of the experimental samples

Scanning electron microscopy

Fibre samples topography of the unbleached and bleached pulps with 5% samples were studied using JSM-T20 Scanning Electron Microscopy JEOL, Japan. Samples were previously coated with gold using "Sputta Coater S 150".

RESULTS AND DISCUSSION

The effect of treatment of unbleached bagasse and rice straw pulps with three different H_2O_2 concentrations for different periods (30,60 and 90 min.) at 70 and 80°C on breaking length, tear factor and degree of brightness are illustrated in Fig. 1, 2 and 3 respectively.

Breaking Length

The breaking lengths of previously mentioned bagasse and rice straw pulps are illustrated in Fig. 1. It is clear that treatments at higher temperatures and concentrations affect the paper strength to a great extent especially with prolonged time of reaction. This effect is expected due to dual oxidation effect of HO^- on the R-O-R glucosidic linkages of the fibre, which increases as the concentration of reactant and the duration of reaction increases, and on the important components such as lignin and hemicelluloses. However from the figure, initial breaking length of bagasse is slightly higher than that obtained in case of rice straw pulp which reflects that bagasse pulp fibre length is slightly higher than that of rice straw pulp. Also, it seems that rice straw pulp withstands degradation to some extent at relatively low temperature (70°C) . For this reason, no effect is observed with unbleached rice straw pulp treated with H_2O_2 for 30 min. at 70°C. This may be due to the silica

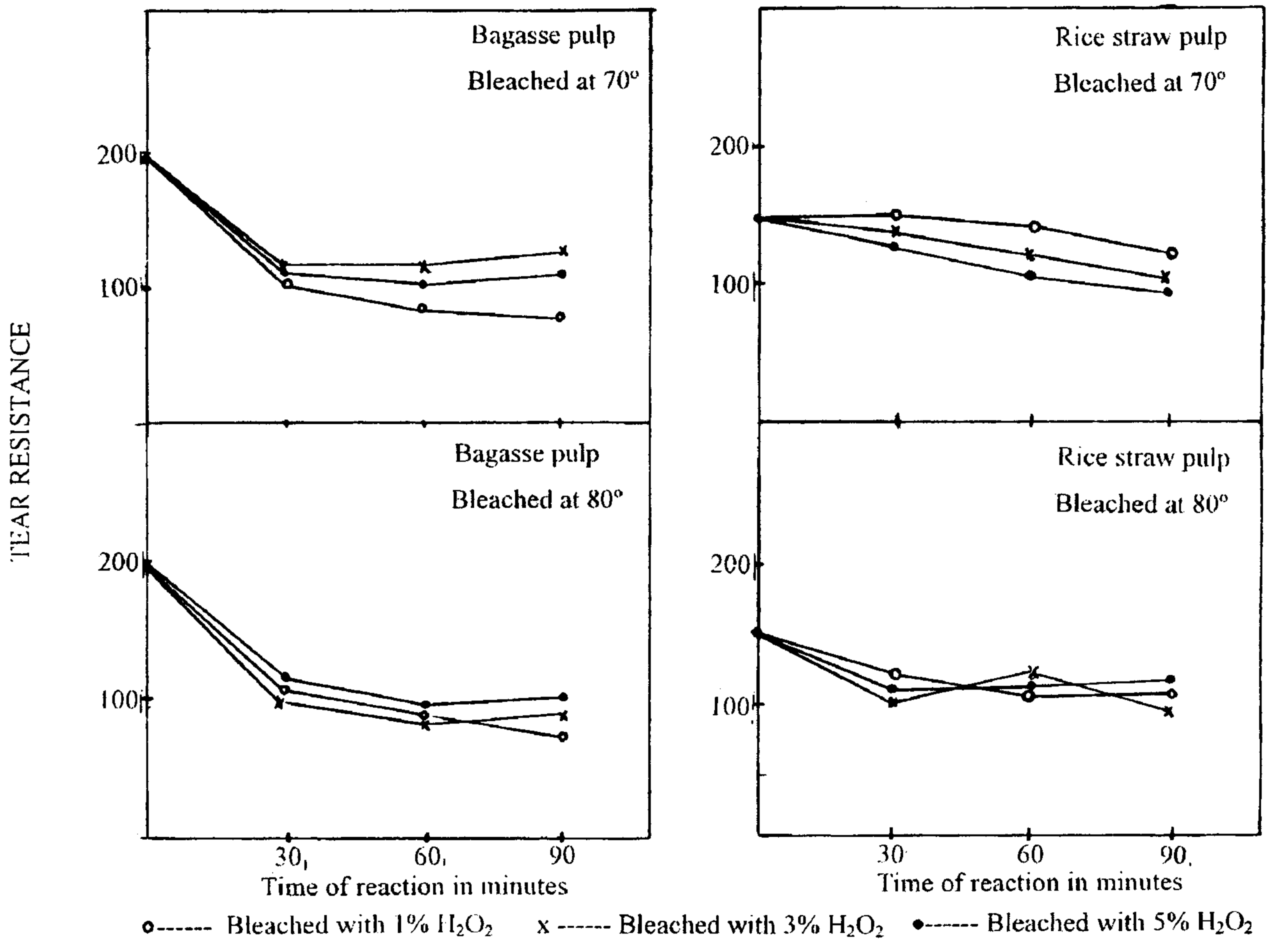


Figure 2. Effect of bleaching time and temperature on the tear resistance of the experimental samples

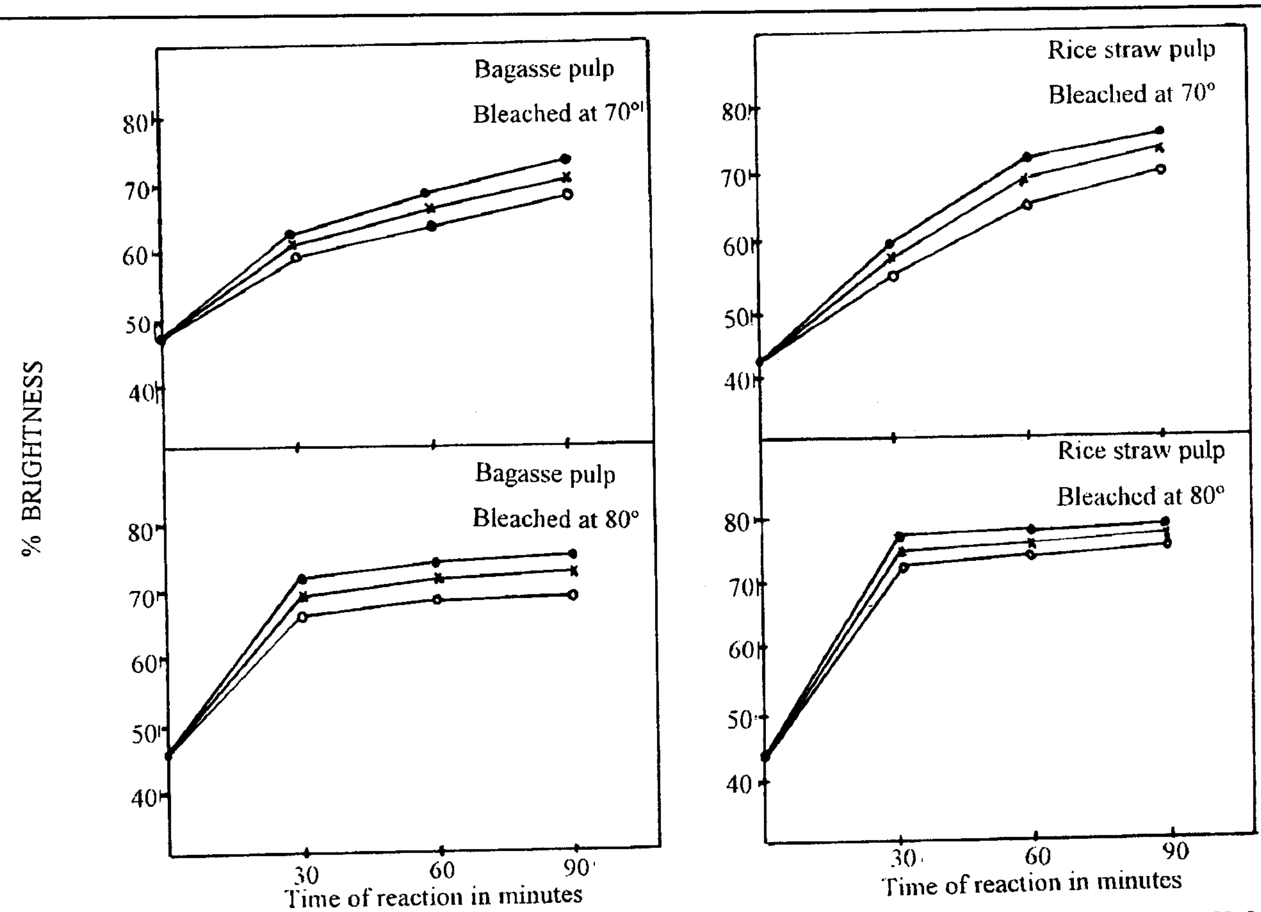
present in considerable amount of which may obscure the oxidizing effect of H_2O_2 for 30 min. at 70°C. However, at higher temperatures the energy of ions, free radicals, as well as the molecules have increased, leading to concomitant degradation in the fiber affecting the inter and intra-bonding strength, resulting in loss in the breaking length of the fibre.

Tear Resistance

From Fig. 2, it is clear that treatments of bagasse and rice straw pulps with H_2O_2 deteriorate the tear resistance. Bagasse pulp shows higher deterioration than rice straw pulp. It should be noted that tear resistance is strongly dependent on fibre length whereas breaking length is influenced to a much smaller extent. Again for this reason, no effects are observed in rice straw pulp treated with H_2O_2 for 30 min. at 70°C. It should be noted that bagasse pulp shows higher initial tear resistance than rice straw pulp Fig. 2. This behavior may be related to increased fibrillation, the presence of lignin and silica may decrease the penetration rate of the OH^- through outer layer, and as a result, the external fibrilation was more pronounced than the internal ones producing less flexible fibres in addition to the increased proportion of the short fibres.

Brightness

From Fig. 3 it is clear that the treatment of either bagasse or rice straw pulps with different H_2O_2 concentration enhances the degree of brightness to a great extent. This improvement increases with increasing H_2O_2 concentration, heating and duration of reaction. This effect may be related to the oxidation or degradation of the coloured components which may affect the brightness. It seems possible to postulate as



o------ Bleached with 1% H_2O_2 x ------ Bleached with 3% H_2O_2 •------ Bleached with 5% H_2O_2

Figure 3. Effect of bleaching time and temperature on the % brightness of the experimental samples

this juncture that H_2O_2 oxidises lignin which may modify the chromophores and decreases the total absorption of light in the visible spectrum, this may be carried out through perhydroxyl anion (HOO^-). It should be noted also that an early stability in the brightness values occurred at high temperature i.e. 80°C (Fig. 3) which may be related to the increased reaction rate at high temperatures.

Infrared investigation

Infrared spectra of the samples are shown in Fig. 4. The absorption intensities of the most important bands of the studies samples are shown in Table 1.

Absorption band at $1110cm^{-1}$ assigned to C-O stretching showed a negligible increase in case of rice straw pulp but a noticeable increase in the bagasse pulp.

Absorption band at $1280cm^{-1}$ belongs to OH deformation, rice straw bleached pulp shows an increased OH group deformation, whereas bagasse pulp behaves differently as decrease in OH deformation values are obtained. This behaviour may be discussed on the basis of the diferences in the chemical constituents of the two samples, and also the changing in the bonding system after treatments with H_2O_2.

Absorption band at $1725cm^{-1}$ is due to C=O stretching. Both samples possess an increase in the C=O values which is expected due to the effect of HOO^- liberated by the dissociation of H_2O_2which led to oxidation of lignin and other components forming carboxylic groups. It should be noted that treatments of bagasse pulp with H_2O_2 lead to increased number of C=O than in case of rice straw pulp; this can be discussed on the basis that silica may obscure some of (HOO) effect.

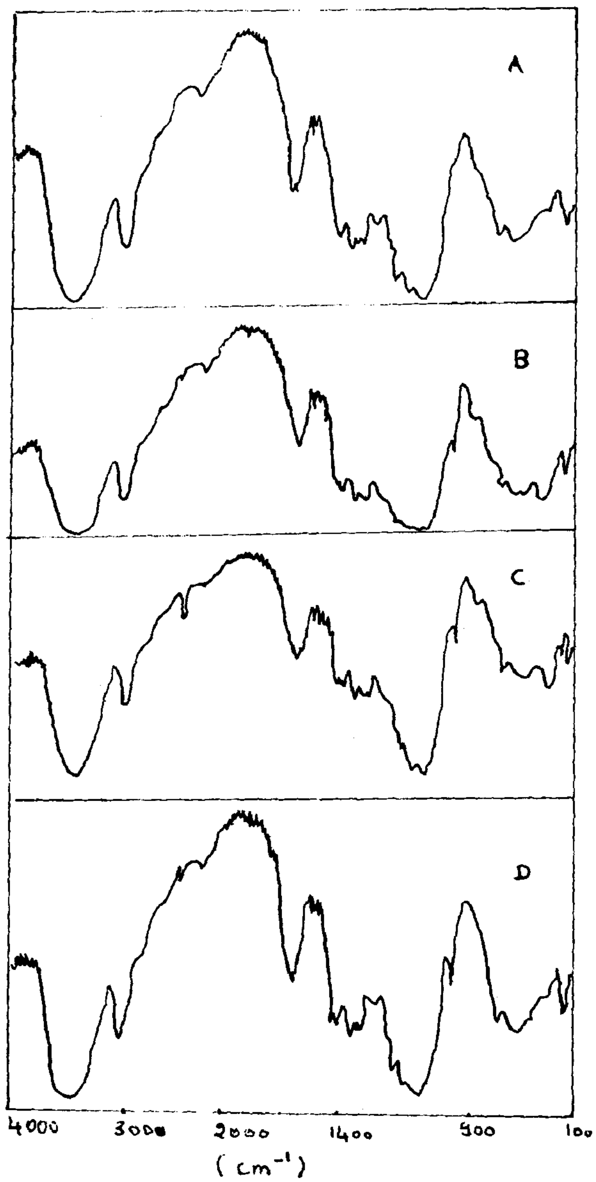


Figure 4. Infra-red spectra of the experimental samples

Absorption band at 3450 cm^{-1} which is ascribed to OH stretching, shows different behaviour for both pulps, as the number of OH groups stretched in case of rice straw decrease but in the case of bagasse pulp this number is greatly increased. It should be noted that bagasse pulp possesses higher brightness than rice straw pulp which reveals that the major part of chromophores which absorb visible light, have been removed through oxidation of lignin in bagasse pulp.

The asymmetry index of the samples which depends mainly on the number of hydroxyl groups entering into hydrogen bonding (13) indicates decrease in the number of OH group forming hydrogen bonding in case of rice straw pulp, whereas a slight increase is observed in case of bagasse pulp. Measuring the crystallinity index (14) shows slight decrease in its values for both samples on bleaching due to the disordering caused by the action of H_2O_2 on the interfibrillar bonding.Estimating the mean hydrogen bond strength shows a great increase in this value for bagasse pulp with no or little changes in case of rice straw pulp. Again, the presence of silica may interfere hydrogen bond formation; it is easy to assume that silica may act as a filler reducing the interfibrillar bonding.

Electron microscopy study on the fibre surface

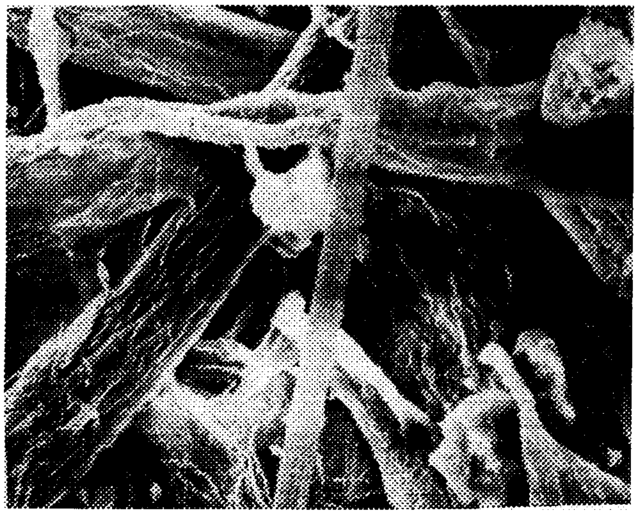
The micrograph shown in Fig. 5 (a) represents for unbleached bagasse pulp in which a ridge-like structure is particularly unevenly distributed. After bleaching, the surface becomes more even, smooth and well defined fibres were obtained with even edge fibres Fig. 5 (b). The micrograph shown in Fig. 5 (c) presents the unbleached rice straw fibres which appear to have a smaller size than bagasse fibres; and after bleaching (d) the fibres become more rigid and possess uneven edges which may be related to the removal of some fibre contents during bleaching.

CONCLUSION

Bleaching of agricultural residues pulps with hydrogen peroxide constitutes a non-conventional way involving oxidation of residual lignin. Thus, considerable improvement in the brightness with a little sacrifice of strength properties was obtained. Hydrogen peroxide bleaching of agricultural residues pulps can be considered as a beneficial way to minimize environmental pollution to a great extent, in addition to its economic value.

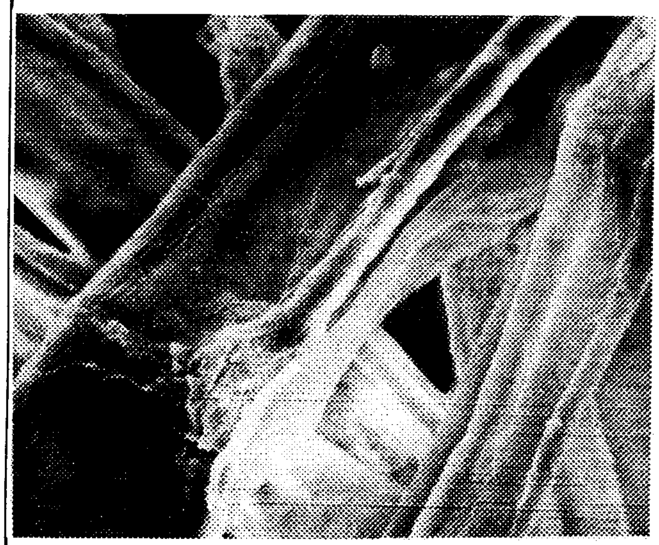
RFERENCES

1. Gierer J. & Jankole Kerstin **J. of Wood Chemistry and Technology.** 13 (4), 561 (1993).
2. Walling C. **Acc. Chem. Res.** 8, 125 (1975).
3. Steenken S. **J. Chem. Soc. Faraday Trans.** I. 83, 113 (1987).
4. Abbot J. & Gintiro T. **J. Pulp & Paper Sci.** 18 (3): J 85 (1992).
5. Tendulkar S.R. & Shinole J.K. **Ippta J.,** (1), (1990).
6. Tendulkar S.R. & Shinole J.K. **Ippta J.,** (3), (1990).

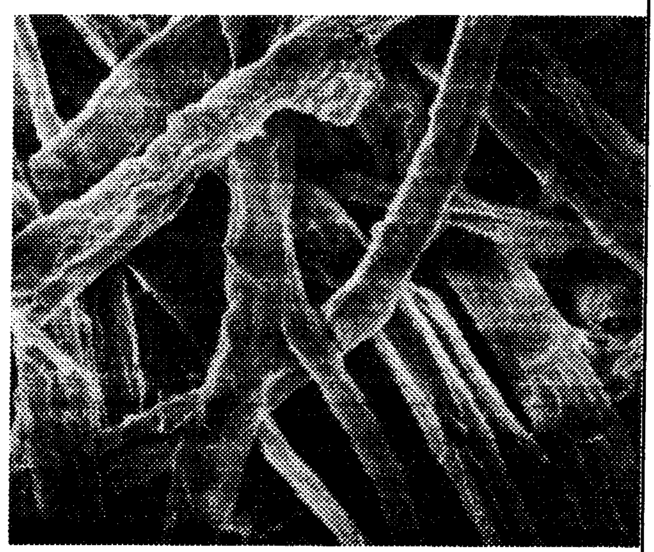


*5 (a) Unbleached bagase pulp (*1000)*

*5 (c) Unbleached rice straw pulp (*2000)*



*5 (b) Bleached bagase pulp (*1000)*



*5 (d) Bleached rice straw pulp (*1000)*

Fig. 5 Scanning Electron Microscopy of Samples.

7. Colodette, J.L.; Rothenberg, S. & Dence, C.W. **J. Pulp & Pap.** Sci. 14 (6): 126 (1988).
8. Colodette, J.L.; Rothenberg, S. & Dence C.W. **J. Pulp & Pap. Sci.** 15 (2): J45 (1989).
9. Ali, T.; McArthur, D.; Stott, D.; Fairbank, M.; & Whiting, P. **J. Pulp & Pap. Sci.** 12 (6): J166 (1986).
10. Rothenberg, S. & Robinson, D.H. **Tappi J.** 63 (9): 117 (1980).
11. Oelert, H.H. & El-Said, H. **J. Appl. Chem. Biotechnology** 28, 480 (1978).
12. Dence, C.W. & Omori, S. **Tappi J.** 69(10): 120 (1986).
13. Yu Levdik, I.; Inshakov, M.D.; Miyurova, E.P. & Nikitim, N.V. Trvses **Nauch-Issled. Inst. Tsellyul. Bum. Prom.** no. 52, 109-116 (1967).
14. Nelson, M.L. & O'Connor, R.T. **J. Appl. Polym. Sci** 8, 1325 (1964).