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Photochemical bleaching of chemical pulps catalyzed by titanium dioxide

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Abstract

A two-stage process for photochemical bleaching of cellulosic pulps is presented. The first, based on the generation of oxygen active species by the photocatalytic action of TiO_2, and the second on the photochemical decomposition of hydrogen peroxide. Both stages are carried out under alkaline pH and at 85°C in aqueous suspension at a consistency of 5%. The experiments were performed on kraft (*Eucalyptus grandis*, *Pinus pinaster* and *Picea mariana*), acesolv (*E. grandis*) and peroxyformic acid (*E. grandis*) pulps. The presence of TiO_2 as photocatalyst showed several advantages, such as reduction of reaction time, preservation of the pulp viscosity, increase of the selectivity during the photobleaching and decrease of the consumption of the bleaching chemicals. UV/Vis and FTIR spectroscopies indicate a decrease of the coniferaldehyde structures during the TiO_2 photocatalyzed stage, whereas quinones entities were found to remain in the residual lignin even after the final hydrogen peroxide stage. TiO_2-photocatalyzed sequence was found to degrade more efficiently the chromophores, especially carbonyl groups, than the sequence carried out in its absence.

Keywords: Cellulosic pulp; Bleaching; Photocatalysis; Titanium dioxide; Lignin; Photobleaching; Oxygen; Hydrogen peroxide

1. Introduction

Photocatalyzed reactions using semiconductor oxides applied to environmental problems have received a considerable attention in the last years [1–17]. Several authors have reviewed the benefits of the oxidation of organic matter via photocatalyzed processes using semiconductors such TiO_2, ZnO, SnO_2, WO_3, ZnS, CdS CdTe [1–5,11]. Titanium dioxide and zinc oxide are the most attractive photocatalysts because they are cheap, friendly to the environment and easy to be recovered [13,17].

They have been used with success to eliminate non-biodegradable pollutant in aquatic environment [12,14–16]. Studies on the action of these photocatalysts on organic derivatives have shown that important reduction of the polluting agents was obtained, in reaction time relatively short, including, in most cases, complete mineralization of the organic pollutant [1–5]. In particular, it was reported that TiO_2 or ZnO are efficient in the photochemical degradation of lignins present in pulping liquor effluents, but the intense brown colour of the liquors have limited the treatment to very dilute solutions [6–10].

Due to stricter pollution regulations, new non-pollutant bleaching processes are highly desired and the photochemical bleaching, based on the generation of oxygen active species, appears very promising [18–21]. We have recently reported a three-stage photochemical bleaching of *Eucalyptus grandis* organosolv pulps [18,22]. The bleaching was attributed to the action of oxygen active species such as superoxide anion, hydroxyl radicals, and singlet oxygen produced by irradiation in alkaline solutions [23–26]. Despite the good results notably observed on peroxyformic acid organosolv from *E. grandis* wood, the final viscosity of the pulp and the amount of hydrogen peroxide consumed have to be improved [22]. In the present work, we report an experimental approach of such an improvement using the photocatalytic properties of TiO_2. The bleaching was performed on three organosolv (acesolv [27] and peroxyformic acid [28]) pulps from *E. grandis* wood, and three kraft pulps from *E. grandis*, *Pinus pinaster* and *Picea mariana* woods. Diffuse reflectance UV/Visible and FT-IR spectroscopies were used in correlation to lignin content and viscosity measurements to assess the structural changes during the bleaching.

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2. Experimental

2.1. Unbleached pulps

The acesolv pulp (AC-E1) [27] was obtained by treatment under pressure of *E. grandis* wood chips with a mixture of acetic acid/ethyl acetate/water (40:40:20 v/v) at 160°C for 3.5 h. After cooking, the pulp was washed with a mixture of acetone/water (9:1 v/v) and with water. One of the peroxyformic acid pulps (PF-E1) was prepared by cooking the *E. grandis* wood chips for 2 h in the presence of formic acid (HCOOH (10)/wood (1), w/w) and hydrogen peroxide (7.5% w/w wood basis) in a closed reactor, at 80°C. Then, the pulp was filtered, treated with NaOH (0.1 mol/l) and rinsed with distilled water to neutral pH. The second peroxyformic pulp (PF-E2) from *E. grandis* wood was prepared in one stage by peroxyformic acid cooking at 80°C followed by formic acid reflux at 110°C as already described by Perez et al. [28]. The kraft pulp (K-E1) from *E. grandis* wood was obtained from LCP-UFV (Brazil), the kraft pulp (K-S1) from black spruce (*P. mariana*) wood was a gift from Norkraft Quévillon, (Canada) and maritime pine (*P. pinaster*) kraft pulp (K-P1) was given by Smurfit Wolrdwild Research Europe (Talence, France). The pulps under study could be considered representative of the traditional and alternative cooking procedures for both softwoods and hardwoods.

2.2. Photobleaching

During the photobleaching, the aqueous suspension containing the pulp (5% consistency) was maintained at 85°C under constant mechanical stirring. The Pyrex cylindrical reactor was placed between the two medium pressure mercury lamps (400 W) used for the irradiation. The Pyrex glass acts as a filter, it eliminates the UV light with wavelength below 300 nm, very detrimental to the cellulosic matrix.

During the first stage, the pulp suspension was irradiated for 1 h in presence of TiO_2 (1% relative to oven dried pulp, o.d.p.), sodium hydroxide (3% o.d.p.) to maintain alkaline the suspension and $MgSO_4$ (0.5% o.d.p.) to prevent the degradation of the pulp. Oxygen was continuously bubbled during this stage. After the irradiation, the pulps were filtered and washed to neutral pH with distilled water. For the second stage, the aqueous suspension included H_2O_2 (6% o.d.p.), NaOH (3% o.d.p.) and also sodium metasilicate (3% o.d.p.) and magnesium sulfate (0.5% o.d.p.) in order to protect the cellulose polymer against the oxygen active species and also to limit the thermal degradation of the hydrogen peroxide. The irradiation was continued for 1 h and after the bleaching, the pulps were washed with water to neutral pH.

2.3. Quantitative and physical measurements

The lignin content of the pulp was estimated using the micro Kappa Number method, according to the Tappi Method UM 246 and the conditions set-up by Berzins [29]. The Klason Lignin content (KL%) was approximately evaluated using the equation: KL% = KN × 0.15 where KN is the Kappa Number [19].

The yield of the bleaching process was measured by the mass loss occurring after the two stages. The viscosity measurements were performed using the capillary viscometer method, according to the ISO 5351/1 method.

Handsheets of paper (10 cm in diameter) were made from the different bleached pulps (basis weight ≈ 450 g/m^2) for DRIFT spectra, brightness index (BI) and UV/Visible diffuse reflectance measurements at infinite thickness expressed by R_∞. Brightness was measured with an Elrepho 2000 Datacolour Reflectometer. UV/Visible diffuse reflectance spectra were recorded on a Hitachi U-3300 spectrometer equipped with an integrating sphere. The DRIFT spectra were obtained using a Perkin-Elmer Paragon 1000 spectrometer using the reflectance accessory.

3. Results and discussion

The photochemical bleaching was performed in two stages in alkaline aqueous medium as previously set-up for similar experiments [18,22]. The first stage is an oxygen photodelignification catalyzed by TiO_2, the second one involves hydrogen peroxide delignification activated by UV light. The combination of the two stages could be beneficial for the delignification as it was already observed with singlet oxygen sensitized photobleaching on an organosolv *E. grandis* pulp [18]. Three organosolv pulps from *E. grandis* wood and three kraft pulps, one from *E. grandis* wood and two from softwoods, were studied (see Section 2).

The results obtained after the first and second stages are reported in Table 1. The same sequences were also carried out in absence of TiO_2 in order to evaluate the extension of its action as photocatalyst. Since the importance of the UV/Vis light in the bleaching has been largely demonstrated in previous papers [18–20,2,22–26], dark experiments were not performed.

The measurement of Kappa Number (KN) and viscosity allowed us the analysis of the selectivity of the delignification. The selectivity, expressed by the percentage ratio of delignification over viscosity loss, is related to the degradation of the carbohydrates matrix damage during the process. The results are presented in Table 2.

3.1. First stage

The photocatalytic action of TiO_2 was used to generate active species to delignify the pulps. The incident radiation provided by the medium pressure mercury lamps and filtered by the Pyrex glass, which eliminates wavelengths below 300 nm, is sufficient to cause an efficient photoexcitation of the catalyst [1,2,14,30]. The UV light promotes electron excitation of the valence band to the conduction band, creating

Table 1

Evaluation of the changes in the properties of the pulps before treatment, after the first stage (TiO_2: 1%, $MgSO_4$: 0.5%, NaOH: 3%, 1 h, 85°C, O_2 bubbled, UV/Vis irradiation) and the second one (H_2O_2: 6%, $MgSO_4$: 0.5%, $NaSi_2O_4$: 3%, NaOH: 3%, 1 h, 85°C, UV/Vis irradiation)

Pulp	Unbleached pulp			After the 1st stage			After the 2nd stage		
	KN	η (dm^3/kg)	BI	KN	η (dm^3/kg)	BI	KN	η (dm^3/kg)	BI
PF-E1	57.7	974	24.5	20.0 [41.7]	778 [667]	36.8 [34.7]	7.6 [9.3]	523 [484]	67.0 [61.3]
PF-E2	15.0	1161	45.1	8.6 [9.3]	1099 [1010]	45.5 [44.9]	3.4 [3.9]	1019 [846]	74.0 [71.7]
K-E1	17.0	1218	29.2	13.3 [14.1]	1155 [1001]	39.2 [38.1]	6.5 [7.5]	894 [787]	69.2 [61.6]
K-S1	20.0	1234	29.6	15.8 [19.6]	1201 [906]	29.5 [30.3]	10.3 [12.1]	1026 [712]	50.4 [51.2]
K-P1	69.1	1260	19.4	45.5 [61.3]	1187 [1107]	19.6 [19.6]	24.7 [41.9]	895 [740]	30.7 [20.5]
AC-E1	65.7	832	20.4	41.9 [46.0]	783 [618]	21.9 [21.6]	9.3 [13.5]	690 [459]	45.1 [60.7]

Non-catalyzed oxygen photobleaching data are given in brackets for comparison.

Table 2

Selectivity parameters for the photobleaching sequence of chemical pulps using TiO_2 photocatalyzed oxygen followed by a hydrogen peroxide (see details in Section 2)

Pulp	After the 1st stage [a]			After the 2nd stage [b]			Global process [a]		
	Delignification (%)	Viscosity loss (%)	Selectivity [c]	Delignification (%)	Viscosity loss (%)	Selectivity [c]	Delignification (%)	Viscosity loss (%)	Selectivity [c]
PF-E1	65.3 [27.7]	20.1 [31.5]	3.25 [0.88]	62.0 [77.7]	32.8 [27.4]	1.89 [2.83]	86.8 [83.9]	46.3 [50.3]	1.88 [1.67]
PF-E2	42.7 [38.0]	5.3 [13.0]	7.99 [2.92]	60.5 [58.1]	7.3 [16.2]	8.31 [3.58]	77.3 [74.0]	12.2 [27.1]	6.32 [2.73]
K-E1	21.8 [17.1]	5.2 [17.8]	4.21 [0.96]	51.1 [46.8]	22.6 [21.4]	2.26 [2.19]	61.8 [55.9]	26.6 [35.4]	2.32 [1.58]
K-S1	21.0 [2.0]	2.7 [26.6]	7.85 [0.08]	34.8 [38.3]	14.6 [21.4]	2.39 [1.79]	48.5 [39.5]	16.9 [42.3]	2.88 [0.93]
K-P1	22.1 [11.3]	5.8 [12.1]	3.81 [0.93]	45.7 [31.6]	24.6 [33.2]	1.86 [0.95]	57.7 [39.3]	29.0 [41.3]	1.99 [0.95]
AC-E1	36.2 [30.0]	5.9 [25.7]	6.15 [1.17]	77.8 [70.7]	11.9 [25.7]	6.55 [2.75]	85.8 [79.5]	17.1 [44.8]	5.03 [1.77]

The results of the same sequences without TiO_2 are presented in brackets for comparison.

[a] With reference to the unbleached pulps.

[b] With reference to the first stage.

[c] Delignification/viscosity loss.

electron–hole pairs at the surface of the catalyst (Eq. (1)) [1–3].

$$\mathrm{TiO_2 + h\nu \rightarrow Ti0_2(e^- – h^+)}. \qquad (1)$$

The high oxidative potential of the holes allows a series of reactions generating hydroxyl radicals from water and/or hydroxyl ions (Eqs. (2) and (3)) [1–3]:

$$\mathrm{TiO_2(h^+) + H_2O \rightarrow TiO_2 + HO^{\bullet} + H^+} \qquad (2)$$

$$\mathrm{TiO_2(h^+) + HO^- + \rightarrow TiO_2 + HO^{\bullet}}. \qquad (3)$$

Another reaction pathway is the direct oxidation of the organic materials (HS) by the hole of TiO_2 (Eq. (4)) [8,9,31].

$$\mathrm{TiO_2(h^+) + HS \rightarrow TiO_2 + HS^{+\bullet}}. \qquad (4)$$

The hydroxyl radical is known to be an extremely strong and non-selective electrophile oxidant. In its reactions with the main components of wood, it attacks preferentially electron-rich aromatic and olefinic groups in lignins, however, it reacts also, at lower rate, with aliphatic side chain of lignin and with carbohydrates [32]. In addition, due to the polymeric nature of lignin, one might consider the involvement of some extracted lignin fragments (formed by the action of the hydroxyl radical) to react with the holes of the catalyst to form cation radicals. The latter can act as a mediator to further oxidize the lignin macromolecule as it was observed for the biodegradation of lignin [33].

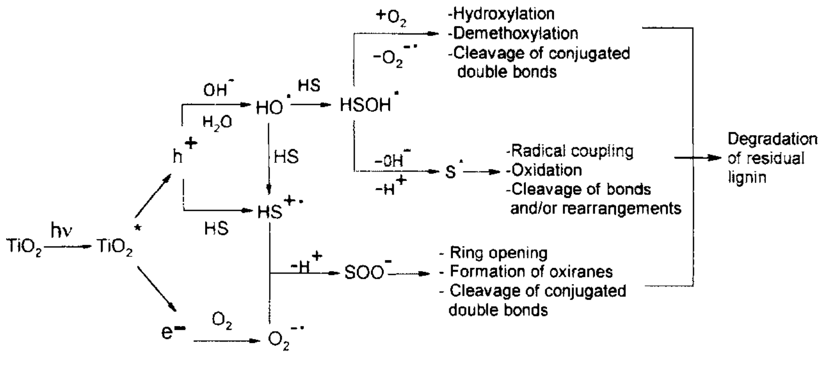
On the other hand, the electron in the conduction band can also reduce the molecular oxygen to superoxide radical (Eq. (5)) [1–3,8,9]; therefore, the presence of molecular oxygen in solution must be considered as a very important parameter of the oxidative process catalyzed by TiO_2.

$$\mathrm{TiO_2(e\ ) + O_2 \rightarrow TiO_2 + O_2^{\bullet}}. \qquad (5)$$

In contrast to the hydroxyl radicals, the anion superoxide does not directly oxidize lignin and carbohydrates; however, its major mode of reaction with the lignin macromolecule is the coupling with radicals generated by the hydroxyl radicals [34]. In addition, the superoxide anion may react with the intermediate species $HS^{+\bullet}$ (generated from holes of the catalyst) to form peroxides (Eq. (6)) [8,9]:

$$\mathrm{O_2^{-\bullet} + HS^{+\bullet} \rightarrow SOOH;\ SOOH + HO^- \rightarrow SOO^- + H_2O}. \qquad (6)$$

A number of reactive species are generated with the catalyst under UV irradiation, nevertheless, hydroxyl and superoxide radicals appear to be the preponderant oxygen active entities. Their action on the lignin macromolecule is depicted in Scheme 1 according to Ref. [34].



HS = lignin macromolecule

Scheme 1. Production of oxygen active species by irradiation in the presence of TiO_2 and their reactions with the residual lignin macromolecule in the chemical pulps, according to Ref. [33].

Due to the reactivity of hydroxyl radicals, the presence of large amount of TiO_2 could lead to degradation of the cellulose matrix [35]. For that reason, we have worked with a low charge of TiO_2 (1% based on pulp). This percentage represents a large economy compared to studies reported by Villasenor and Mansilla [8] and Mansilla et al. [9] on the degradation of kraft effluents by ZnO using a ratio ZnO/lignin equal to 42.5/1 and by Ohnishi et al. [36] reporting a ratio of 50/1 using TiO_2.

From the data presented in Table 1, it is clearly seen that the pulps bleached with TiO_2/UV light and oxygen present a higher viscosity and lower Kappa Number than the non-catalyzed ones; however, no significant brightness increase was observed. The discrepancy between the delignification level and the brightness gain after photochemical bleaching was already observed for the oxygen steps of a photochemical bleaching in three stages developed in our laboratories [18]. The behaviour of viscosity data is somewhat surprising because we expected some damage on the carbohydrate matrix due to the formation of hydroxyl radicals. Nowadays, we are working on the mechanistic aspects of the reaction in order to understand the overall process.

The disparity observed in the delignification efficiencies has to be related to the various lignin content of the pulps, to the nature of the pulping process and/or to the starting raw material. The pulps PF-E1 and AC-E1 were obtained from the same wood, *E. grandis*, with different pulping, they present approximately the same lignin content, nevertheless, the photodelignification of the peroxyformic acid pulp is better than acesolv one. This behaviour can be explained by the presence of numerous phenolic groups in the residual lignin of the peroxyformic acid pulp, which are formed by saponification of the phenolic formic esters formed during the cooking [22,28]. In contrast, the acetylation of the phenolic groups in the residual lignin of the acesolv pulp shown by the FTIR spectra (vide supra) explains its lower delignification compared to the peroxyformic acid. This is consistent with the high reactivity of the oxygen active species, generated from TiO_2 or ZnO, on phenols already reported [13,15,16]. Comparison of the data for PF-E2 and K-E1 pulps shows again for pulps with similar lignin content, the easiest photodelignification for the peroxyformic acid pulp, probably due to a higher phenolic content caused by the saponification of the phenolic formates.

The weak changes in the brightness index values during the first stage with TiO_2 indicate that although lignin was removed, several coloured chromophores remain in the pulps. Nevertheless, it was observed that, in the second stage, the pulp was more prone to colour removal as it was already observed for the classical photobleaching involving three stages [18].

The presence of molecular oxygen in solution is fundamental for an efficient delignification. This is exemplified by PF-E1 pulp submitted to a photobleaching in the absence of oxygen bubbling. After the first stage, the pulp without oxygen has a lignin content 3.8% compared to 1.14% with oxygen.

Finally, the photocatalytic action of the TiO_2 was confirmed by the values of the selectivity parameter (Table 2) for all pulps which are considerably higher than those observed for non-photocatalyzed process.

3.2. Second stage

The second stage is very similar to the last one of the classical photobleaching in three stages [18]. It used hydrogen peroxide (6% based on pulp) as source of oxygen active species, generated mainly by the UV light. The delignification pathways are preponderantly due the action of hydroxyl and superoxide radicals [25]. Evidences that singlet oxygen is also present in the reaction medium have been shown [23,24], but it seems that it is partly consumed by the reaction with the hydroxyl anions present in the solution, to form superoxide radical [25,26]. The hydroxyl radicals are produced mainly by cleavage of the peroxydic bond by UV light, nevertheless, the alkaline pH favour a major participation of the superoxide radical [4,19,23–25], less oxidant and more selective than the hydroxyl radical. It has been reported [19] that H_2O_2 photobleaching occurs with less damage on the cellulosic matrix and major efficiency when the pH of the suspension is maintained higher than 10. However, despite all these observations, the reduction of the pulp viscosity in the second stage is slightly higher in absolute values than the one observed for the first stage. Nevertheless, a gain was found when the viscosity loss is compared to the photobleaching process without catalyst in the first stage (Table 2).

The final delignification is better for all the pulps studied, and this has to be attributed to the TiO_2 photocatalytic action. Moreover, the properties of the pulps bleached with the photocatalyzed sequence were found better than those of the pulps bleached without TiO_2 (Tables 1 and 2). The residual lignin, after the first stage, should probably have incorporated changes, such as hydroxylation and formation of peroxidic entities [25,37,38], which made possible this efficient delignification.

Again, it is possible to observe that organosolv pulps employed in this work presents a superior bleachability than the kraft pulps. The percentages of delignification and viscosity loss, and consequently, the selectivity of the process, are clearly higher for the acesolv and peroxyformic acid pulps than for the kraft pulps, except for PF-E1 due the reasons already mentioned.

The second stage is very important for the brightness gain, as it can be seen in Table 1. Nevertheless, the pre-treatment with an oxygen-based stage appears to be essential in order to decrease the lignin content and to reach high brightness values.

3.3. *Effect of the temperature*

In order to evaluate the effect of the temperature on the performance of the system, the pulp PF-E2 was photobleached at 40°C with the same two-stages sequence using TiO_2 in the first one. A decrease of the delignification efficiency was noted at lower temperature where the final KN was found equal to 17.9, while at 85°C, it was equal to 7.6. This observation shows that the process is temperature-dependent in agreement with the results obtained by Villasenor and Mansilla [8] and Mansilla et al. [9] in a study involving the degradation of lignin fragments using ZnO as catalyst.

3.4. *Diffuse reflectance UV–Vis spectroscopy*

Diffuse reflectance UV–Vis spectroscopy was used to follow the changes occurring during the bleaching sequences. The spectra were measured for the unbleached pulps, after the first and second stages for both TiO_2 photocatalyzed and non-catalyzed sequences. An example is given for the eucalyptus peroxyformic acid (PF-E2), softwood (K-S1) and hardwood (K-E1) kraft pulps. They are presented in Figs. 1–3.

Examination of the figures indicates that a higher colour removal is operating in two stages for the TiO_2 photobleached eucalyptus pulps; no difference was noted for the spruce and both pine pulps; the TiO_2 sequence is only beneficial for the hydrogen peroxide stage.

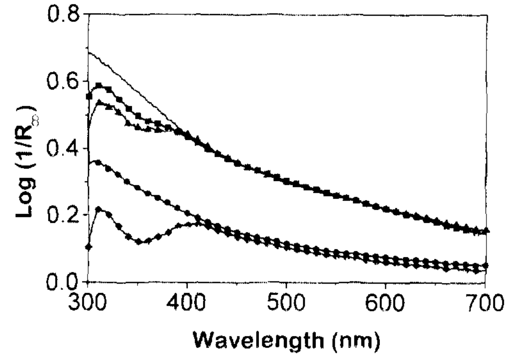


Fig. 1. Diffuse reflectance UV/Vis spectra, expressed as log $(1/R_\infty)$, of the PF-E2 pulp handsheets (~450 g/m²) made from: unbleached pulp (—); first stage: oxygen photobleaching in the presence (-▲-▲-▲-) and in the absence (-■-■-■-) of TiO_2; second stage: hydrogen peroxide photobleaching of the pulps obtained in the first stage without (-●-●-●-) and with (-◆-◆-◆-) TiO_2.

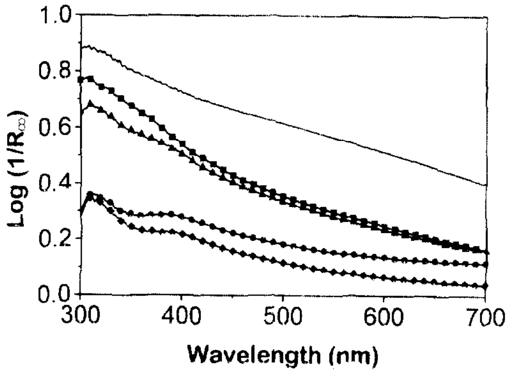


Fig. 2. Diffuse reflectance UV/Vis spectra, expressed as log $(1/R_\infty)$, of the K-E1 pulp handsheets (~450 g/m²) made from: unbleached pulp (—); first stage: oxygen photobleaching in the presence (-▲-▲-▲-) and in the absence (-■-■-■-) of TiO_2; second stage: hydrogen peroxide photobleaching of the pulps obtained in the first stage without (-●-●-●-) and with (-◆-◆-◆-) TiO_2.

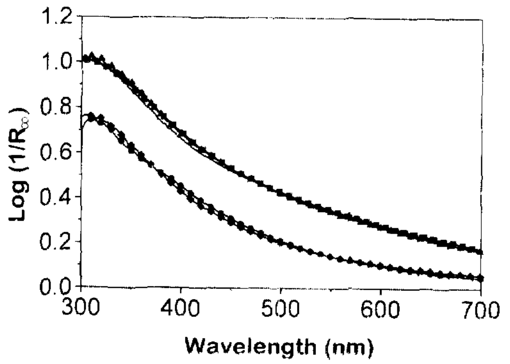


Fig. 3. Diffuse reflectance UV/Vis spectra, expressed as log $(1/R_\infty)$, of the K-S1 pulp handsheets (~450 g/m²) made from: unbleached pulp (—); first stage: oxygen photobleaching in the presence (-▲-▲-▲-) and in the absence (-■-■-■-) of TiO_2; second stage: hydrogen peroxide photobleaching of the pulps obtained in the first stage without (-●-●-●-) and with (-◆-◆-◆-) TiO_2.

The pulp PF-E2 (Fig. 1) presents a peculiar behaviour among the eucalyptus pulps. The first stage does not bring changes at wavelength higher than 400 nm, this indicates that quinones structures are not destroyed. But the reduction of the band at 350 nm, due to coniferaldehyde groups, is clearly observable [39]. The spectra of K-E1 PF-E1, and AC-E1 display similar behaviour, so for clarity, only the K-E1 curves are shown (Fig. 2). Some colour removal was observed when oxygen photobleaching was carried out and a slight improvement was noticed when TiO_2 was introduced. These results are in accordance with the brightness measurements presented in Table 1.

The effect of TiO_2 on the softwood pulps, exemplified in Fig. 3 for spruce pulp is negligible, nevertheless, the lignin structure of the softwood pulp was probably affected by the catalyzed first stage, improving the colour removal during the second one. The continuous aspect of the spectra for the softwood pulps does not bring information about the chromophores involved in the bleaching process, as it was found for the eucalyptus wood pulps.

The second stage brings a substantial colour removal for all the pulps and the gain in whiteness is higher for the TiO_2/O_2 pre-treated pulps than for the pulps treated in absence of the TiO_2. The reduction of coniferaldehyde structures absorbing at 350 nm is observed for all eucalyptus pulps. In contrast, both the bands near 320 nm, due to coniferyl alcohol, biphenyl and other lignin structures, and 400 nm, attributed to quinone type structures, remain in the residual lignin. It appears clearly that some oxygen active species, generated by TiO_2 in the first stage, promote some oxidation of the lignin, which very beneficial for the hydrogen peroxide bleaching in the second stage.

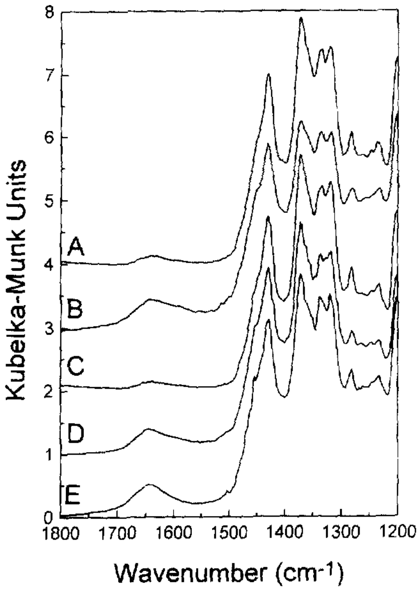


Fig. 4. DRIFT spectra of the PF-2 pulp handsheets (~450 g/m^2) made from: unbleached pulp (A); first stage: oxygen photobleaching in the presence (B) and in the absence (C) of TiO_2; second stage: hydrogen peroxide photobleaching of the pulps obtained in the first stage with (D) and without (E) TiO_2.

3.5. Diffuse reflectance infrared (DRIFT) spectroscopy

DRIFT spectroscopy was employed in order to identify some structural changes in the lignocellulosic matrix. Figs. 4–6 show the IR spectra of PF-E2, K-E1, and AC-E1 pulps before and after all bleaching (first and second stages). The spectra related to PF-E1, K-S1 and K-P1 pulps are not shown

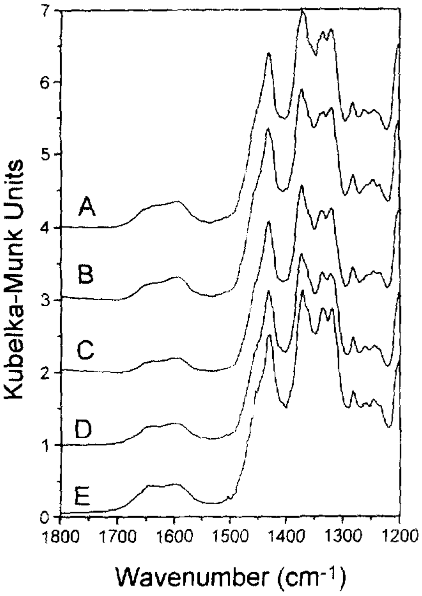


Fig. 5. DRIFT spectra of the K-E1 pulp handsheets (~450 g/m^2) made from: unbleached pulp (A); first stage: oxygen photobleaching in the presence (B) and in the absence (C) of TiO_2; second stage: hydrogen peroxide photobleaching of the pulps obtained in the first stage with (D) and without (E) TiO_2.

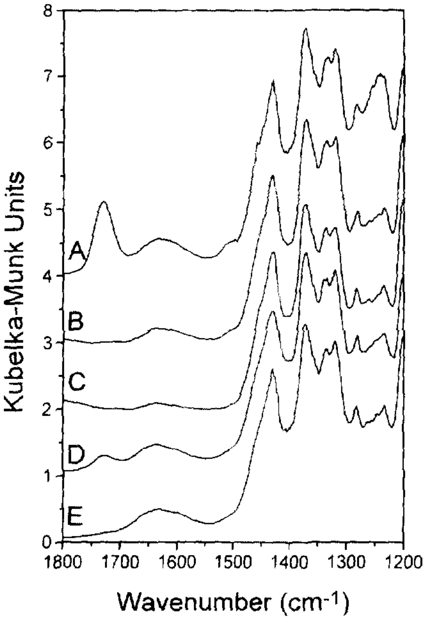


Fig. 6. DRIFT spectra of the AC-E1 pulp handsheets (~450 g/m^2) made from: unbleached pulp (A); first stage: oxygen photobleaching in the presence (B) and in the absence (C) of TiO_2; second stage: hydrogen peroxide photobleaching of the pulps obtained in the first stage with (D) and without (E) TiO_2.

because the bands do not bring further significant information. The regions of the spectra between 4000–1800 and 1200–400 cm^{-1} were omitted for clarity of the figures because they do not present significant changes.

The DRIFT technique was used on pulp dried at 70°C under vacuum in order to avoid the presence of the water traces which give a strong absorption band at 1640 cm^{-1} when the transmission mode is employed [40].

The efficiency of the delignification can be observed in all the spectra around 1260 cm^{-1} attributed to the guaiacyl units of the lignin polymer [41]. The region between 1800 and 1500 cm^{-1} displays some of the most noticeable changes experienced by the functional groups during the bleaching. The PF-2 unbleached pulp spectra presents a band centred at 1640 cm^{-1} assignable to quinones [41] and also to conjugated carbonyl groups such as coniferaldehydes [42]. It is clearly seen that destruction of chromophores absorbing in this region is operating during the TiO_2-photocatalyzed sequence. In contrast, an increase of the same band is observed for the non-catalyzed process, suggesting that new carbonyl groups are formed during the bleaching. This observation agrees with the results reported by Michell et al. [40] about the generation of new carbonyl groups during the photobleaching of eucalyptus soda pulp. Their presence might be a source of thermal and or light instability [43].

The spectra recorded for the KE1 pulp reveal, beside the band at 1640 cm^{-1} discussed above, a band centred around at 1595 cm^{-1}. This band, which is due to the aromatic skeletal vibrations, does not considerably decreases during the bleaching sequences. This is in accordance to the moderate delignification degree observed for the kraft pulps in this work.

For the acesolv pulp AC-E1, beside similar changes already discussed for PF-2 and KE-1 pulps, an almost complete disappearance of the band at 1729 cm^{-1} due to acetylated phenols formed during the pulping is also observed. The presence of TiO_2 in the first stage bleaching leads to a more efficient saponification of these acetate groups. This observation on ACE-1 pulp and the good bleachability noted for PF-E2 pulp, in which many phenolic groups are formed by the alkaline treatment after the pulping, suggest that the good performance of the first stage depends, between several other factors, on the amount of phenolic groups in the residual lignin, as already observed in earlier works [18,22,23,26].

3.6. Mechanistic considerations

Although the mechanistic aspect was not the main purpose of this study, UV–Vis and IR spectroscopies gave us some important information about the chemical pathways occurring along the process. The first stage, when it is operating with TIO_2, does not create new carbonyl groups in contrast to the sequence carried out in the absence of the semiconductor. This point, allied to a higher selectivity observed for the first bleaching stage in the presence of TiO_2, suggests that different mechanisms are operating for the catalyzed and non-catalyzed systems. The direct oxidation of the lignin fragments in the activated holes associated with the action of the superoxide anion radical, largely generated by the electron in the conduction band appear to be an important path for the lignin oxidation. On the other hand, the hydroxyl radical action seems to be the preponderant pathway for the non-catalyzed sequence, that could explain its lower selectivity. In fact, hydroxyl radicals do not promote aromatic ring opening without the cooperation with superoxide anion radicals [34]. Moreover, the more effective oxidation of the residual lignin after the first stage in presence of TiO_2 appears to be decisive point for a successful H_2O_2/UV stage.

4. Conclusion

The photobleaching in two stages, using TiO_2 in the first one, presented in this study shows an efficiency comparable to a three stages photochemical bleaching developed in our laboratories [18], but a net decrease of the irradiation time of the pulp was obtained. The amount of chemicals was drastically reduced and the consistency of the pulp in the suspension increased (from 0.7% to 5%) if the bleaching is compared with a process performed in one stage [19]. A good improvement was obtained in relation to the preservation of the viscosity of the pulp. With reference to results reported by Marcoccia et al. [20,21], based on the generation of active species from oxygen, we have worked with pulp consistencies five times higher, and with a lower global reaction time, to obtain reproducible results. However, in contrast with Marcoccia's findings, experiments using just oxygen at alkaline pH even at 85°C do not lead for kraft pulps to a large gain in delignification and/or brightness index. Even though mechanistic studies are needed for a better understanding, the results obtained on the photobleaching of the peroxyformic acid and kraft pulps from *E. grandis* pulps are encouraging and give confidence to promote a process able to produce pulps with good properties at reasonable cost.

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