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Photodelignification of *Eucalyptus grandis* organosolv chemical pulp

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Abstract

Efficient delignification of *Eucalyptus grandis* organosolv pulp was achieved. The process, which was chlorine and sulphur free, removed 88% of the lignin (kappa number (KN) 65 to 8) with moderate viscosity loss (η = 19 cP to 12 cP). The best sequence involved three photochemical stages in alkaline medium (NaOH) at 85 °C. The first stage involved oxygen treatment; this was followed by the action of excited singlet oxygen produced by methylene blue (4.5×10^{-5} mol l^{-1}). The last stage, using hydrogen peroxide (6% relative to the weight of oven dried pulp (odp)), was the most efficient, the structure of the lignin having been prepared by the first two stages. The mechanism of the overall process remains unknown.

Keywords: Pulp; Photobleaching; Hydrogen peroxide; Singlet oxygen; Lignin

1. Introduction

The importance of minimizing the use of chlorine- and sulphur-based chemicals in wood pulping and bleaching has increased in recent years because of stricter pollution regulations. One response to this problem involves the use of organosolv pulping, followed by a bleaching sequence based on active oxygen derivatives. The University of Uberlandia (Brazil) has developed a new, efficient organosolv pulping method for *Eucalyptus grandis* which is chlorine and sulphur free [1]. It uses only acetic acid, ethyl acetate and water at 160 °C for 3.5 h [1]. The use of active oxygen species in conjunction with UV light is very attractive for the bleaching of *Eucalyptus* pulp; the potential benefits of using UV light in pulp bleaching have been recognized for chlorine [2], hypochlorite [2], chlorine dioxide [3], oxygen [4–6] and hydrogen peroxide [7].

It has been shown by Machado et al. [8,9] that hydrogen peroxide in alkaline medium and UV light promote strong delignification of various soluble lignins and lignin models. Quenching experiments support the involvement of singlet oxygen, produced by the decomposition of hydrogen peroxide at alkaline pH, as the main cause of the rapid breakdown of the lignin polymer [8,9]. Delignification of organosolv pulp, using alkaline hydrogen peroxide and UV light, was first performed by Nascimento et al. [10], using large quantities of hydrogen peroxide and sodium silicate. In this work, we investigate the possibility of photodelignification of unbleached organosolv chemical pulp in alkaline medium using oxygen, hydrogen peroxide and a singlet oxygen sensitizer (methylene blue (MB)). The bleaching sequences were designed to reduce the amounts of chemicals used and to shorten the irradiation time.

2. Experimental details

2.1. Pulp

Eucalyptus grandis organosolv pulp [1] was obtained by treatment under pressure of wood chips (40 g) with a mixture of acetic acid (160 ml), ethyl acetate (160 ml) and water (80 ml) at 160 °C for 3.5 h. After cooking, the pulp was washed with a mixture of acetone (360 ml) and water (40 ml) at 100 °C for 30 min. After cooling to approximately 60 °C, the pulp was filtered and washed with a mixture of acetone (180 ml) and water (20 ml) and then with water (500 ml). After drying, the pulp was analysed for lignin content and viscosity (kappa number (KN) = 65, η = 19 cP).

Before the bleaching experiments, the pulp was treated with a chelating agent, diethylenetriaminepentaacetic acid (DTPA), to remove metal ions, which could promote an

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increase in the degradation rate of hydrogen peroxide [11]. DTPA (1% relative to the weight of oven dried pulp (odp)) was added to a suspension of the pulp and deionized water. The suspension was maintained with stirring for 60 min at 60 °C. The pulp was then washed with deionized water and dried at 50 °C for 1 day.

2.2. Bleaching

Bleaching tests were performed in the dark and on exposure to UV light. In the photochemical process, the reactor, a Pyrex cylindrical flask with a diameter of 7.5 cm, was fitted between two 400 W medium pressure mercury lamps (Mazda HPLN), 10 cm from each lamp. The Pyrex glass acts as a filter, avoiding the wavelengths below 300 nm which might be very detrimental to the cellulose polymer matrix.

The experiments were usually performed at 85 ± 5 °C, using aqueous suspensions with a pulp consistency of 5%. The action of oxygen on the bleaching process was evaluated by bubbling oxygen into the suspension at basic pH (3% NaOH odp) and in the presence of $MgSO_4$ (0.5% odp).

A process using MB to produce singlet oxygen by photosensitization was developed. MB (4.5×10^{-5} mol l^{-1}) was added to a suspension of the pulp (5% consistency) in the presence of sodium hydroxide (3% odp) and $MgSO_4$ (0.5% odp). The mixture was irradiated at 85 °C for 1 h with oxygen bubbling in the suspension.

In the process using hydrogen peroxide, sodium metasilicate (3% odp) and magnesium sulphate (0.5% odp) were used to protect the cellulose pulp against oxygen active species and also to limit the thermal degradation of hydrogen peroxide. The concentration of hydrogen peroxide was 6% odp, and that of sodium hydroxide was 3% odp; the consistency of the pulp was 5%.

In all experiments, the amount of sodium hydroxide was sufficient to maintain the pH of the suspensions alkaline during the bleaching process.

2.3. Physical and analytical methods

The lignin content of the pulp was estimated by KN, using the Tappi method (T236 os 76). Insoluble sulphuric lignin (Klason lignin) was estimated for some pulps according to the usual procedures (T222 om 83). Viscosity measurements were performed using an electronic viscometer (Lab-Line instrument ELV-8, 4537) according to a methodology based on the Tappi method (T230 om 82).

Paper sheets (22 cm × 22 cm) were made from the different bleached pulps (approximately 50 g m^{-2}) on a Noble Wood former. The brightness index (BI) was measured with an Elrepho 2000 Datacolor reflectometer. The UV–visible diffuse reflectance was recorded between 290 and 700 nm using a Hitachi U-3300 spectrometer equipped with an integrating sphere. The K and S values were estimated only for paper bleached with the sequence G (oxygen–light/MB–light/peroxide–light) (Table 1), where the difference between black- and white-backed reflectance curves was sufficient for calculation using the Kubelka–Munk formalism [12]. The IR spectra were measured with a Perkin Elmer Paragon 1000 FTIR spectrometer; the Kubelka–Munk calculations were made by the resident software of the spectrometer. The different bleaching sequences used in the present work are reported in Table 1.

3. Results and discussion

3.1. Bleaching in one stage

In order to assess the importance of the photochemical step in the bleaching process, since there is competition between the photochemical and thermal routes, two different bleaching processes were considered. One involves hydrogen peroxide and the other oxygen. Both bleaching reactions were performed at alkaline pH in the dark and under the action of UV light; the temperature was maintained at 85 ± 5 °C.

3.1.1. Hydrogen peroxide (B1 and B2)

With hydrogen peroxide, the best delignification was found for the reaction induced by UV light. This can be seen in Table 2 where KN values were measured before and after bleaching with and without light. The quantity of lignin (expressed as Klason lignin, KL) can be approximately evaluated by the formula: $\%KL = KN \times 0.15$. The results in Table 2 are in accordance with the kinetics of Machado et al. [8,9]. They found a strong increase in the rate of delignification when alkaline peroxide bleaching was performed on exposure to UV radiation. Moreover, examination of the BI numbers (Table 2) indicates that UV light promotes the preferential destruction of the coloured chromophores.

Comparing the IR spectra (Fig. 1), a considerable reduction in the band at 1736 cm^{-1} can be seen. This band can be assigned to carboxylic derivatives (lignin and carbohydrates) and unconjugated carbonyl groups in lignin [13]. The band at 1646 cm^{-1}, due to quinonoid and conjugated carbonyl groups of the lignin polymer [13], suffers little change when compared with the unbleached pulp. Moreover, for the dark process, a decrease in absorbance is observed for the band at 1250 cm^{-1}, which can be attributed to guaiacyl groups in lignin [13].

3.1.2. Oxygen (C1 and C2)

For delignification using oxygen, the reactions were performed at alkaline pH. The results are presented in Table 3. Due to the high lignin content in the three samples (R, C1 and C2) and for better accuracy, the delignification was estimated by performing a Klason lignin determination (%KL). In contrast with Marcoccia's findings [6], our experiments show that the photochemical procedure, using oxygen in alkaline medium, does not lead to a large improvement in delignification. The time of reaction in both experiments was fixed to 1 h. The relatively low sensitivity of the pulp to oxygen

Table 1
Bleaching treatment of *Eucalyptus grandis* organosolv pulp (see Section 2)

Sample	Bleaching treatment
R	Without
B1	Without UV light; time, 1 h; temperature, 85 °C H_2O_2 (6% odp)/NaOH (3% odp)/$MgSO_4$ (0.5% odp)/metasilicate (3% odp)
B2	With UV light; time 1 h; temperature, 85 °C H_2O_2 (6% odp)/NaOH (3% odp)/$MgSO_4$ (0.5% odp)/metasilicate (3% odp)
C1	Without UV light; time, 1 h, temperature, 85 °C O_2 (bubbling)/NaOH (3% odp)/$MgSO_4$ (0.5% odp)
C2	With UV light; time, 1 h; temperature, 85 °C O_2 (bubbling)/NaOH (3% odp)/$MgSO_4$ (0.5% odp)
D1	Stage 1 Without UV light; time, 1 h; temperature, 85 °C O_2 (bubbling)/NaOH (3% odp)/$MgSO_4$ (0.5% odp) Stage 2 Without UV light; time, 2 h; temperature, 85 °C H_2O_2 (6% odp)/NaOH (3% odp)/$MgSO_4$ (0.5% odp)/metasilicate (3% odp)
D2	Stage 1 With UV light; time, 1 h; tmeperature, 85 °C O_2 (bubbling)/NaOH (3% odp)/$MgSO_4$ (0.5% odp) Stage 2 With UV light; time, 2 h; temperature, 85 °C H_2O_2 (6% odp)/NaOH (3% odp)/$MgSO_4$ (0.5% odp)/metasilicate (3% odp)
D3	Stage 1 With UV light; time, 1 h; temperature, 85 °C O_2 (bubbling)/NaOH (3% odp)/$MgSO_4$ (0.5% odp) Stage 2 With UV light; time, 1 h; temperature, 85 °C H_2O_2 (6% odp)/NaOH (3% odp)/$MgSO_4$ (0.5% odp)/metasilicate (3% odp)
E1	With UV light; time, 1 h; temperature, 45 °C Methylene blue (MB, 4.5×10^{-5} mol l^{-1})/O_2 (bubbling)/NaOH (3% odp)/$MgSO_4$ (0.5% odp)
E2	With UV light; time, 1 h; temperature, 85 °C MB (4.5×10^{-5} mol l^{-1})/O_2 (bubbling)/NaOH (3% odp)/$MgSO_4$ (0.5% odp)
F	Stage 1 With UV light; time, 1 h; temperature, 85 °C O_2 (bubbling)/NaOH (3% odp)/$MgSO_4$ (0.5% odp) Stage 2 With UV light; time, 1 h; temperature, 85 °C MB (4.5×10^{-5} mol l^{-1})/O_2 (bubbling)/NaOH (3% odp)/$MgSO_4$ (0.5% odp)
G	Stage 1 With UV light; time, 1 h; temperature, 85 °C O_2 (bubbling)/NaOH (3% odp)/$MgSO_4$ (0.5% odp) Stage 2 With UV light; time, 1 h; temperature, 85 °C MB (4.5×10^{-5} mol l^{-1})/O_2 (bubbling)/NaOH (3% odp)/$MgSO_4$ (0.5% odp) Stage 3 With UV light; time, 2 h; temperature, 85 °C H_2O_2 (6% odp)/NaOH (3% odp)/$MgSO_4$ (0.5% odp)/metasilicate (3% odp)

bleaching, even in the ground state, can probably be ascribed to the fact that some reactive phenols are acetylated during the pulping process and are not available for electron transfer to the oxygen molecule. Almost no change is observed before and after oxygen bleaching in the UV–visible diffuse reflectance spectra (not shown) or the BI numbers. In contrast, the IR spectra of the pulps are modified by oxygen treatment (Fig. 2). As for peroxide bleaching, after reaction, the band at 1730 cm^{-1} disappears almost completely and the band at 1640 cm^{-1} remains pratically the same. Also, for the dark process, a decrease in the intensity is observed for the band at 1250 cm^{-1}; this may be attributed to the breakdown of guaiacyl groups in lignin [13].

3.2. Bleaching in two stages using oxygen and hydrogen peroxide (D1, D2 and D3)

The bleaching sequence O/P is commonly used in totally chlorine free (TCF) bleaching [14]; we have applied this

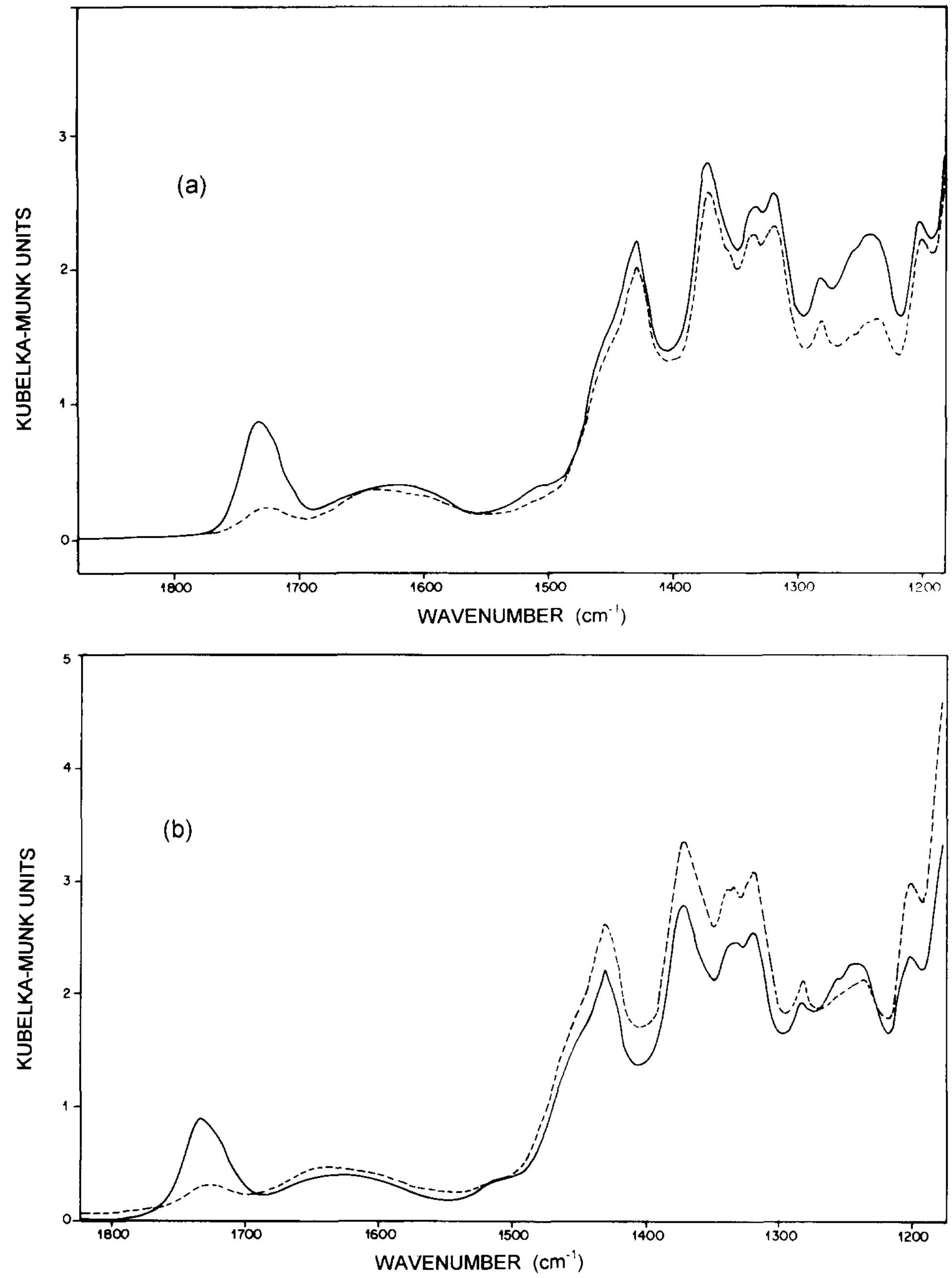

Fig. 1. DRIFT spectra of papers (approximately 50 g m^{-2}) made from unbleached pulp (full line), bleached pulp B1 (broken line, (a)) and bleached pulp B2 (broken line, (b)).

Table 2
Bleaching of organosolv pulp in one stage with hydrogen peroxide (6% odp) and sodium hydroxide (3% odp) at 85 °C for 1 h

Bleaching sequence	Illumination	KN	BI
R	Control	65	20.4
B1	Dark	35	39.4
B2	Light	20	50.7

Table 3
Bleaching of organosolv pulp in one stage with oxygen (bubbling) and sodium hydroxide (3% odp) at 85 °C for 1 h

Bleaching sequence	Illumination	% KL	BI
R	Control	9.3	20.4
C1	Dark	7.1	21.6
C2	Light	6.9	21.8

combined stage to the organosolv pulp. The experiments were performed with and without light. The results are reported in Table 4. The photochemical process, in a global form, gives the best results. This can be seen when the thermal process, involving 1 h with oxygen and 2 h with hydrogen peroxide (KN = 14), is compared with the photochemical process

(KN = 11). Another way to see the effect of light is to compare sequences D1 and D3, where similar KN values are obtained, but the second stage of D3, involving hydrogen peroxide, is decreased to 1 h. The UV-visible diffuse reflectance spectra and the BI values of samples D2 and D3 are approximately the same (Table 4 and Fig. 3) indicating similar breakdown of the chromophores. It is noticeable that H_2O_2 has a stronger discolouration effect on the pulp than oxygen (Fig. 3). As already observed for oxygen and peroxide bleaching, DRIFT spectroscopy shows an almost

Table 4

Bleaching of organosolv pulp in two stages: (1) O_2 (bubbling) and NaOH (3% odp) at 85 °C; (2) H_2O_2 (6% odp) and NaOH (3% odp) at 85 °C

Bleaching sequence	Illumination	Step 1 (O_2)	Step 2 (H_2O_2)	KN	BI
R	Control			65	20.4
D1	Dark	1 h	2 h	14	40.2
D2	Light	1 h	2 h	11	59.9
D3	Light	1 h	1 h	13.5	60.7

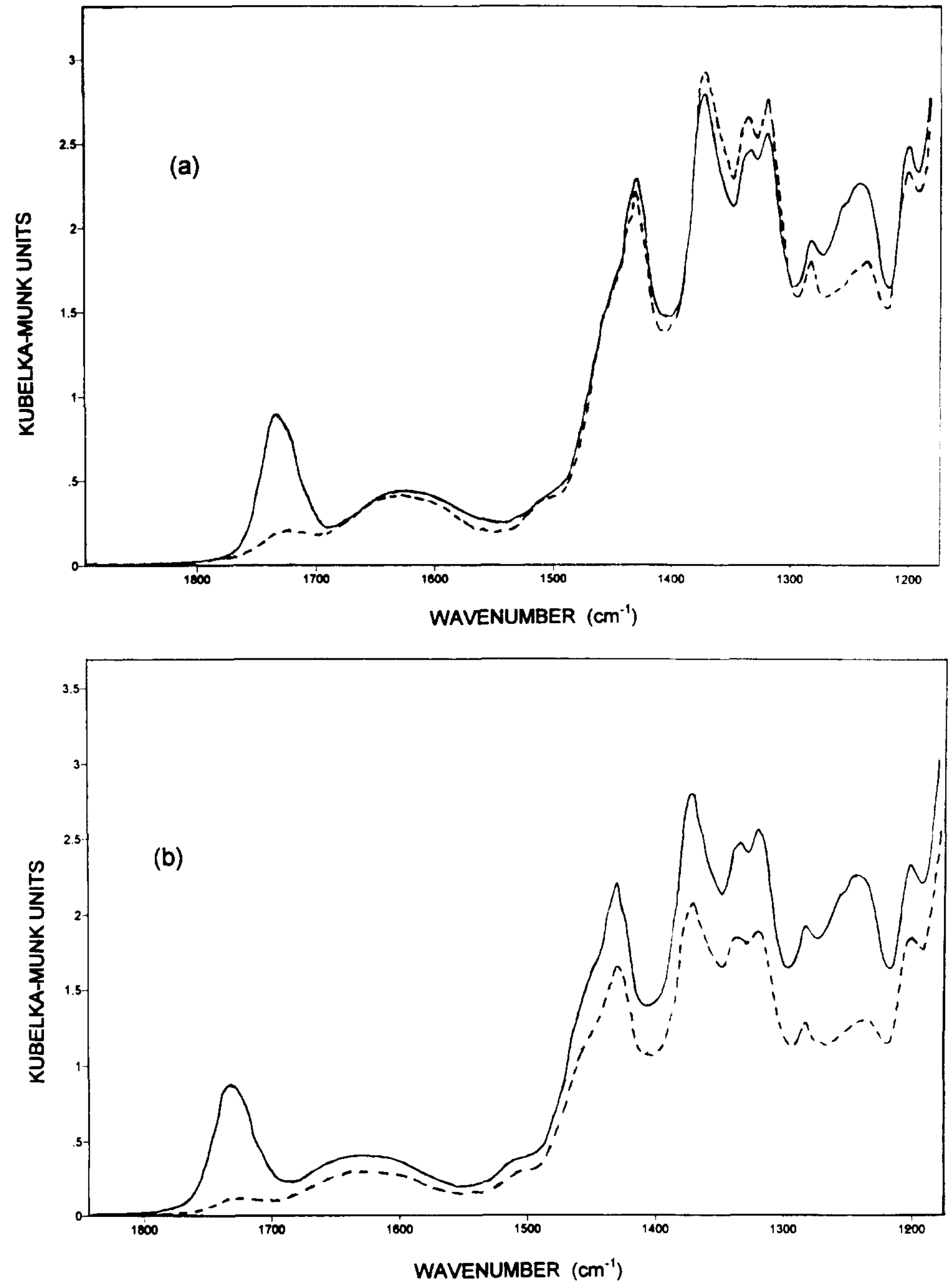

Fig. 2. DRIFT spectra of papers (approximately 50 g m^{-2}) made from unbleached pulp (full line), bleached pulp C1 (broken line, (a)) and bleached pulp C2 (broken line, (b)).

Table 5

Bleaching organosolv pulp with methylene blue (MB): (1) O_2 (bubbling) and NaOH (3% odp) at 85 °C; (2) MB (4.5×10^{-5} mol l^{-1}), O_2 (bubbling) and NaOH (3% odp); (3) H_2O_2 (6% odp) and NaOH (3% odp) at 85 °C

Bleaching sequence	Illumination	Step 1 (O_2)	Step 2 (MB + O_2)	Step 3 (H_2O_2)	KN	BI
R					65	20.4
E1	Light		1 h, 45 °C		65	22.1
E2	Light		1 h, 85 °C		63	21.3
F	Light	1 h	1 h, 85 °C		50	26.9
G	Light	1 h	1 h, 85 °C	2 h	8	70.2

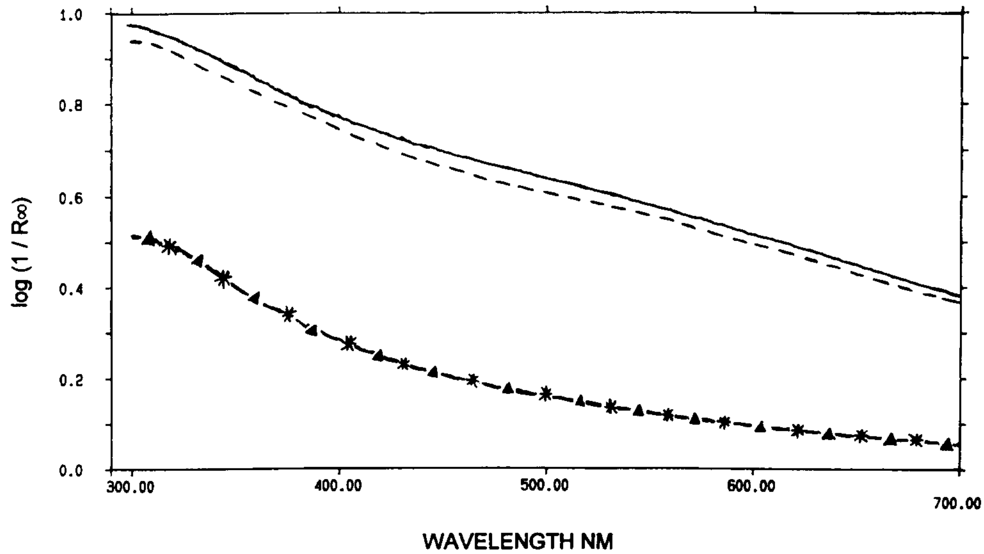

Fig. 3. UV–visible diffuse reflectance spectra, expressed as log($1/R_\infty$), of papers (approximately 50 g m^{-2}) made from unbleached pulp (full line), bleached pulp C2 (broken line), bleached pulp D2 (▲) and bleached pulp D3 (*).

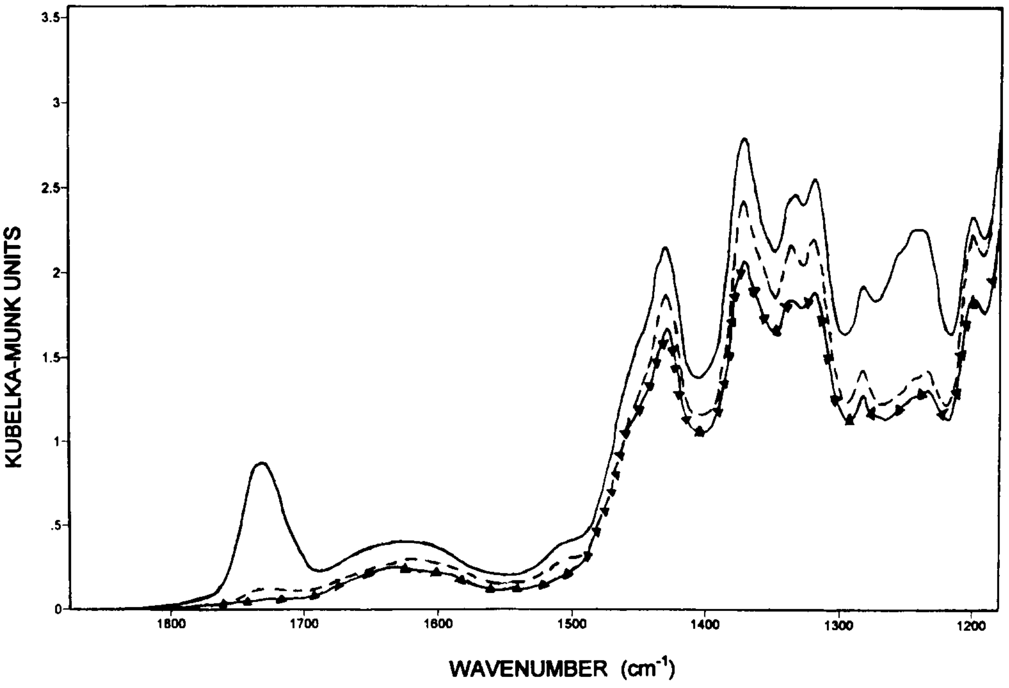

Fig. 4. DRIFT spectra of papers (approximately 50 g m^{-2}) made from unbleached pulp (full line), bleached pulp C2 (broken line) and bleached pulp D3 (▲).

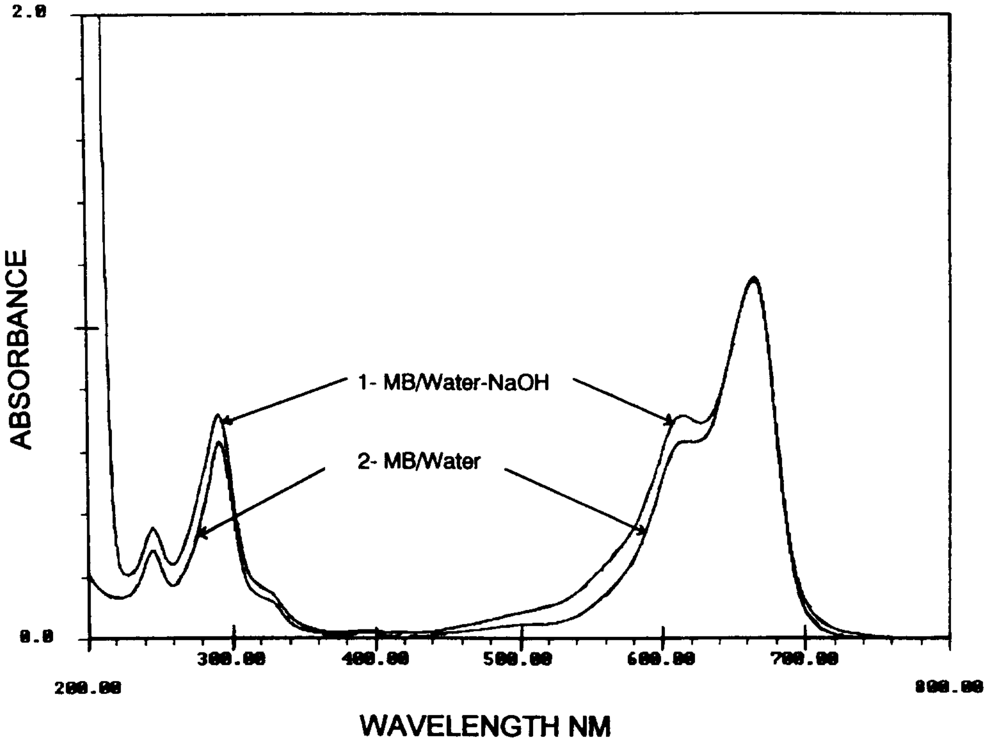

Fig. 5. UV–visible absorption spectra of MB in water (2.1×10^{-5} mol l^{-1}) and in water + NaOH (0.5% w/w).

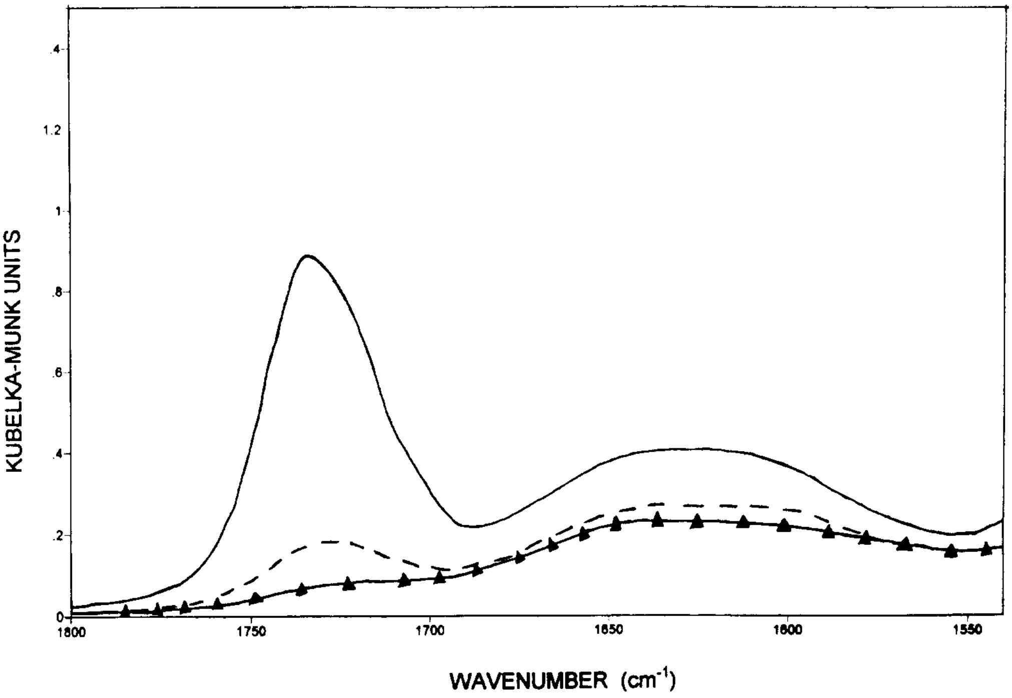

Fig. 6. DRIFT spectra of papers (approximately 50 g m^{-2}) made from unbleached pulp (full line), bleached pulp E2 (broken line) and bleached pulp E1 (▲).

complete disappearance of the band at 1740 cm^{-1}, due to unconjugated carbonyl groups and carboxyl groups, and constant intensity of the band at 1646 cm^{-1}. Also, the breakdown of some guaiacyl structures, characterized by the band at 1250 cm^{-1}, is observed (Fig. 4).

3.3. Bleaching with a singlet oxygen sensitizer MB

3.3.1. Bleaching in one stage (E1 and E2)

The introduction of singlet oxygen in the bleaching sequence was performed by using MB which is very soluble

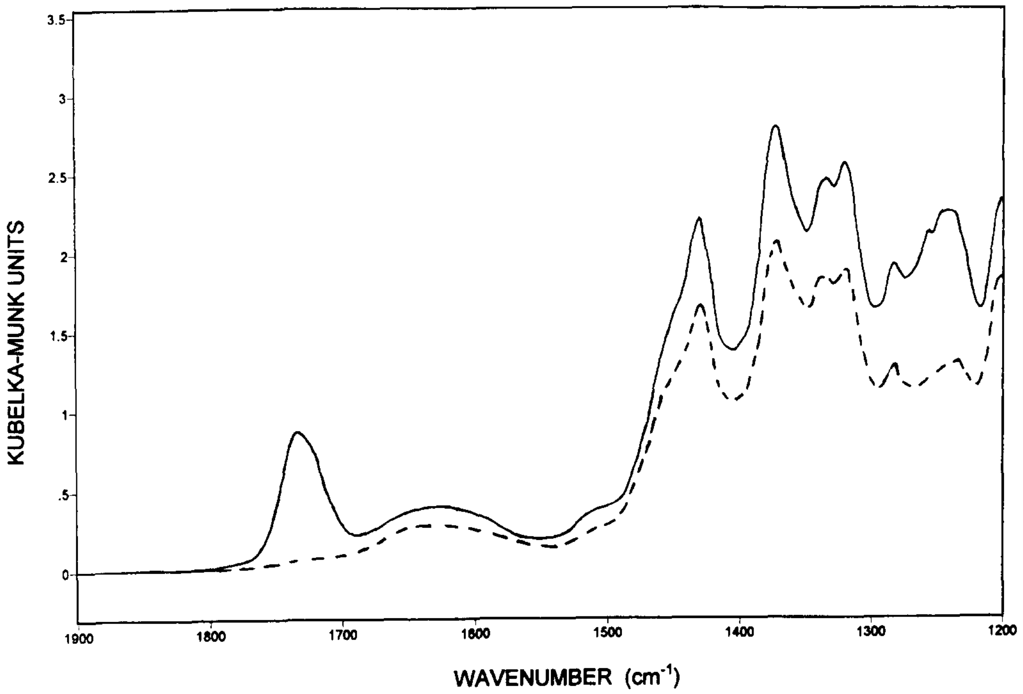

Fig. 7. DRIFT spectra of papers (approximately 50 g m^{-2}) made from unbleached pulp (full line) and bleached pulp F (broken line).

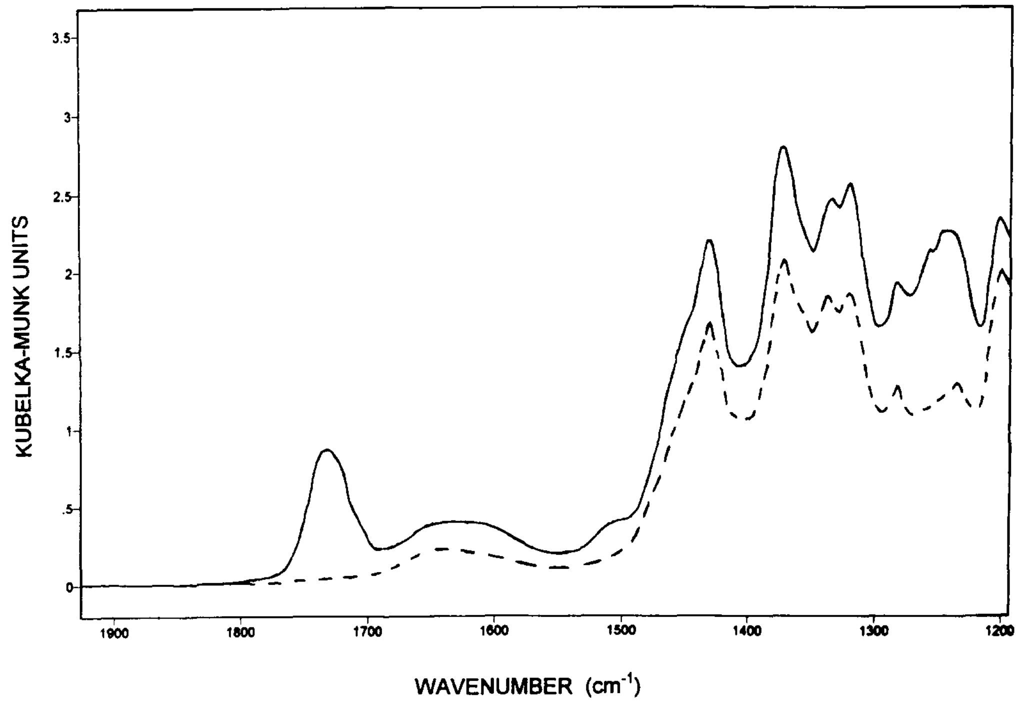

Fig. 8. DRIFT spectra of papers (approximately 50 g m^{-2}) made from unbleached pulp (full line) and bleached pulp G (broken line).

in water and exhibits similar UV–visible absorption properties in water at neutral and alkaline pH (Fig. 5). The bleaching reactions were performed at alkaline pH because the degradation kinetics of some lignin models are higher in alkaline medium [15].

The treatment involving MB in one stage was performed at two different temperatures (45 and 85 °C). The results are presented in Table 5 (experiments E1 and E2). According to KN, it appears that the delignification is not successful, although the BI numbers increase slightly. However, from the IR spectra (Fig. 6), it can be seen that the structure of lignin is changed by this treatment. The experiment performed at 45 °C is more efficient than that at 85 °C. This is in agreement with that expected for reactions involving singlet oxygen [9], which benefit from a decrease in temperature. In the process at 45 °C, almost all the band at 1740 cm^{-1}

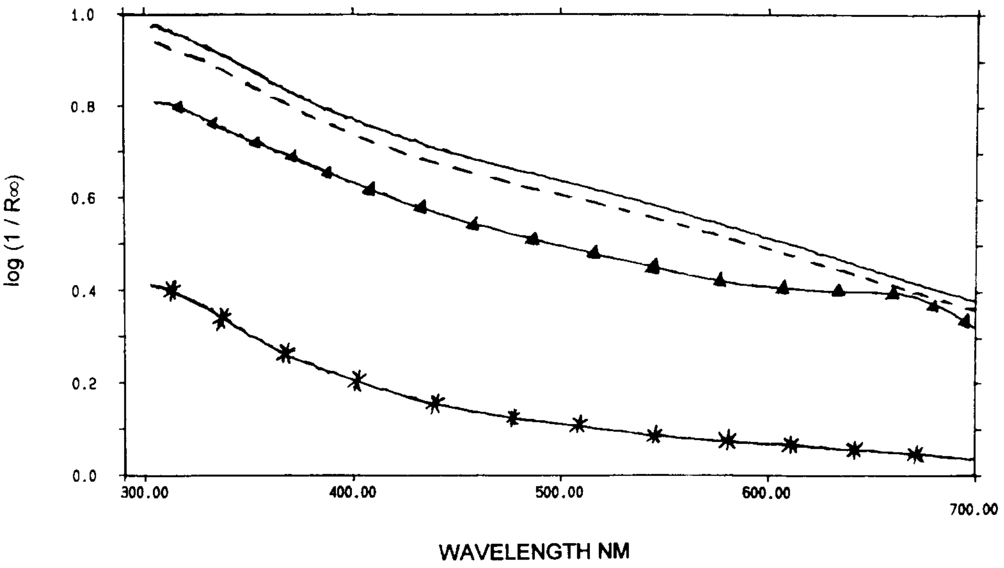

Fig. 9. UV–visible diffuse reflectance spectra, expressed as log($1/R_\infty$), of papers (approximately 50 g m^{-2}) made from unbleached pulp (full line), bleached pulp C2 (broken line), bleached pulp F (▲) and bleached pulp G (*).

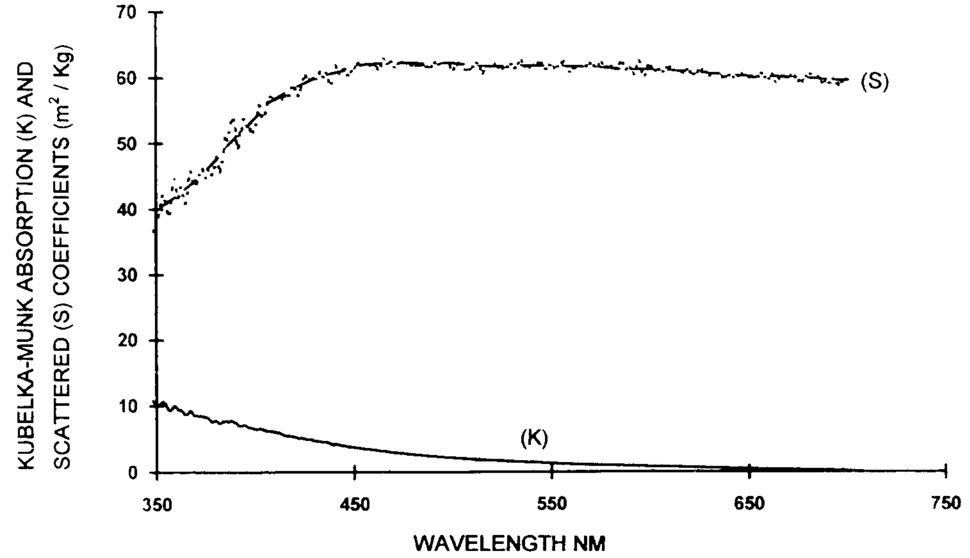

Fig. 10. Kubelka–Munk absorption coefficients K and S of paper (approximately 50 g m^{-2}) made from bleached pulp G [12,16].

disappears. Moreover, the band at 1630 cm^{-1} partially disappears in both cases.

3.3.2. Bleaching in two stages (F)

Reaction in two steps of 1 h in the presence of light and with the temperature fixed at 85 °C was performed; the first step is identical to process C2 (O_2), and the second is similar to process E2 (MB). The results are reported in Table 5. The increase in BI is low; nevertheless, partial delignification (23%) is observed. However, the pulp after this process is more susceptible to delignification. The IR spectra (Fig. 7) show that this treatment removes practically all the unconjugated carbonyl and carboxyl groups, and partially reduces the intensity of the band around 1640 cm^{-1} related to quinones and conjugated carbonyls. Also, the species absorbing at 1250 cm^{-1} is removed. This is an indication of changes in the lignin polymer structure. The UV–visible diffuse reflectance spectra (Fig. 9, see Section 3.3.3) show the presence of some residual MB, characterized by a band with a maximum near 650 nm, which may perturb the BI value found for sample F. In the next section, it is shown that the two-stage process increases significantly the level of delignification achieved with hydrogen peroxide; the residual MB is removed by the third stage with hydrogen peroxide.

3.3.3. Bleaching in three stages (G)

It is observed by FTIR spectroscopy that the sequence F modifes the lignin structure even though delignification only reaches 23%. The introduction of a third stage involving hydrogen peroxide/NaOH and light is very efficient for delignification and whitening of the pulp as shown in Table 5.

A comparison between the IR spectra of unbleached pulp and pulp bleached using sequence G (Fig. 8) indicates that, in the bleached pulp, only the band at 1640 cm^{-1} remains. This is indicative of the presence of some conjugated carbonyl groups in the remaining lignin. The light pale yellow colour observed in pulp G (BI = 70.2) also gives some evidence of the presence of residual quinonoid derivatives in the lignin part. The UV–visible diffuse reflectance spectra (Fig. 9) also show a good performance for the pulp bleached in three stages. The presence of coloured lignin derivatives in samples R, C2 and F is probably responsible for the shape of the spectra in the visible region. It is noticeable that, during the third stage, the residual MB is completely removed. The spectrum of sample G, expressed by the absorption and scattering coefficients (K and S respectively) vs. wavelength (Fig. 10), is very similar to that found for TCF pulp bleached with oxygen and hydrogen peroxide [16]. According to viscosity measurements, the photobleaching in three stages (sequence G) maintains relatively good properties to the cellulose pulp (pulp R, $\eta = 19$ cP; pulp G, $\eta = 12$ cP) for a photochemical bleaching [6,10].

Light at wavelengths greater than 320 nm is responsible for the decomposition of hydrogen peroxide molecules into hydroxyl radicals [9]. These radicals act on hydrogen peroxide and perhydroxyl ions to give many active oxygen species. Alkaline pH increases the presence of perhydroxyl ions in the suspension, resulting in a minor participation of hydroxyl radicals in the delignification process, and so minor degradation of the cellulose pulp [9]. It is very difficult to determine the nature and efficiency of the active oxygen species in the third stage without a better knowledge of the residual lignin structure and the photochemical mechanisms involved. For this reason, new experiments are currently under way. In addition, the improvement of the photobleaching process to attain complete removal of lignin in the pulp, with the retention of good cellulose quality, is our next objective.

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