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Dyeing Capacity of *Eucalyptus globulus* L. on Chemical Pulp: An Overview

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This paper presents a study on the dyeing capacity of *Eucalyptus globulus* L. bark on chemical pulp. *Eucalyptus globulus* L. bark is a natural source of polyphenolic compounds such as tannins and flavonoids, which are natural colourants. First of all, the effect of the bark granulometry on dyeing capacity was investigated. The greater dyeing capacity noted in the range between 1.4 and 1.0 mm. Subsequently, the effect of conventional aquatic extraction and ultrasound assisted extraction were studied in a wide range of different conditions such as temperature and residence time. Ultrasound assisted extraction gave evidence of being the most effective method. Furthermore, the effects of conventional dyeing (impregnation of the pulp in the dye bath) and ultrasound assisted dyeing were evaluated, with the last one showing a significant improvement of dyeing capacity. Also, the effect of the change in the ratio of the weight of extractable quantity of the plant to the weight of dry pulp on the dyeing capacity of eucalyptus was examined. In addition, tests about the colour stability took place by measuring the colour difference of the dyed paper in several time periods. The estimation of dyeing capacity occurred through the determination of colour coordinates of the dyed paper, according to CIE L*a*b* system. By controlling these parameters we can optimize the dyeability of chemical pulp which is critical for the paper industry.

1. Introduction

Since the beginning of the 20th century, dyes are produced almost exclusively from by-products of the petrochemical industry, such as alizarin and other aromatic derivatives. Until then the synthesis of dyes was based on natural resources, mainly plants. Nowadays there is a worldwide resurgence of interest in natural dyes. This trend is based firstly on the fossil fuel depletion and the widespread turn to the renewable sources and secondly on the increasing public awareness of the environmental and health hazards related to the synthetic dyes (Gilbert, et al. 2001). In the frames of this work the investigated natural resource was the *Eucalyptus globulus* L. bark, which contains great quantity of tannins and flavonoids, colourants that gives yellowish-brown hues (Bechtold and Mussak, 2009; Nisar and Hussain, 2007; Mongkholrattanasit, et al. 2011).
The application of natural dyes in paper industry shows great importance considering their limited resistance against leaching, which is the case of paper recycling. Furthermore, the study of dyeability of chemical pulp is very important as it consists almost the 70% of the worldwide produced pulp from wood annually, because of the improved properties paper that produces. Moreover, studies have shown that the absence of lignin in chemical pulp leads to the need of using larger amounts of dye in

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order to obtain the required colour comparing with mechanical pulp (Bechtold and Mussak, 2009; Drzewinska, 2009). Thus, the optimization of chemical pulp dyeing is a matter of further study.
According to the literature there are great evidence that different drying, extraction and dyeing methods affect drastically the dyeing capacity of various plants (Socaciu, 2007; Sivakumar, et al. 2011). The scope of this work was the evaluation of all these parameters on the dyeing capacity of Eucalyptus globulus L. bark on chemical pulp.

2. Materials and methods

2.1 Materials

Chemical pulp originated from spruce softwood was used. The supplied chemical pulp was torn into small pieces by hand and added into deionized water (2 % w/w mixture consistency).Then, vigorous mixing of the resulting mixture took place for 6 h using a mechanical mixer at 2000 rpm. After filtration, the produced pulp had moisture content of 92 % w/w and was stored in an airtight plastic pot at 4 ^{o}C.
The bark of *E. globulus* L. is a great source of natural dyes as it contains numerous dyestaff components such as tannins and flavonoids, with most important the eriodictyol, naringenin, quercetin, rhamnazin, rhamnatin and taxifolin (Mongkholrattanasit, et al. 2011; Nisar, et al. 2007). Moreover, it consists forest industry residue, which means zero supply cost and zero environmental impact. The bark was air dried in dark place at room temperature (~ 45 % Relative Humidity), ground in several sizes (Fritsch Cutting Mill Pulverisette 15) and stored in dark and dry place. Moreover, grain size classification took place, using the Fritsch Vibratory Sieve Shaker Analysette 3 Spartan (measuring range: 19.1 - 0.063 mm, sieving time: 10 min, middle amplitude).

2.2 Extraction

For the production of the natural dyes, conventional and ultrasound assisted aquatic extraction took place. In the case of conventional extraction, the examined extraction conditions varied from 40 to 80 ^{o}C extraction temperature (T_e) and from 15 to 60 min residence time (t_e), all the possible combinations were examined. On the other hand, in ultrasound assisted extraction the experimental conditions varied from 25 to 80 ^{o}C T_e and from 5 to 15 min t_e. A Vibre-Cell VC 750 ultrasonic processor set at 250 W and 20 kHz was used during the ultrasound assisted extraction.
In both cases, specific amounts of the ground bark were extracted with 125 mL of deionized water. In each experiment the determination of the specific amounts of extracted plant material resulting from the Φ/X ratio, which derives from the oven dry weight of the extracted plant material divided by the oven dry weight of the pulp dyed with the plant extract. The final extract obtained after filtration of the insoluble residues through a copper filter fabric.

2.3 Dyeing

All the produced extracts were used for the dyeing of chemical pulp. Conventional and ultrasound assisted process took place. The simple impregnation of the pulp in the dyebath is defined as conventional dyeing. In this case, the dyeing conditions varied from 25 to 80 ^{o}C dyeing temperature (T_d) and from 15 to 60 min residence time (t_d). For the ultrasound assisted dyeing the prementioned ultrasonic processor was used in the same settings. The examined conditions in this case varied from 25 to 80 ^{o}C T_d and 5 to 15 min t_d. In both cases, the dyeing was realised using a liquor ratio of 55:1 ml/g.

2.4 Handsheet formation

Isotropic handsheet derived from dyed and undyed pulp were formatted according to SCAN-C-26:76 and SCAN-C-M5:76 methods using the Lorentzen and Wettre standard equipment (sheet former model SCA, sheet press and rapid dryer). The characteristics of the produced handsheets are 155 mm diameter and 1.8 ± 0.05 g oven dry mass. The handsheets were stored in a dark and dry place for at least 24 h before their colour determination.

2.5 Colour measurement

The colour of the produced sheets was determined according to CIE L*a*b* system using a Dr. Lange colourimeter. The final dyeing result derived from the total colour difference ΔE^*_{ab} between each dyed sheet and a reference sample (undyed sheet). The total colour difference is given from the following equation:

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

where $\Delta L^* = L^*_{sample} - L^*_{reference}$, $\Delta a^* = a^*_{sample} - a^*_{reference}$ and $\Delta b^* = b^*_{sample} - b^*_{reference}$

3. Results and Discussion

Savvidou M. and Economides D. (2006; 2007) showed that severe extraction and dying conditions ($T_e = T_d = 80$ ^oC and $t_e = t_d = 60$ min) give tense dyeing result. Moreover, they introduced the term “limiting saturation value”, which describes the fact that beyond this limit any increase of the Φ/X ratio is unable to cause any further colour change, as the pulp fibers cannot absorb any more dye. Papadaki et al. (2012) showed that even in mild conditions the limiting saturation value for *E. globulus* L. bark is around Φ/X = 1.4. Therefore, the experiments for optimization of grain size, extraction and dyeing method occurred with extracts produced at Φ/X ratio of 0.4 and 0.6 units, respectively. By avoiding the saturation limit, every colour change would be significant.

In Figure 1, the effect of grain size on the ΔE^*_{ab} is presented at severe conventional extraction and dyeing conditions. According to this Figure, the optimum grain size ranges from 1.4 to 1.0 mm. The decrease of ΔE^*_{ab} as the grain size increases is significant. The ΔE^*_{ab} could be tripled by using the optimum grain size. From this point all the experiments occurred at the optimum grain size.

In Figure 2, the effect of conventional and ultrasound extraction on ΔE^*_{ab} in various conditions is presented. According to Papadaki et al. (2012), an efficient pair of conventional dyeing conditions is $T_d = 25$ ^oC and $t_d = 30$ min, so the study of extraction conditions occurred in combination with these dyeing conditions. The ultrasound assisted extraction is preferred as in mild conditions such as $T_e = 25$ ^oC and $t_e = 10$ min show the same dyeing result as in the case of conventional extraction at high temperature and residence time. Moreover, these mild conditions ensure a low cost operation with minor environmental impact.

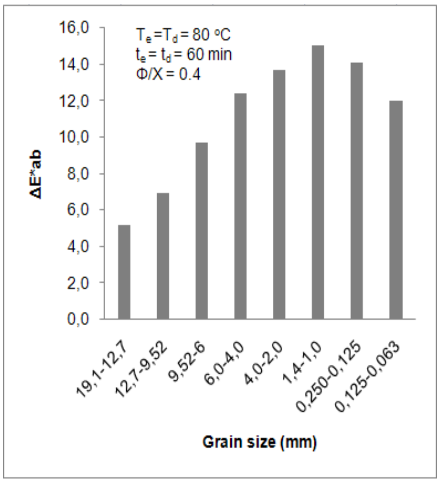

Figure 1: Grain size effect on total colour difference (ΔE^*_{ab}) at severe extraction and dyeing conditions.

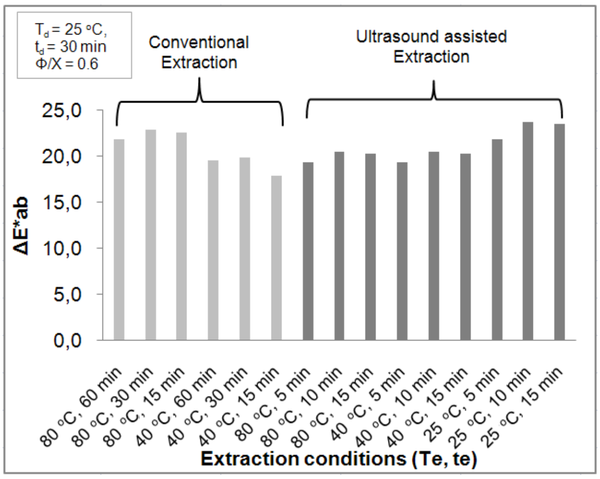

*Figure 2: Effect of extraction methods on total colour difference (ΔE*ab) in various conditions.*

The effect of the dyeing method on the ΔE^*_{ab} in various conditions is presented in Figure 3. Referring to this Figure, the ultrasound assisted dyeing shows significant dyeing result in extra mild conditions, even for $t_d = 10$ min. Therefore, ultrasound dyeing is preferred from conventional one despite the fact that the second at severe conditions presents better dyeing result. After this study, it is interesting to present the dyeing result for the most effective and less effective combination of extraction and dyeing conditions (Figure 4). The effectiveness refers not only to the strongest dyeing result but also to the low cost and environmental impact (milder conditions).

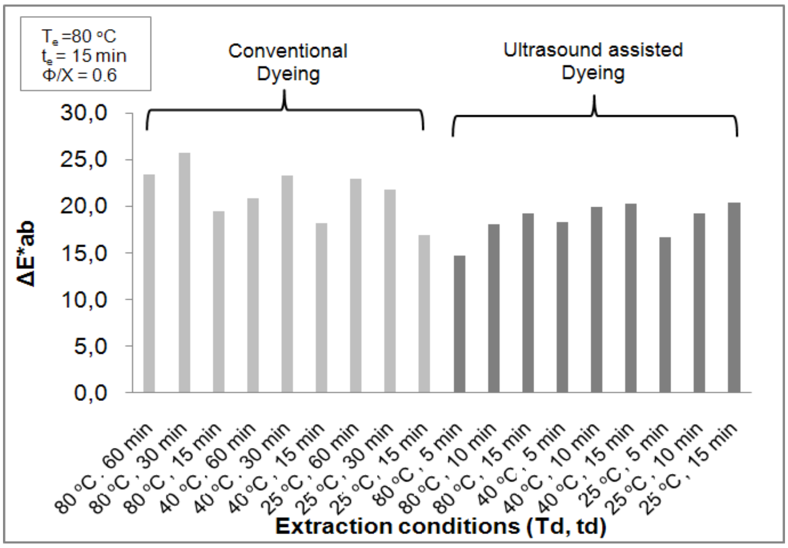

Figure 3: Effect of dyeing methods on total colour difference (ΔE^*_{ab}) in various conditions.

The colour stability against ageing was also examined as it is presented in Figure 5. Relatively mild conditions of conventional extraction and dyeing were selected in order to study the colour stability. Colour measurements took place on dyed handsheets four days and one month after their dyeing. According to Figure 5, the dyeing result of *E. globulus L.* bark on chemical pulp show significant stability against ageing.

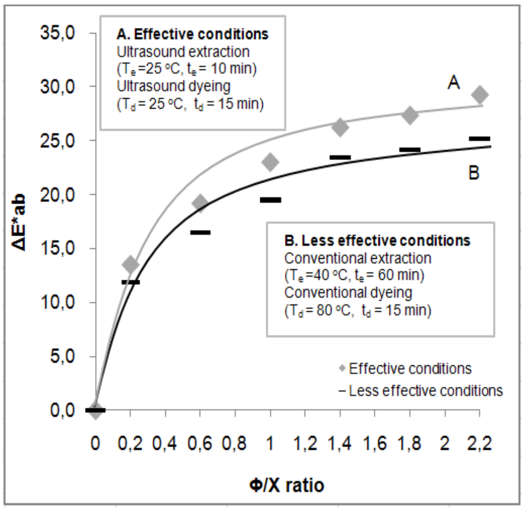

Figure 4: ΔE^*_{ab} related with the Φ/X ratio, comparison of effective and less effective conditions.

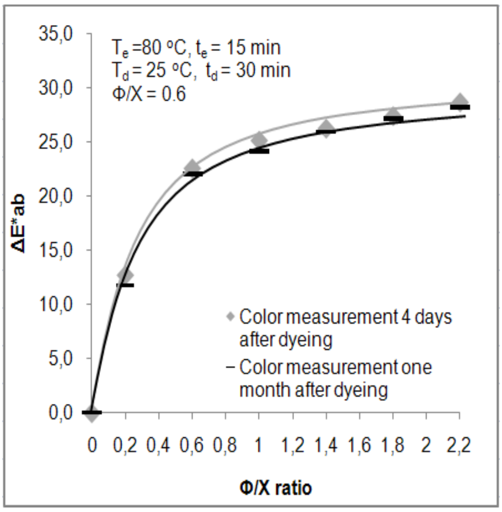

Figure 5: Colour stability against ageing.

Moreover, the effect of extraction methods on achieved colour shades is presented in an a*b* plot

(Figure 6). As it was expected the chromatic coordinates show higher values as the conditions turn severer. According to Figure 3, in the case of conventional dyeing a lower ΔE^*_{ab} is observed at T_d = 40 and 80 ^oC for 60 min t_d, than at shorter t_d (30 min). This fact may be due to the destruction of some colorants at high t_d values. In the case of even shorter t_d the dyeing result is very weak. On the other hand, in the case of ultrasound assisted dyeing the ΔE^*_{ab} increases with the increase of t_d, while strong dyeing result even in short t_d is observed. The above observations would be better justified in Figure 7, where the effect of dyeing process on color coordinates a*b* is presented. From Figures 6 and 7, it turns out that *Eucalyptus globulus* L. bark gives yellowish-brown hues on dyed chemical pulp as the experimental points move in the yellow – red area of the a*b* plot.

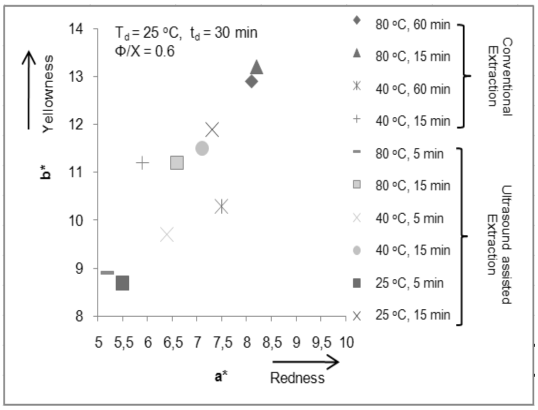

Figure 6: The impact of extraction methods on colour shade of dyed chemical pulp in various conditions.

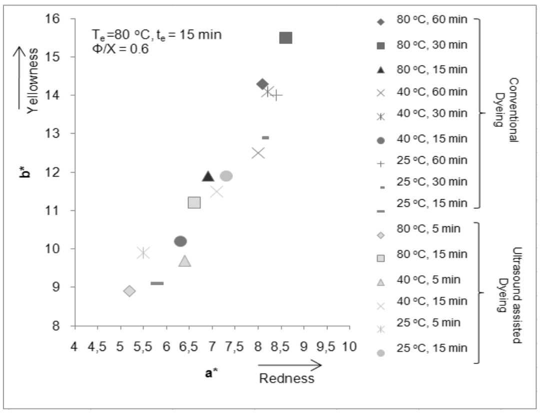

Figure 7: The impact of dyeing methods on colour shade of dyed chemical pulp in various conditions.

4. Conclusions

In the frames of this work, the optimization of crucial factors that affect the dyeing capacity of *E. globulus* L. bark on chemical pulp was occurred. The presented results prove that the *E. globulus* L. bark can be used as a source of natural colourants for the chemical pulp.

According to this study, the grain size affect drastically the dyeing capacity of the bark and the optimum grain size was experimentally determined in the range of 1.4 and 1.0 mm. Furthermore, the relatively low dyeing temperature and short extraction residence time that were achieved show great industrial interest because of their low cost and environmental impact. At this point, it is important to notice that in both cases of extraction and dyeing, the ultrasound assisted processes gave strongest dyeing result in shorter time and lower temperature in comparison with the conventional ones. Additionally, in this case "the limiting saturation value" was achieved in lower Φ/X ratios. Moreover, the dyed handsheets showed great colour stability in ageing, a fact that presents the *E. globulus* L. bark as a promising dyestuff material with application mainly in packaging products.

For further study, the use of other technologies such as microwave on the extraction and dyeing process or different drying methods of the dyestuff material are suggested. In this case, the achievement of tense dyeing result is expected at even lower temperature, shorter residence time and lower Φ/X ratio.

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