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Application of Forest Byproducts in the Textile Industry: Dyeing with Pine and Eucalyptus Bark Extracts †

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Abstract: The main by-product generated in the forestry industry is bark, derived from the debarking process. Pinus and eucalyptus are nowadays two of the most important tree species exploited by the forestry industry in southwestern Europe. This work investigates the application of Maritime pine (*Pinus pinaster* Ait.) and Eucalyptus (*Eucalyptus globulus* Labill.) barks as a source of high polyphenolic content extracts, to be used as natural dyes in the textile industry. We demonstrated that it is possible to use the extracts obtained from both forest by-products as textile dyes without need for using any metallic mordant.

Keywords: natural dye; bark; pine; *Eucalyptus*; forest byproducts; polyphenols; tannin

1. Introduction

High water consumption, together with the use of synthetic dyes and metallic mordant agents, contribute to the high environmental impact of the textile industry. Numerous investigations have focused on the search for more sustainable raw materials and processes for this sector. One of the most promising solutions is to look towards forest by-products as a sustainable source of fibrous raw materials to substitute plastic fibers and replace partially cotton. In addition, forest by-products could also be a good source of natural dyes and textile additives, replacing synthetic ones. The main by-product generated in the forestry industry is bark, derived from the debarking process. Pinus and eucalyptus are nowadays two of the most important tree species exploited by the forestry industry in southwestern Europe. *Eucalyptus globulus* Labill. bark has shown to be a valuable source of extracts with high content of hydrolysable tannins, and especially of gallotaninns, similar to those present in commercial tannic acid [1,2]. Pine bark probably is one of the most investigated raw material to obtain extracts with high polyphenolic content, highlighting the presence of condensed tannins [3] with applicability as a component of adhesives [4], or biopolymers [5]. Recent studies have shown that tannins and tannic acid could be an interesting alternative to metallic mordant in the dyeing industry[6].

This work investigates the application of Maritime pine (*Pinus pinaster* Ait.*)* and the Eucalyptus (*Eucalyptus globulus* Labill.) barks as a source of high polyphenolic content extracts, to be used as natural dyes in the textile industry. Extraction was performed with water in alkali conditions. The influence of the extraction conditions to obtain the extracts used as natural colorant and the dyeing conditions (pH, temperature, use of mordant) on the properties of the dyed textile sample was evaluated. It was shown that the pH and the extraction conditions used were the variables with the greatest influence on the final properties of the dyed textile. In addition, this work also demonstrated that it is possible to use the extracts obtained from both forest by-products as textile dyes without need for using any metallic mordant.

2. Material and Methods

2.1. Raw materials

Eucalyptus globulus Labill. (EB) and *Pinus pinaster* Ait. (PB) bark were grounded in a cutting mill (Retsch, Haan, Germany) equiped with a 4 mm sieve. The products were oven-dried at 60 °C until attaining the equilibrium moisture content. Then the PB and EB particles were subjected to a vibratory sieve shaker (Retsch, Haan, Germany). The particles between 0.5 and 2 mm were selected as raw material to obtain the extracts. These were the used for dyeing 100% cotton knit samples. The textile samples were supplied by TINTEX-TEXTILES, S.A. Sodium hydroxide was provided by Acros Organics (New Jersey, USA), and Sodium sulphite anhydrous by PanReac AppliChem (Barcelona, Spain.)

2.2. Extraction

The extractions were performed using only water as solvent, avoiding the use of organic compounds. As extraction agents were sodium hidroxide and sodium sulfite. The bark particles and water were mixed at room temperature, heated and, once the selected temperature was reached, the alkali was added. After the selected contact time, the suspension was vacuum filtered and the extracts were concentrated in a rotary evaporator (BÜCHI, Flawil, Switzerland). The extraction conditions tested are shown in Table 1:

Table 1. Extraction conditions on the extraction yield.

Raw material	Extraction agent NaOH(%)	Na_2SO_3(%)	Temperature (°C)	S/L	Time (min)	ID code
Eucalyptus Bark	1	1	95	1/15	60	EB_{E1}
Eucalyptus Bark	1	1	80	1/10	30	EB_{E2}
Pine Bark	5	2.5	80	1/5	30	PB_{E1}
Pine Bark	1	2	60	1/5	30	PB_{E2}

S/L: Solid liquid relation

The extraction yield was calculated by measuring the weight difference between the initial dry material weight and the final residue dry material (Equation 1).

$$\boldsymbol{EY}(\%) = \frac{\boldsymbol{Raw\ material}(\boldsymbol{g}) - \boldsymbol{Residue\ material}(\boldsymbol{g})}{\boldsymbol{Raw\ material}(\boldsymbol{g})} \times \mathbf{100}, \textbf{Eq. 1}$$

2.3. Dyeing process

The dyeing of the cotton knit samples was carried out using the concentrated extracts of pine and eucalyptus bark (at 10% concentration) as dyes, with a liquor ratio of 1/15 (mass of dry textile product / mass of dyeing solution). Samples were dyed in an ultrasonic bath (Sonorex Super RK 512 H, Bandelin, Berlin, Germany). Cotton knit samples of 5 ± 0.5 g were mixed with the dyeing liquor (2% g dry extract/ g textile sample) in a closed bottle

(500 ml) and placed in the ultrasonic bath, at the temperature and during the time defined for each test. Once the dyeing stage was finished, the dyed textile samples were washed first with cold water, then with water at 40 ± 5 °C and Cottoblanc STM (CHT Germany) as a soap agent, and finally with cold water. The influence of the extraction conditions used to obtain the extracts (Table 1), and the dyeing process conditions such as temperature (60-80 °C), the pH of the dyeing liquor (7-9) and the use of mordant with alum was tested.

2.4. Characterization of extracts by UV-VIS spectroscopy

The extracts were characterized using a FLEX-STD-UV-Vis (IS) 25 μm spectrometer; Light source LS-DW (Deuterium Tungsten); Transmission probe, 400 μm core diameter fibers, 200 cm, stainless steel (Sarspec, Vila Nova de Gaia, Portugal). The evaluation of the color of the dyed textile samples was carried out with the same spectrometer equipment using a reflectance probe, with 400 μm core diameter fibers and 1.5 m stainless steel with a standard probe holder measured at 45 degrees. Measurements were made in quintuplicate at certain points of the textile samples.

3. Results and Discussion

3.1. Extraction

Eucalyptus and Pine bark were extracted using an alkali extraction methodology, to obtain an extract solution with potential applicability in the dyeing process of cotton textile products. Thinking of a future industrial application and from an economic point of view, the viability of the process will be conditioned by the extraction yield of the process. Table 2 shows the extraction conditions influence on the extraction yield obtained.

Table 2. Extraction yield for different extraction conditions.

Nomenclature	Extraction Yield (%)
EB_{E1}	10.0 ± 1.2
EB_{E2}	5.1 ± 0.6
PB_{E1}	13.0 ± 2.3
PB_{E2}	7.14 ± 0.8

Regarding the values obtained, the highest extraction yield values were achieved when the "harshest" extraction conditions were used, in terms of temperature or percentage of extraction agent.

3.2. Characterization of extracts by UV-VIS spectroscopy

The two main tannin groups, condensed and hydrolyzable tannins, can be distinguished by their UV spectra. Condensed tannins present a single absorption maximum between 260 and 270 nm, while hydrolisable tannins have two absorption peaks at 255 and 365 nm [7].

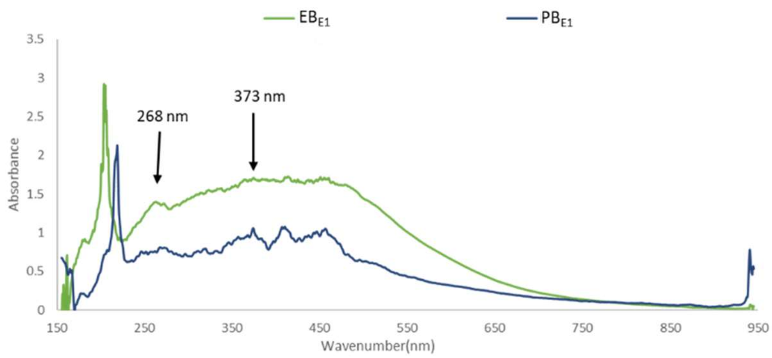


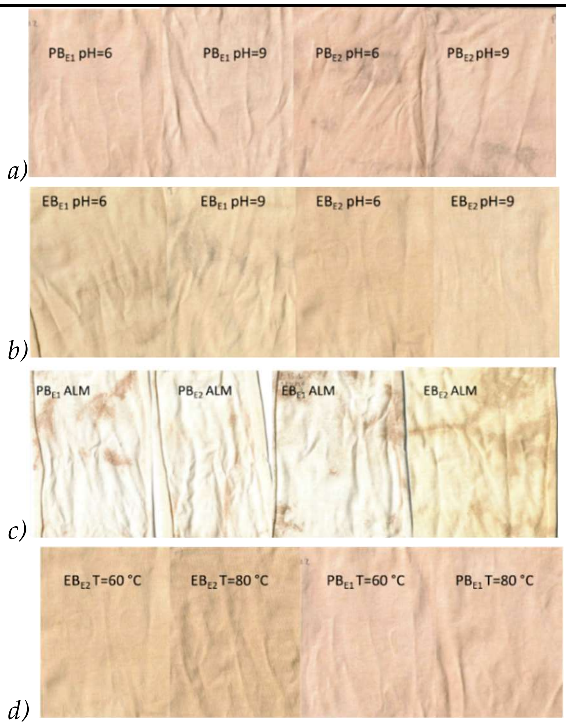
Figure 1. UV-VIS spectra of PB$_{E1}$ and EB$_{E1}$ extracts.

As shown in Figure 1, the pine bark extracts presented an absorption peak in the low wavenumber region, characteristic of condensed tannins. However, eucalyptus bark extracts showed a broad band that could be explained by the presence of a high proportion of gallotannins and ellagitannins that have an additional absorption maximum between 350 and 450 nm.

3.3. Dyeing with natural extracts

The first set of experiments was carried out to understand the feasibility of both extracts to be used as a colorant in the textile industry, together with the influence of the extraction conditions used. In a second stage, the dyeing conditions were tested. Figure 2 shows the textile samples dyed with pine and eucalyptus bark extract.

Figure 2. Cotton textile samples: (**a**) Dyed with PB$_{E1}$ and PB$_{E2,}$ pH influence; (**b**) Dyed with EB$_{E1}$ and EB$_{E2}$ pH influence; (**c**) Dyed with PB$_{E}$ and EB$_{E}$ Alum as Mordant influence, (**d**) Dyed with EB$_{E2}$ and PB$_{E1}$, Dyeing temperature influence.



pH unmodified, Dyeing conditions: S/L=1/15, 30 min, 60 °C. Values are presented as mean ± standard deviation (n=6).

Table 3. Color evaluation of the textile cotton samples dyed with EB_E and PB_E.

Samples / Dye	L*	a*	b*
Cotton textile sample	95.4 ± 2.0	0.9 ± 0.3	-3.3 ± 1.4
EB_{E1}	72.5 ± 9.3	16.1 ± 2.2	31.5 ± 4.0
EB_{E2}	69.1 ± 0.9	19.4 ± 0.7	29.8 ± 1.7
PB_{E1}	86.2 ± 4.9	19.79 ± 1.7	22.5 ± 4.6
PB_{E2}	72.1 ± 5.8	25.3 ± 2.2	18.1 ± 4.5

Table 3 shows the color of the dyed textile samples, in the CIELAB color space, evaluated by UV/VIS spectroscopy, using a reflectance probe with a standard probe holder measured at 45 degrees.

As for the influence of the extraction conditions, it was greater for the PB extracts than for the EB extracts. It was observed the appearance of stains in the dyed textile samples, which is an undesirable effect. The samples dyed with the EB_{E1} and PB_{E2} extracts were those with the highest number of stains.

The next step was to evaluate the influence of the dyeing conditions. Table 4 show the color changes produced by the variation in pH, the addition of alum as mordant, and the increase in dyeing temperature, respectively.

Table 4. Evaluation of the dyeing conditions: pH, Mordant and dyeing temperature influence.

Samples / Dye	L*	a*	b*
pH influence evaluation*[1]			

EB_{E1}	76.4 ± 2.6	11.9 ± 0.9	27.7 ± 2.0
EB_{E2}	77.6 ± 1.8	16.2 ± 0.7	23.1 ± 2.6
PB_{E1}	74.5 ± 6.2	21.9 ± 2.9	24.3 ± 10.7
PB_{E2}	53.5 ± 7.7	33.0 ± 4.1	37.9 ± 11.5
Alum influence evaluation*2			
EB_{E1}	93.0 ± 8.4	6.9 ± 0.3	0.9 ± 0.3
EB_{E2}	73.8 ± 12.9	11.6 ± 3.2	30.7 ± 18.3
PB_{E1}	94.5 ± 1.8	11.0 ± 1.6	1.2 ± 1.9
PB_{E2}	89.5 ± 3.2	10.7 ± 2.6	4.1 ± 4.4
Dyeing temperature influence evaluation*3			
EB_{E2}	64.1 ± 1.0	19.3 ± 1.5	23.9 ± 2.9
PB_{E1}	59.7 ± 1.4	29.3 ± 1.7	27.2 ± 3.4

Dyeing conditions: *1, pH= 9-10, S/L=1/15, 30 min, 60 °C; *2, pH= unmodified, S/L=1/15, 30 min, 60 °C, Alum 3 g/L; *3, pH= unmodified, S/L=1/15, 30 min, 80°C.

Table 4 shows the color evaluation of the cotton knit dyed with the PB and EB extracts using NaOH as alkali agent to increase the pH of the dye bath to a pH=9.5 ± 0.5. The solubility, viscosity and reactivity of pine and eucalyptus bark extracts is influenced by the pH [4,8,9]. Regarding this, the PB_{E2} extract was the one that presented the greatest variation due to the increase in pH, followed by the EB_{E2} extract. However, the influence of pH on the color achieved with the PB_{E1} and EB_{E1} extracts was low.

With respect to the mordant influence, alum produced the precipitation of the high molecular weight polyphenols present in the extract by complexation, due to the metallic character of the Alum, and this produced a poor distribution of the dye in the textile sample.

Finally, the dyeing temperature has shown an important influence on the final color achieved in the textile samples when PB extract was used in the dyeing process, but not when the EB extract was used.

The influence of dyeing conditions (pH, temperature) on the final color of cotton fabrics was low when EB extracts (with high hydrolysable tannin content) were used as dyes, which represents an important industrial advantage.

4. Conclusions

This work demonstrated that the valorization of the most important by-products generated by the forestry industry, such as eucalyptus and pine bark, is possible in the production of extracts with high applicability in the textile industry. In addition, this work also demonstrated that it is possible to use the extracts obtained from both forest by-products as textile dyes without the need to use any metallic mordant. Polyphenolic extracts have been used to protect against UV light in the development of body creams or in the treatment of wood due to their antioxidant properties. Future work will focus on evaluating the impact of this and other properties of the extracts on the dyed textile samples.

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Data Availability Statement: :Data is contained within the article.

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