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Article

The Improvement of the Bleaching of Peroxyformic Sugar Cane Bagasse Pulp by Photocatalysis and Photosensitization

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Um novo processo de branqueamento em dois estágios combinando fotocatálise e fotosensibilização foi aplicado sobre a polpa celulósica obtida por polpação do bagaço de cana-de-açúcar com ácido peroxifórmico. O primeiro estágio consiste na irradiação (1 h) da polpa em meio alcalino em suspensão aquosa à consistência de 5%, empregando lâmpadas de tungstênio ou mercúrio, em presença de TiO_2, como agente fotocatalisador, azul de metileno (MB), ácido 3,4,9,10-perileno-tetracarboxílico ou 4, 4’4”,4’”-tetra-sulfotalocianina de Fe(II) (TSPC) (concentaração ≈ 10^{-5} mol L^{-1}) como agentes fotosensibilizadores, oxigênio e peróxido de hidrogênio. O segundo estágio, conduzido sob peróxido de hidrogênio, completa eficientemente a deslignificação, permitindo a obtenção de elevado grau de alvura, bem como a remoção completa do fotosensibilizador absorvido sobre a polpa. Empregando esta seqüência, resultados altamente satisfatórios foram obtidos na presença de luz UV/visível e de PTCA ou MB (polpa não branqueada - número de Kappa: 13, índice de alvura: 44, viscosidade: 900 dm^3 kg^{-1} ; polpa branqueada - número de Kappa: 1.2-1.3, índice de alvura: 86, viscosidade: 510-550 dm^3 kg^{-1}), bem como sob luz visível na presença de MB (número de Kappa: 1.7, índice de alvura: 80, viscosidade: 625 dm^3 kg^{-1}). Apesar dos bons resultados apresentados, mecanismos com vistas ao aumento de selectividade e eficiência do processo de fotobranqueamento deverão ser desenvolvidos futuramente.

Presented here is a new process in two stages for bleaching peroxyformic sugar cane bagasse pulp combining photosensitization and photocatalysis. The first stage consists of an irradiation (1h), with tungsten or mercury lamps, of the pulp under alkaline pH in aqueous suspension at a consistency of 5% with TiO_2 and methylene blue (MB) or 3,4,9,10-perylenetetracarboxylic acid (PTCA) or Fe (II) 4,4’,4’’,4’’’-tetrasulfophthalocyanine (TSPC) (concentration ≈ 10^{-5} mol L^{-1}) in the presence of bubbling oxygen and hydrogen peroxide (2% pulp basis). The second photobleaching stage performed with hydrogen peroxide (3%) efficiently completed the delignification and the brightness gain, removing completely the sensitizer from the pulp. Under those conditions, efficient bleaching of the pulp was obtained, using uv/vis light and PTCA or MB (unbleached pulp: kappa number: 13, brightness: 44, viscosity: 900 dm^3 kg^{-1}; bleached pulp: kappa number: 1.2-1.3, brightness: 86, viscosity: 510-550 dm^3 kg^{-1}) or visible light with MB (kappa number: 1.7, brightness: 80, viscosity: 625 dm^3 kg^{-1}). The mechanisms of photobleaching to increase the selectivity and the efficiency of the process remain to be established.

Keywords: *cellulosic pulp, bleaching, photocatalysis, titanium dioxide, lignin, photobleaching, oxygen, hydrogen peroxide, photosensitization, singlet oxygen*

Introduction

The principal goals of chemical pulp bleaching are to remove residual lignin and to decolorize the pulp without adversely damaging the cellulosic matrix. Due to stricter pollution regulations, new non-pollutant bleaching processes are highly desired and the Totally Chlorine Free (TCF) bleaching technology based on the action of oxygen, ozone, hydrogen peroxide and peracids appears to fulfill the conditions for a closed cycle mill[1]. The delignification performed in the TCF bleaching is mainly based on redox reactions[2]. It is known that excitation of molecules in their electronic excited states increases their redox properties compared to the ground state[3]. In that respect, the photochemical bleaching, based on the generation of oxygen active species, appears very promising[4-7]. We have recently reported a three stage photochemical bleaching of *Eucalyptus grandis* organosolv pulps[4,8]. The bleaching was attributed to the combined action of superoxide anions, hydroxyl radicals, and singlet oxygen produced by irradiation in alkaline solutions[8-12]. Some improvement in the photobleaching was reached by the use of the photocatalytic action of TiO_2 [13]. The presence of TiO_2 as a photocatalyst showed several advantages such as the reduction of reaction time, preservation of the pulp viscosity, increase of the selectivity during the photobleaching process and decrease of the consumption of the bleaching chemicals[13]. This article describes the photobleaching of chemical pulp combining the use of a photocatalyst TiO_2, and a photosensitizer. The study was focused on peroxyformic sugar cane bagasse pulp, because it was easy to obtain and the process involves a very abundant raw material in Brazil[14]. The role of the sensitizer is to absorb most of the light in the range 300-800 nm, the ultimate goal being to set up a technology based on sunlight energy to bleach pulps which might be used in sunny countries located in equatorial and tropical areas. The bleaching sequences were accomplished using oxygen and hydrogen peroxide as the source of oxygen active species in the presence of uv and visible light. The relative contribution of the uv and visible parts of the light was changed by varying the nature of irradiating sources: mercury versus tungsten lamps.

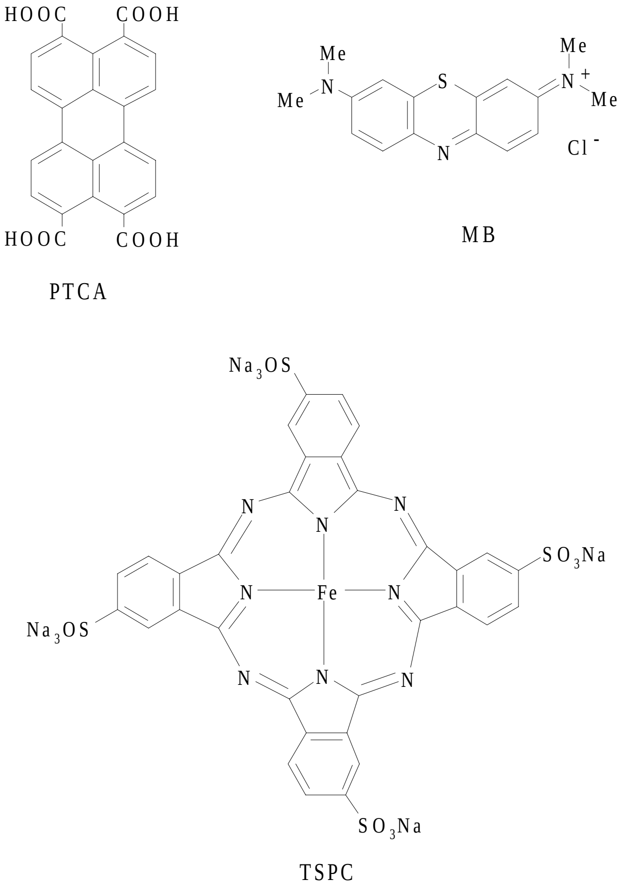
Experimental

Pulp

The unbleached pulp was prepared from sugar cane bagasse using the one stage peroxyformic procedure previously described[14]. The pulping of the bagasse was carried out at 75 °C (3 h) to profit from the action of peroxyformic acid, followed by a formic acid reflux (110 °C, 2 h), using the same liquor. The pulping process was completed by a 0.25 N NaOH extraction of the pulp at 60 °C in order to dissolve more lignin. Good quality unbleached pulps were obtained. The pulp used in this study has the following characteristics: kappa number (KN) = 13, intrinsic viscosity $[\eta] = 900\ dm^3\ kg^{-1}$ and brightness index (BI) = 44.1.

Photobleaching

During the photobleaching, the aqueous suspension containing the pulp (5% consistency) was kept at constant temperature (40 or 85 °C) with constant stirring. The Pyrex cylindrical reactor was placed between two lamps during the irradiation. Two medium pressure mercury lamps (Mazda 400 W) and two tungsten lamps (Mazda Iodine 500 W)) were used for the uv/visible and visible irradiations respectively. The Pyrex glass acts as a filter, it eliminates the uv light with wavelengths below 300 nm, which are very detrimental to the cellulosic matrix. The bleaching was done in two stages. During the first stage, the pulp suspension was irradiated for 1 h in the presence of TiO_2 (0.5 % relative to oven dried pulp, odp), hydrogen peroxide (2% odp), sodium hydroxide (3% odp) to maintain alkaline the suspension and $MgSO_4$ (0.5% odp) to prevent the degradation of the pulp. A dye, methylene blue (MB), 3,4,9,10-Perylene tetracarboxylic acid (PTCA) or Fe(II) 4,4',4'',4'''-tetrasulphophtalocyanine (TSPC) (Fig. 1) was added to the solution (final concentration $\approx 5 \times 10^{-5}\ mol\ L^{-1}$)



Scheme 1. Formulae of the photosensitizers.

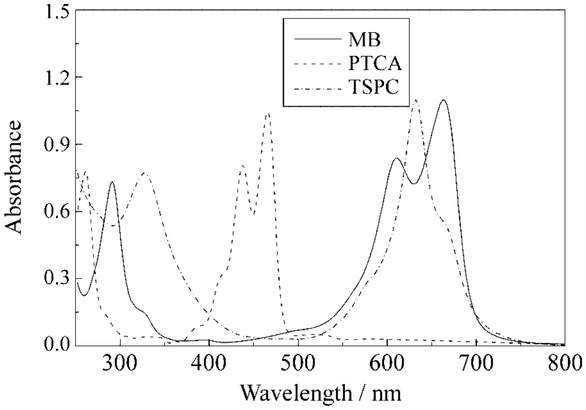


Figure 1. Absorption spectra of the sensitizers in alkaline water solutions (pH = 11; concentration ≈ 2 x 10^{-5} mol L^{-1}).

in order to absorb the uv/visible light and therefore to increase the photobleaching of the pulp. Oxygen was continuously bubbled through the solution during irradiation. After the irradiation, the pulp was filtered and washed to a neutral pH level with distilled water. For the second stage, the aqueous suspension included H_2O_2 (3% odp), NaOH (3% odp), bubbling oxygen and also sodium metasilicate (3% odp) to limit the thermal degradation of the hydrogen peroxide. The irradiation was maintained for 1 h and after the bleaching, the pulps were washed with water to a neutral pH.

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. The viscosity measurements were performed using the capillary viscometer method, according to the ISO 5351/1 method. Handsheets of paper (10 cm of diameter) were made from the different bleached pulps (basis weight ≈ 450 g m^{-2}) for measuring, brightness and uv/visible diffuse reflectance spectra at infinite thickness expressed by R_∞. The brightness at 457 nm was obtained with an Elrepho 2000 Datacolor Reflectometer and the uv/visible diffuse reflectance spectra were recorded with a Hitachi U-3300 spectrometer equipped with an integrating sphere.

Results and Discussion

The photobleaching was performed on sugar cane bagasse, which appears to be the most promising raw material pulped with peroxyformic acid[14]. It was performed in two stages using both uv/visible and visible lights. The experimental conditions for the uv/visible irradiations are very similar to those previously reported[13], the same setup was used for the visible irradiations, the medium pressure Hg lamps (400 W) being replaced by quartz/iodine tungsten lamps (500 W). The experiments were conducted at 40 °C and at 85 °C in order to know the effect of thermal activation. The bleaching performance was evaluated by measuring the amount of residual lignin (kappa number), pulp viscosity (η) which is indicative of the damage of the cellulosic chain) and brightness (BI) of papers made from the pulp after each stage. The bleaching yields were found to be greater than 90%.

In the first stage of the photochemical bleaching, the pulp was treated with oxygen and hydrogen peroxide in the presence of both a photosensitizer and a photocatalyst (TiO_2) in an alkaline medium. The beneficial effect of TiO_2 to delignify and to bleach the chemical pulps under uv/visible irradiation had already been observed[13]. The presence of the sensitizer should allow the utilization of both uv and visible light to photobleach the pulp, and may eventually allow the use of sunlight as an irradiation source. The second stage gives high brightness to the pulp as well as eliminating the residual dye over the pulp arising from the first stage. Among different sensitizers which might be used, we have selected methylene blue (MB) for its singlet oxygen sensitizer ability and because it was shown to efficiently photobleach the pulp[4,8]. 3,4,9,10-Perylenetetracarboxylic acid (PTCA) has been described as a potential visible light transfer agent semiconductors[15]. Finally, Fe(II) 4,4',4'',4'''-tetrasulphophtalocyanine (TSPC) was used to promote the thermal oxidative degradation of catechol[16] and veratryl alcohol[17] in the presence of hydrogen peroxide. All these compounds are water-soluble at alkaline pH and their absorption spectra are given in Fig. 2. In an alkaline water solution, MB and TSPC have an intense absorption between 520 and 720 nm, whereas the absorption of PTCA is centered at 450 nm.

The results of the photobleaching of the sugar cane bagasse pulp at 85 and 40 °C respectively are shown in Tables 1 and 2 and for the experiments performed at 85 °C, in the form of a bar chart in Fig. 2.

Examination of Tables 1 and 2 shows that the bleaching of the peroxyformic bagasse pulp was operating quite well without light in two stages at 85 °C and was very poor at 40 °C. Even for the thermal process, important viscosity loss was observed (37% at 85 °C and 23% at 40 °C). This could be due to the detrimental action of metal ions such as Fe^{2+}, Fe^{3+}, Mn^{2+} on the cellulosic matrix during the peroxide bleaching[18], as no chelating treatment was done on the unbleached pulp; though the objective of the study was to evaluate the improvement of the bleaching using light in the presence of a dye and a photocatalyst.

Comparison of the data on Tables 1 and 2 clearly indicates that the enhancement of the bleaching by light is temperature-dependent and that it is very poor at 40 °C. It is likely that the oxygen active species, such as singlet oxygen, superoxide anion and other delignifying radicals, do not migrate sufficiently to reach and react with the residual lignin structure. Nevertheless, some enhancement

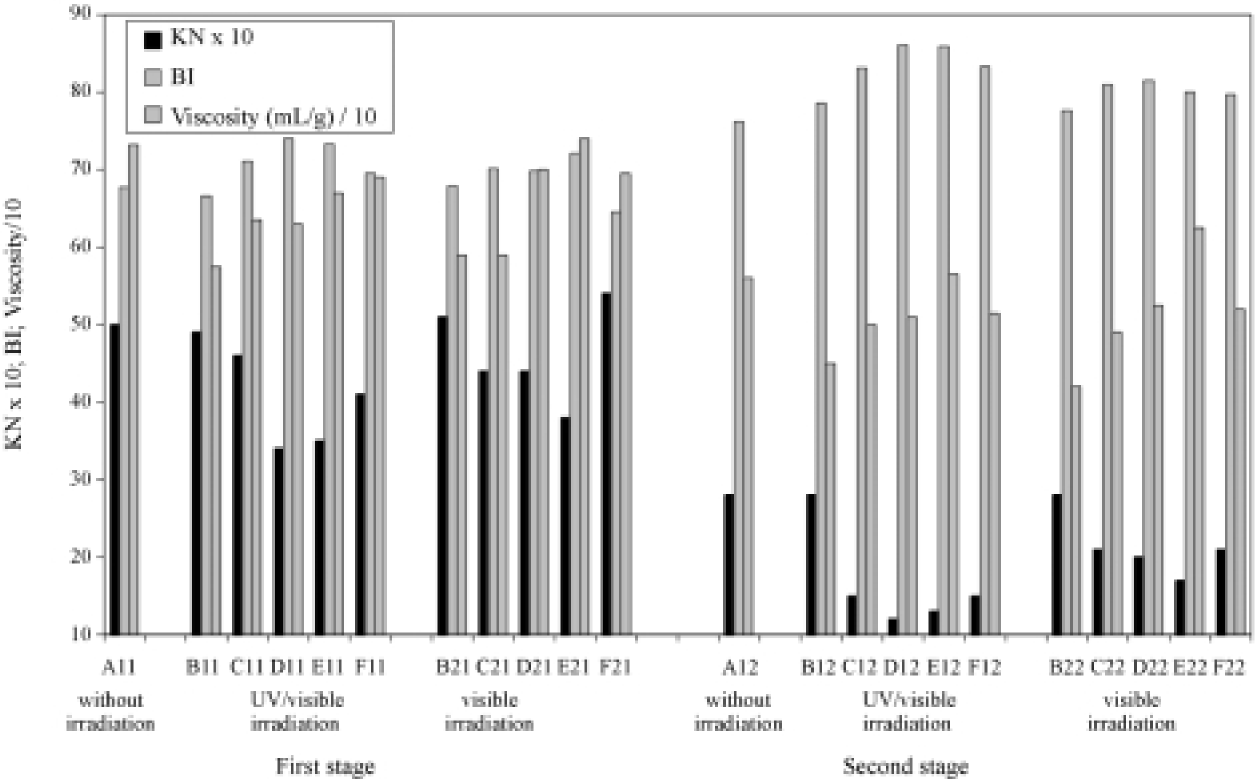


Figure 2. Performance of the photobleaching of peroxyformic sugar cane bagasse pulp in two stages at 85 °C. (For an easier comparison the kappa numbers are multiplied by 10 and the viscosity numbers divided by 10; moreover the experiments were labeled Nxy with x identical as in Table 1 and y = 1 for the first stage, y = 2 for the second one).

was observed using the combination TiO_2/PTCA in the presence of UV/VIS and visible light (experiments D1 and D2) with very low viscosity loss compared to the thermal process (Table 2).

As previously observed[13], the presence of TiO_2 alone improves the photodelignification in the first stage and consequently in the second one but this improvement is dependent upon the nature of the irradiation light. At 85 °C in the first stage, the use of tungsten lamps, which display a higher visible component, brings an increase in delignification of 14% instead of 6% with the Hg lamps which emit more uv light. This effect is reversed in the second stage with a 46% improvement with the Hg lamps and 25% with the tungsten lamps. This is clearly seen in Fig. 2 by comparing the B11:C11 bars to the B21:C21 ones for the first stage and the B12:C12 bars to B22:C22 ones for the second stage. The global action of TiO_2 is better with the uv/vis irradiation than with the visible light. Also, as previously observed[13], the photocatalyst limits the viscosity loss and improves the brightness of the pulp with the experiments performed at 85 °C being the best.

Water soluble iron and manganese sulfoporphyrins and sulfophthalocyanines have been developed during the last decade as ligninase substitutes to degrade aromatic derivatives[16]. In that respect, the iron (II) sulfophthalocyanine TSPC was found to be very efficient for thermal degradation of catechols[16]. We have used this compound to enhance the photodelignification because in addition to its thermal ability to degrade lignin model compounds, it has an important absorption band in the visible region which is very similar to the one of methylene blue (Fig. 1). Examination of Table 1 and Fig. 2 (experiments F1 and F2) indicates that the compound TSPC does not bring significant enhancement to the delignification process. One can relate these results to those observed by Hampton and Ford[17] on the thermal oxidation of 3,4-dimethoxybenzyl alcohol by TSPC where the authors noticed a complete decomposition of TSPC solution in two minutes. Thus TSPC, due to its oxidative instability, is not the most useful sensitizer and is unable to augment the activity of TiO_2 in the photochemical bleaching of pulps. Due to the lack of results with this sensitizer at 85 °C, irradiations at 40 °C were not performed.

In contrast to TSPC, methylene blue (MB) and the perylenetetracarboxylic acid (PTCA) enhanced the delignification and the brightness gain and limited the viscosity loss under both the tungsten and mercury lamp irradiations with the latter being the most efficient (Table 1 and Fig. 2). As observed before, the process is thermally activated, almost no enhancement was observed at 40 °C (Table 2).

Table 1. Photobleaching of peroxyformic sugar cane bagasse pulp in two stages at 85 °C

		After the first stage			After the second stage		
System		KN	BI	[η] ($dm^3\ kg^{-1}$)	KN	BI	[η] ($dm^3\ kg^{-1}$)
A	pulp+TiO_2	5.0	67.7	732	2.8	76.2	560
B1	pulp+uv/vis	4.9	66.6	575	2.8	78.6	450
C1	pulp+TiO_2+uv/vis	4.6	71.1	635	1.5	83.1	500
D1	pulp+TiO_2+PTCA+uv/vis	3.4	74	630	1.2	86.1	510
E1	pulp+TiO_2+MB+uv/vis	3.5	73.3	670	1.3	85.9	565
F1	pulp+TiO_2+TSPC+uv/vis	4.1	69.5	690	1.5	83.3	515
B2	pulp+vis	5.1	67.9	590	2.8	77.6	420
C2	pulp+TiO_2+vis	4.4	70.1	590	2.1	81.0	490
D2	pulp+TiO_2+PTCA+vis	4.4	69.8	700	2.0	81.5	525
E2	pulp+TiO_2+MB+vis	3.8	72.1	740	1.7	80.0	625
F2	pulp+TiO_2+TSPC+vis	5.4	64.5	695	2.1	79.7	520

Unbleached pulp (15 g, 5% consistency): KN = 13; BI = 44.1; η = 900 mL/g. *First stage*: TiO_2 0.5% oven dry pulp (odp) ; H_2O_2 2% odp; $MgSO_4$ 0.5% odp; NaOH 3% odp, O_2 bubbling; photosensitizer ≈ 5×10^{-5} mol L^{-1}; irradiation time 1 h. *Second stage*: H_2O_2 3% odp; $MgSO_4$ 0.5% odp; NaOH 3% odp, O_2 bubbling; $NaSi_2O_3$ 3% odp; irradiation time 1 h. Uv/vis: two medium pressure Hg lamps (400W) with Pyrex vessel; Vis: two tungsten lamps (500 W) with pyrex vessel.

Table 2. Photobleaching of peroxyformic sugar cane bagasse pulp in two stages at 40 °C.

		After the first stage			After the second stage		
System		KN	BI	[η] ($dm^3\ kg^{-1}$)	KN	BI	[η] ($dm^3\ kg^{-1}$)
A	pulp+TiO_2	11.1	52.7	775	9.9	55.8	690
B1	pulp+uv/vis	11.1	55.1	660	9	57.9	550
C1	pulp+TiO_2+uv/vis	10.8	54.6	740	8.7	59.1	570
D1	pulp+TiO_2+PTCA+uv/vis	10.6	56.4	750	7.8	60.4	665
E1	pulp+TiO_2+MB+uv/vis	11.2	54.2	740	8.5	56.4	645
B2	pulp+vis	11.4	54.1	670	9.3	59.4	575
C2	pulp+TiO_2+vis	10.5	56.7	755	8.9	58.1	600
D2	pulp+TiO_2+PTCA+vis	10.9	55.6	770	8.8	61.4	670
E2	pulp+TiO_2+MB+vis	11.2	54.2	740	8.5	56.4	645

Same conditions as for Table 1.

In the first stage with uv/vis irradiation, a very similar increasing delignification was observed for MB (26%) and PTCA (24%). Using tungsten lamps, no delignification enhancement was obtained with PTCA whilst 13% was gained using MB. The different proportion of visible light absorbed by PTCA and MB might explain this result.

After the second stage, both MB and PTCA, in conjunction with TiO_2 and uv/vis light, were able to cause delignification to a great extent (PTCA: 64%; MB: 63%) reaching similar brightness levels (BI ≈ 86). Moreover, MB brings some protection to the cellulosic matrix, the viscosity loss being less than with PTCA or without a sensitizer. Investigation, on a β-O-4 lignin model compound[12] pointed out the role of the superoxide anion in the photosensitized irradiations in an alkaline medium. This activated oxygen species, which appears less detrimental to the cellulosic matrix than hydroxyl radicals might explain the result observed for MB.

The combined action of TiO_2 and MB with visible light is quite efficient in terms of delignification and viscosity loss. Nevertheless some chromophores absorbing in the visible region are still remaining in the pulp as shown in Fig. 3. It is also clearly seen that the second stage very efficiently removes the sensitizer from the pulp. Similar observations were made with the two other dyes (curves not shown).

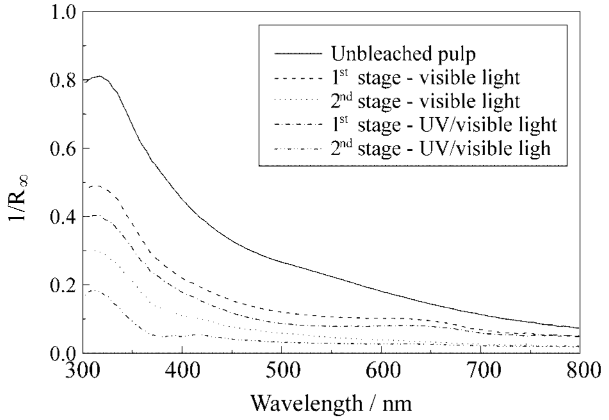


Figure 3. UV/Vis diffuse reflectance spectra of paper sheets made from pulps obtained with TiO_2/MB photobleaching under UV/Vis and Vis irradiations.

One might speculate as to the respective roles of TiO_2 and of the sensitizer in the bleaching process but the main objective of the study was to demonstrate the viability of this new method to produce bleached chemical pulps using the combined action of light, photocatalyst, sensitizers in presence of oxygen and hydrogen peroxide. The nature of the oxygen active species and their mechanism of action in the delignification and brightening processes are still unknown, they are currently being studied in our laboratories and should give clues as to how to increase the selectivity of the photochemical process to an acceptable level.

Conclusion

The present study is an approach to produce chlorine- and sulfur-free bleached pulp under mild conditions from a lignocellulosic raw material, sugar cane bagasse. It demonstrates that the combination of peroxyformic acid pulping followed by photochemical bleaching using a photocatalyst TiO_2, dyes such as 3,4,9,10-perylenetetracarboxylic acid (PTCA) or methylene blue (MB) can produce almost fully bleached pulp with uv/vis light (KN = 1.2-1.3; BI = 86; η=510-550 dm^3 kg^{-1}) or with visible light (KN = 1.7-1.3; BI = 80; η = 625 dm^3 kg^{-1} for MB/TiO_2). Nevertheless, it is necessary to improve the efficiency and the selectivity of the system photocatalyst/sensitizer, to bring solar photobleaching to an acceptable level for use. Efforts are being made in this direction in our cooperative program CAPES/COFECUB between the University of Uberlandia and the University of Bordeaux.

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