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SOLAR-DRIVEN PHOTOBLEACHING OF LIGNOCELLULOSIC BIOMASS

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Abstract: *Lignocellulose material is the main natural resource for the pulp and paper industry, and for its application the material should have a degree of whiteness as high as possible. For this reason, different bleaching treatments were applied during time. In this paper, the photobleaching induced by solar light of a lignocellulosic biomass using NaClO was studied. The colorimetric measurements, UV spectra absorption, and FTIR spectra changes are evaluated and discussed in this paper. The changes of L*a*b parameters can be considered a proof of the reactions generated by hypochlorite radicals during solar light exposure, leading to a biomass whitening.*

Keywords: lignocellulose biomass, solar-driven, bleaching, UV irradiation, colorimetric tests, kappa number

1. INTRODUCTION

Lignocellulosic biomass (LC), one of the most abundant and inexhaustible natural resource, is composed from cellulose, hemicellulose and lignin and it has a complex, rigid structure due to the covalent bonds that are established between these biomacromolecules [1]. Lignin acts as a "glue", linking hemicellulose and cellulose through ester bonds (by intra- and intermolecular bonds) and hydrogen bonds, respectively [2, 3]. The separation processes are thus greatly hampered by these molecular interactions, but imperious for its further utilization. LC is a raw material for the pulp and paper industry, applications focused on the separation of lignin and cellulosic fractions of the biomass. Also, the pulp must have a degree of whiteness as high as possible, and different bleaching treatments were applied during time [4].

Solar photochemical energy is an important long-range option for meeting future energy needs. The intensity of solar radiation in the Earth's distance from the sun is approximately 1353 kW/m^2, a number also called the solar constant. The solar radiation is emitted from the sun's photosphere at 6000 K temperature, which gives it a spectral distribution resembling closely that of a black body at the corresponding temperature. Passing through the Earth's atmosphere, the solar radiation is attenuated by scattering from the air molecules, aerosols and dust particles, as well as through absorption by the air molecules, in particular oxygen, ozone, water vapor, and carbon dioxide. This gives a characteristic fingerprint to the solar radiation spectrum on the Earth's surface [5].

The spectral range of sunlight is very large, from nanometric wavelengths (gamma, X-rays) to metric ones (radio waves). The energy flux is divided into ultraviolet (UV) radiation (λ<400nm) that accounts for less than 9% of the total flux, visible light (Vis) (400nm < λ < 700nm) for 39%; and infrared (IR) for about 52% from the total [6].

The bleaching of lignocellulosic biomass is an important industrial process, consisting in the chemical processing of a dark-colored cellulose into a raw material with a high degree of whiteness, especially through the selective removal of residual lignin from LC. Among the methods applied in the bleaching process are the use of chlorinated compounds or hydrogen peroxide. H_2O_2 is the main bleaching agent in the pulp industry [7, 8]. The per hydroxyl anion (HOO^-) removes the conjugated carbonyl groups from the lignin structure. The decomposition of hydrogen peroxide results in the hydroxyl radical ($HO^\bullet$) and superoxide ($O_2^\bullet$) which can remove lignin from the ligno-cellulosic mass. Modern wood pulp bleaching technologies, which use their chlorine-free oxidizing habits (H_2O_2, O_2, O_3 or peracids), do not lead to a high degree of whiteness (maximum 65%), and an additional step is required, bleaching with chlorine dioxide for example, to achieve an optimal

degree of whiteness. Chlorinated compounds have the ability to form covalent groups, by breaking the bonds of lignin. The major disadvantage of this method is the high toxicity of the reaction products [9].

An efficient bleaching method consists in a near complete in situ delignification of pulping with oxidative agents, by nucleophilic / electrophilic / radical / oxidation reactions [9, 10] when chromophores (unsaturated aldehydes, ketones, phenolic ring-conjugated ethylenic or carbonyl groups) are transformed to their non-chromophore counterparts [11]. Thus, the chloride-based chemicals (ClO_2, $NaClO_2$, NaClO) were intensively studied. The mechanism of bleaching consists in hypochlorite ion' attack on the aromatic ring and olefinic side chains of lignin when a phenoxy radical is formed that facilitates lignin oxidation with carboxyl- and carbonyl-based fragmentations, and CO_2 releasing.

In the same time, cellulose can be affected by the chemical reactions when the functional hydroxyl groups can be transformed first in carboxyl and then in carbonyl groups, and polysaccharides degrade. Figure 1 evidenced the NaClO change on the quinone type of lignin, simultaneously with decomposing the aliphatic side chain.

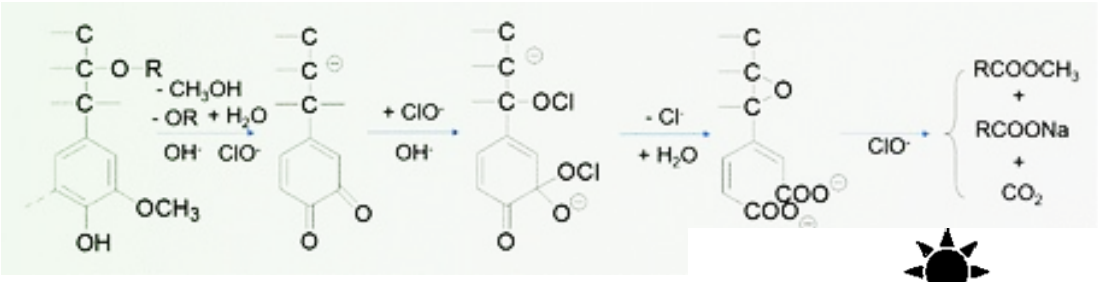


Figure 1. Pulp delignification using NaClO *[12]*

In this work, the photobleaching induced by solar light of a lignocellulosic biomass using NaClO was studied. The changes of L*a*b parameters, can be considered a proof of the reactions generated by hypochlorite radicals during solar light exposure, leading to a biomass whitening before using it in the paper industry.

2. EXPERIMENTAL PART

The photobleaching process of LC was carried out by using sodium hypochlorite (Chimcomplex, Romania), 20% solution in distilled water, as the oxidizing agent. A quantity of 60 ml of oxidizing agent was added to 1g of grounded sample, the solution being kept for 0.5h at room temperature and then irradiated with sunlight (1450 W/cm^2), in a glass reactor with quartz window, to initiate the radical reaction of lignin structure modification, Figure 2. Samples were collected at 30, 40, and 60 minutes of exposure, in order to motorize the oxidation process. The separation from the solution was done by vacuum filtration, washing with distilled water 5 times and drying the sample at room temperature.

The chromatic parameters before and after each bleaching process have been recorded with a Chroma Meters CR-410 colorimeter (Konica Minolta, Tokyo, Japan). The measurements were expressed according to the International Commission on Illumination (CIE) L*a*b* system. The total color differences $\Delta E^*_{x\ ab}$ was estimated according to ASTM 2244 [13], and calculated using Equation (1):

$$\Delta E^*_{x\ ab} = \sqrt{(\Delta L^*_x)^2 + (\Delta a^*_x)^2 + (\Delta b^*_x)^2} \qquad (1)$$

where, ΔL^* is the difference in lightness ($\Delta L^* = L^*_{bleached} - L^*_{native}$), Δa^* is the chromatic deviation of the a coordinates (red and green color) ($\Delta a^* = a^*_{bleached} - a^*_{native}$), and Δb^* is chromatic deviation of the b coordinates (yellow and blue color) ($\Delta b^* = b^*_{bleached} - b^*_{native}$).

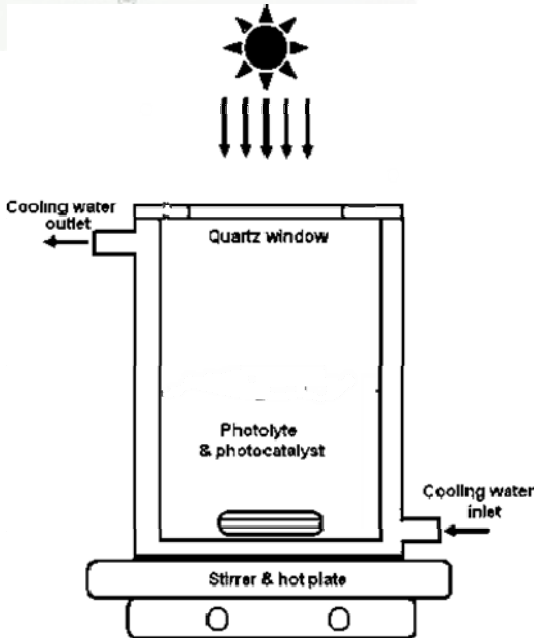


Figure 2. Schematic representation of the photobleaching process

The kappa number of the pulp, determined before and after the sunlight exposure, was used to analyze the delignification process. The kappa number is defined as the amount of potassium permanganate solution (0.02 mol/l) consumed by 1g of oven-dried pulp. Its value is determined in the conditions established in ISO 302:2004 [14]. A specific amount of dried pulp was first disintegrated into distillated water. Then, a mixture of potassium permanganate solution (0.02 mol/l) and sulfuric acid solution (2 mol/l) was added to the aqueous suspension and the reaction was terminated by adding potassium iodine solution (1 mol/l). The free iodine was then titrated with sodium thiosulphate (0.2 mol/l) in the presence of starch indicator. The temperature was monitored throughout the analyze in order to a temperature correction of kappa number value.

The ATR-FTIR spectra were recorded using a GX-type FTIR spectrometer (Perkin Elmer) from 4000 to 400 cm-1 include a resolution of 4 cm-1 with 32 cycles.

The DR-UV spectroscopy was conducted using a T60 UV–VIS spectrophotometer (PG Instruments, Lutterworth, UK) with split-beam technology, a sample analyzer, and a monochromator in a Czerny–Turner mount 1200 lines/mm. A spectral range of 190–1100 nm was utilized with a $BaCO_3$ pellet serving as a white reference standard. The analysis took place at a controlled temperature of 25 °C.

3. RESULTS AND DISCUSSION

The schematic representation of the solar-driven bleaching process, evaluated by chromatic changes, is shown in Figure 3. As can be observed, the samples' visible appearance is significant changed, the samples become more porous, with a higher surface area due to the bleaching effect on the fibers' cell wall by removing residual lignin and its chromophores [15]. The color is modified from light brown to a dirty white tone, the color tone varying with the exposure time. After 30 minutes of sun exposure, the color is very less modified, with a slightly whitening degree. The higher difference of color as compared to the initial sample, can be observed for the LC specimen exposed to the sunlight for 40 minutes. For the maximum exposure time, of 1 hour, the change in color is medium. Possible secondary reactions occur and hamper the bleaching process.

By measuring the CIELab parameters, the changes in lightness, green-red (a*) and blue-yellow (b*) color coordinates that could sustain the visible color modification can be achieved. In Figure 4, the values variation of the chromatic parameters of LC samples with the exposure time can be observed.

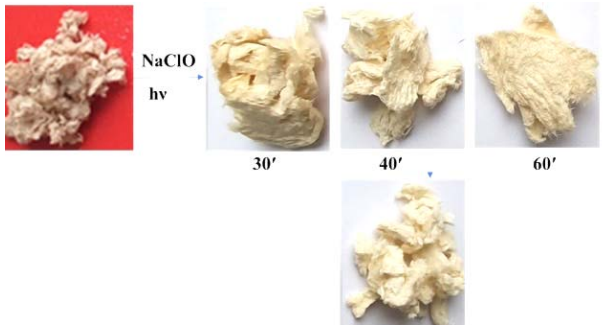


Figure 3. The aspect of photobleached samples

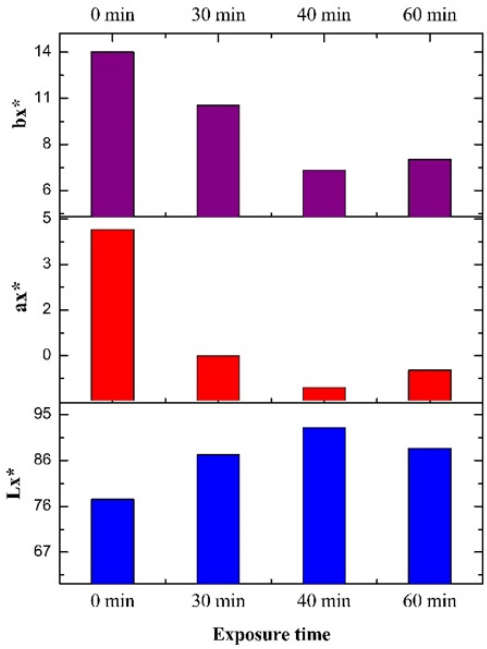


Figure 4. CIELab parameters of initial and exposed samples to sunlight

Lighter color is obtained after sunlight exposure. L_x^* parameter increase with 12-14% for the specimens exposed 30 and 60 minutes to UV radiation and with 17% as compared to initial color for the sample kept 40 minutes in sunlight. For this latter sample, the lightness value is above 90, showing the proximity to white. The value of the a_x^* parameter characterize the change in color tone, the exposed samples being more reddish than the initial one. Another important change in samples' color is evidenced by b_x^* value, the yellow shade being the most marking in the initial sample appearance. The important decrease of the parameter value can be considered for LC bleaching. After 30 and 60 minute of sun exposure, the blue-yellow factor decreases with 23% and 45% respectively. The most significant change in yellowness is observed after 40 minutes exposure when

the reduction is with more than half as compared to the control sample.
Using the CIELab representation, the change in color can be expressed more accurate, Figure 5, being evidenced the transition to higher L^* and lower a^* and b^*.

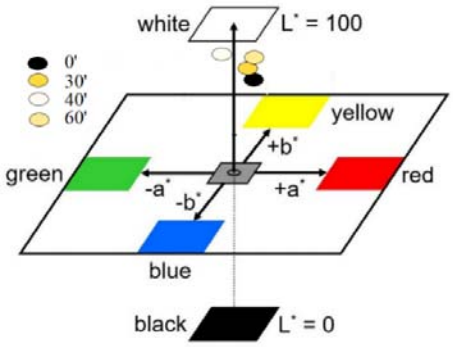


Figure 5. CIELab schematic representation of samples' color

The total color differences calculated based on L*, a*, b* parameters are presented in Figure 6. It can be observed that the highest change results for the sample exposed 40 minutes. To mark the correct color tone and the saturation of the specimens' color, hue angle h_{ab} and Chroma G were calculated and represented using the exposure time, according to equations (2) and (3):

$$h_{ab} = \tan^{-1}\frac{b*}{a*} \quad (2)$$

$$C^*_{ab} = \sqrt{(a)^2 + (b^*)^2} \quad (3)$$

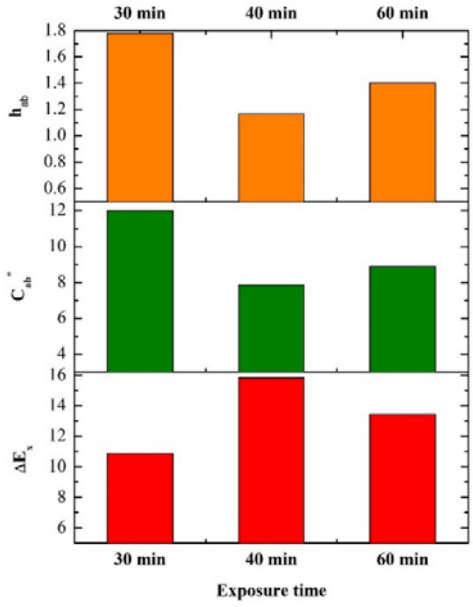


Figure 6. Variation of the total color change, chroma G, and Hue angle

The values of hue angle and Chroma are in accordance with the above-mentioned conclusions. The smallest value of h_{ab} characterize the less yellow sample and the smallest C_{ab}^* is a proof of the closest value to L-axis.
The change in these color parameters can be considered a proof of the bleaching process using NaClO and UV light.

As well-known, lignin is a cross-linked aromatic macromolecule, hydroxylated and methoxylated, that impart to LC the color, besides the resistance to biological attack with its high structural rigidity and important chemical resistance [11, 16]. The variation of lignin content during the experimental procedure of photobleaching with sodium hypochlorite solution was estimated using the kappa number. The measured valued are presented in Table 1.

Table 1. Kappa number variation with the exposure time

Sample	Kappa number
0 min	28.44
30 min	18.88
40 min	11.51
60 min	13.43

The kappa number of bleached LC pulp decrease substantially after 30 minutes of exposure, with approx. 34%, so a high content of lignin was removed in the first period of time. By maintaining the samples to sunlight, the mechanism of blocking the lignin chromophores was continued with lignin removing, until a kappa number with more than 50% lower compared to the initial LC pulp. In accordance with the colorimetric analysis, the lowest kappa number results for the specimen irradiated for 40 minutes. The maximum bleaching time seems to be this latter time interval, after 40 minutes secondary processes occur and chromophores groups are restored.

Spectroscopy is a useful non-invasive, high throughput technique that can provide important qualitative and quantitative results, with easy sample preparation and small trial amount. The most important absorptions given by LC, initial and exposed to sunlight in NaClO presence, according to literature [17, 18], are presented in Table 2 and Figure 7.

Lignin removal from LC pulp after NaClO beaching can be proved by the most important peaks specific for lignin, cellulose and hemicellulose that have intensities lower, influenced by the exposure time. The absorption of 1600 cm^{-1} band decrease with 12.5% than for initial LC for 40 minutes exposed sample. In fact, all the bands recorded in FTIR spectra have intensities lower for 30 and 60 minutes, and the lowest being noted for the specimen 40' exposed.

The lignin content was quantified using the ratio between the lignin 1600 cm^{-1} band and cellulose 1096 cm^{-1} band [19, 20]. Lignin index decrease from 1.22 in the initial LC, to 1.16 and 1.14 for samples exposed to sunlight for 30, 60 minutes respectively, and to 1.10 for the whitest specimen.

Table 2. The intensity of the LC most important peaks before and after bleaching

Peak / Sample	Absorption, a.u			
	Initial	30‘	40‘	60‘
3314: O-H stretching vibration	0.91447	0.88206	0.84696	0.87863
2880: C–H stretching vibration	0.94281	0.92231	0.89994	0.92276
1635: O-H bending from the absorbed water	0.9508	0.93269	0.91728	0.9352
1600: aromatic skeletal vibration in L – COO- stretching in H	0.98259	0.92901	0.86227	0.92565
1508: aromatic skeletal vibration in L	0.94439	0.94392	0.92184	0.93798
1420: C-H bending in CH_3 for L – O-H in place bending for H/C	0.92104	0.90353	0.86714	0.90596
1320: C–H-bending vibration in L - O-H in place bending for H/C	0.91309	0.88592	0.85833	0.88632
1170: asymmetric stretching C1-O-C4’ for H/C	0.91226	0.89029	0.86502	0.89235
1106: carbonyl stretching vibration for L and aromatic ring	0.84537	0.80319	0.7598	0.80101
1096: C2-O2H stretching for H/C	0.81106	0.80173	0.78258	0.80919
896 (C-O-C stretching at β-glycosidic linkages in H/C)	0.88413	0.84536	0.81559	0.85138

L-lignin; H-hemicellulose; C-cellulose

The main photo yellowing mechanism of lignin-based materials can be divided into three steps [21]:

1. Energy absorption (UV/Vis radiation) by photo-activation of lignin groups.

2. Forming intermediate structures, as for example, phenoxyl radicals.

3.Forming chromophores from the previous intermediates that could absorb the visible light.

In addition, other reactions, not necessarily involving phenoxyl radicals, could influence color formation and lignin photodegradation.

The UV–Vis spectra corresponding to the lignocellulose solutions upon irradiation time, in the 250-350 nm domain, are represented in Figure 8. An absorbance that supports a bathochromic shift is observed. Furthermore, a decrease of the absorbance value with increasing the photobleaching time, as compared to the control sample, sustain the previous results. This reducing of absorbance can be considered another proof of the photodegradation of the lignocellulosic material. According to literature, a partial demineralization process of organic part and the formation of compounds with less absorbing properties are related to LC photodegradation [22, 23].

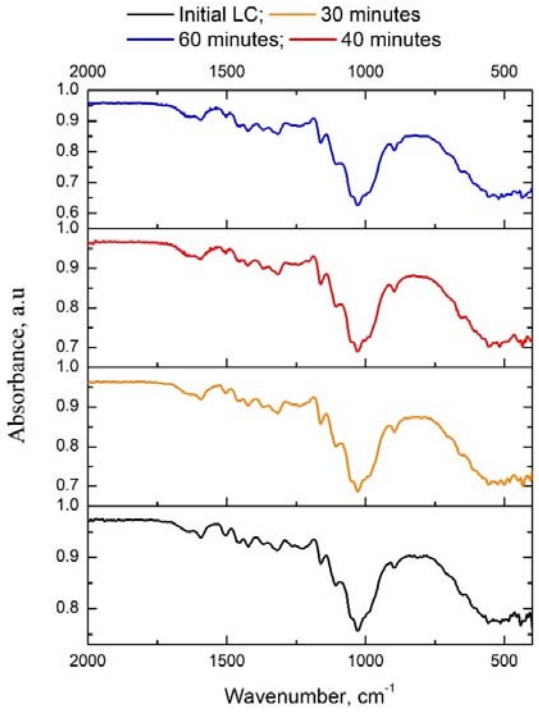


Figure 7. The FTIR spectra of initial and photobleached samples

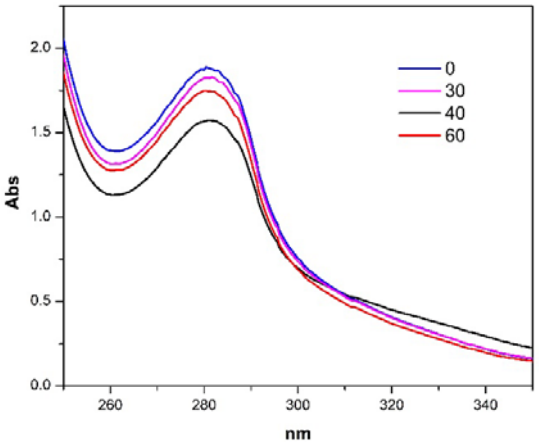


Figure 8. The UV absorption spectra changes of lignocellulose suspension under solar light irradiation

Correlating the results, it can be concluded that NaClO can be used for LC bleaching, process activated by the sunlight, with maintaining the time moderate.

Due to the complexity of lignin, analyzing lignin in the solid state is difficult (due to its complex structure and interference with other components) and efforts to isolate lignin without affecting the chemical structure often have a low yield due to oligomerization and reactions with the substrate.

4. CONCLUSIONS

The lignocellulose biomass was photobleached by solar light irradiation in the presence of NaClO. The irradiation conditions have been established in this paper, by UV-Vis absorption spectra, FTIR spectra, colorimetric data, and kappa number determination.

As observed based on the visual aspect of samples after irradiation, lighter color is obtained after sunlight exposure of LC samples. As compared to the initial sample, the higher difference of color is observed for the LC specimen exposed to the sunlight for 40 minutes.

The values of hue angle and Chroma are essential in these experiments. The smallest value of h_{ab} characterize the less yellow sample and the smallest C_{ab}^* is a proof of the closest value to L-axis. The change in these color parameters can be considered a proof of the bleaching process using NaClO and UV light.

The kappa number of bleached LC pulp decrease substantially with sunlight exposure, with maximum decrease at 40 minutes. Also, the lignin index decreases from 1.22 in the initial LC, to 1.16 / 1.14, and 1.10 for the whitest specimen. An absorbance that supports a bathochromic shift is observed based on UV-Vis spectra.

Based on this study, the solar-driven photobleaching of lignocellulose biomass using NaClO can be considered as an efficient method of conditioning the raw material before using in pulp and paper industry.

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