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Eucalyptus globulus Bark as Source of Tannin Extracts for Application in Leather industry

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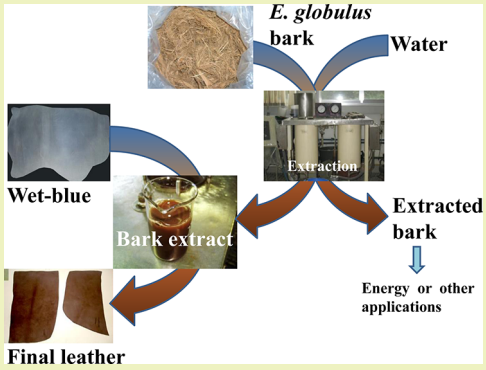
ABSTRACT: This paper reports the extraction of *Eucalyptus globulus* bark and a concentration strategy to obtain a phenolic-rich extract for application in the leather tanning industry. The profiles of total phenolic compounds (TPC) and tannins contents in water and dilute alkali as a function of extraction temperature and time led to the selection of the best conditions concerning extraction yield and selectivity. The selectivity profile for TPC and tannins was established, and a maximum of 20 g per kg of bark was found, representing 2.5 g per L of extract produced. On the basis of these results, the conditions selected to produce the extract for the application envisaged in this work were: water, 140 °C and 120 min. To increase the extract concentration, recirculation of the extracts over fresh bark (similar to a continuous bark extraction process) was performed and evaluated. The increment in phenolic compounds was about 4, attaining the final concentration of 8.6 g/L for TPC and 6.5 g/L for tannins. The final extracts showed leather retanning aptitude equivalent to a commercial extract of chestnut and revealed good performance in the production of leather articles like box-calf and nubuck.



KEYWORDS: *Eucalyptus globulus bark, Biorefinery, Phenolic compounds, Tannins, Water extraction, Retanning, Leather*

INTRODUCTION

E. globulus is the main wood species used in Portugal for the production of high quality pulp and paper, with an annual production of about 2 million tons of pulp.[1] In this industrial activity, around 0.2 million tons of bark are generated annually as byproduct, being directly burnt for power generation. However, this raw material can be considerably valorized through the extraction of high-value added compounds without compromising its conventional end use. This vision is in tune with the search for more favorable processes for upgrading different types of forest residues, in accordance with the new strategic objectives for the European Forest-Based Sector[2]. This will form the basis for a new forest-based value chain by the integration of the biorefinery-related processes in already existing industrial units and could significantly reduce actual dependence on oil-derived chemicals.[3−5]

The chemical composition of *E. globulus* bark is rather similar to that of wood, in concerns to the main structural components. Data reported in the literature refer to about 19−23 wt % of lignin, 42−55 wt % of cellulose, and 7−18 wt % of xylans.[6−8] However, some important quantitative differences concerning extractives turn unfavorable its incorporation in the pulping process. One of the most significant differences between bark and wood is their water and alkali soluble compounds. The values reported for hot water solubility and alkaline solution (1% NaOH) of *E. globulus* wood are 2−6% wt and 13−23% wt,[6,9] respectively; whereas for bark the range of values are 5−8% wt and 20−31% wt,[6,7] respectively. These differences clearly point out the high content of polar compounds of bark and foresee an exploitation potential of these fractions as sources of chemicals.

Several authors have been reporting yields and composition of the extracts obtained with different solvents and mixtures as methanol and methanol/water,[10−13] ethanol and ethanol/water, NaOH, and Na_2SO_3 aqueous solutions.[7,8,14,15] A variable range of yields has been reported depending of the extraction solvent and conditions and also on the quantification method. *E. globulus* bark contains simple phenolics (such as gallic acid, ellagic acid, protocatechuic acid) and derivatives,[16] flavonoids,[13] and more complex polyphenolic compounds, such as ellagitannins (hydrolyzable tannins)[11,17] and proanthocyanidins (condensed tannins).[8] Therefore, *E. globulus* barks can be considered a promising source of phenolic compounds for several applications.

Phenolic compounds could find a wide range of valuable applications such as antioxidants[18−20] and as bioactive components;[8,21,22] in particular, tannins have been referred in applications where the capacity of complexing metal ions and

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proteins is the chief mechanism, such as clarification of beverages, antimicrobial activity, and leather tanning.[23]

"Leather tanning" is a general term for the numerous processing steps involved in converting animal hides or skins into finished leather. First, the hides are processed in successive unit operations aiming to clean and prepare them for tanning. Tanning is the process that converts the protein of the raw hide or skin into a stable material that will not putrefy and is suitable for a wide variety of end applications. The tanning chemical process consists, roughly, in the linkage of tanning agent to the functional groups of collagen, the main leather component, imparting it physical and chemical resistance. Therefore, the tanning effect depends mainly on the extent of cross-linking between collagen macromolecules and the thermodynamic stability of the new bonds. The most commonly used tanning agent is chromium(III) sulfate, which imparts the leather with a pale blue color after tanning. Chrome-tanned leather obtained is called wet-blue. Then, the wet-blue pieces follow to the crusting process where they are retanned, dyed, and fatliquored. The tanned leather is retanned with the general objective of getting the fullness and roundness and other important properties of leather for its final use.[24]

Vegetable tannins (e.g., mimosa, chestnut tree, and quebracho extracts) and syntans (synthetic tannins) have been used for leather tanning and retanning.[25] The tanning activity of these agents is therefore related with multiple hydrogen-bonding and/or ionic interactions with the protein functional groups.[24,25] The aim of this work is to produce an aqueous extract of *E. globulus* bark with suitable composition and concentration for application in leather retanning as an alternative to the conventional vegetal extract.

EXPERIMENTAL SECTION

Bark was collected at the end of the debarking process of a pulp mill using *E. globulus* as the raw material, and it was air-dried in the dark until reaching constant moisture content (near 15 wt %). Wet blue pieces were obtained by chrome-tanned leather from bovine at CTIC, Technological Center for Leather Industry, Portugal.

Extraction of Bark. Batch extractions were performed in a M/K system batch digester (5 L capacity) with temperature and time control and liquid phase recirculation using water or aqueous alkaline media (NaOH 0.1% and NaOH 0.5%). The extraction temperatures were 80, 120, and 140 °C. A ratio of 500 g bark:4 L of extraction media was used. Figure 1 represents the time and temperature profiles used for extractions, where the dots represent the sampling points.

Concentration Processes. On the basis of evaluation of TPC content from the previous experimental stage, the conditions selected to produce the *E. globulus* bark extract were: water, extraction temperature 140 °C and total extraction time 120 min. However, the tannin concentration achieved, about 2.5 g/L, is below the values of commercial liquid extracts typically applied in retanning process (10 g/L). In this work, a strategy to increase the concentration of tannins/phenolic compounds was developed aiming to obtain a suitable liquid extract for application in the leather industry, allowing the benchmarking with the commercial ones. For that, the selected extract from the previous phase was concentrated by recirculation over fresh bark, simulating a continuous bark extraction process, to obtain at least 2 L of concentrated extract (tannin concentration 8–10 g/L) for analysis and testing in leather retanning; the sequential extractions of fresh bark were performed using the extract from the previous stage as extraction medium. The scheme of Figure 2 illustrates the concentration stages performed.

The first stage (I) involved eight extractions. The extracts were combined, and a final volume of 24 L was obtained and fully used for the six subsequent extractions. From stage II, 18 L of extract was obtained, and 2 L was reserved for analysis and testing. The remaining

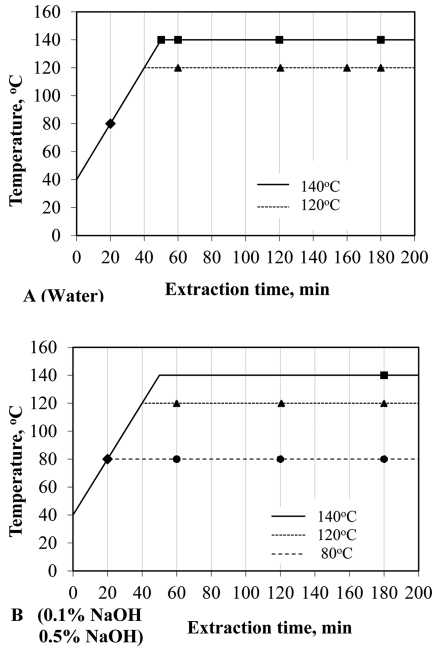

Figure 1. Time and temperature profiles applied in water (A) and alkaline (B) extractions. The dots represent the sampling points.

was applied in the next stage (III), resulting in 12 L, and the process was repeated up to stages VI and VII. In these last steps, the bark weight and liquid were decreased, keeping the ratio of extraction media/bark to obtain 2 L of concentrated extract.

Characterization of Extracts. The extracts were analyzed in terms of total nonvolatile solids, ashes, total phenolic compounds, and tannins. All quantifications were performed at least in triplicate, and the mean value was calculated.

Nonvolatile solids in the extracts were quantified following the standard TAPPI method T652m-89. Briefly, 10.00 or 20.00 mL of extract was added to previous calcined crucibles containing sand (sieved to remove dust). The crucibles were dried at 105 °C until constant weigh. Extraction yield was calculated as the weight of nonvolatile solids (without ashes) per 100 g of oven-dried (o.d.) bark. Inorganics in the extract were evaluated following the TAPPI T211 om-93 standard proceeding for each dried extract and subtracted to nonvolatile solids value.

Total phenolic content was quantified by the Folin-Ciocalteu method[26] as described in the literature.[7] Gallic acid was the standard for the calibration curve, and the results are expressed as total phenolic compounds (TPC) in gallic acid equivalents (GAE) per 100 g of o.d. extract (% $TPC_{extract}$) or per 100 g of o.d. bark (% TPC_{bark}).

Tannin content was assessed by the hide-powder method (ASTM D6401-99(2004)) being defined as the portion of the soluble solids of the extract that is absorbed or bounded by a standard hide powder material. Therefore, the tannins content (%) was obtained as the difference between the soluble solids (%) and the nontannins (%). The final value is presented in tannin content per 100 g of o.d. extract (% $TaN_{extract}$) or 100 g o.d. bark (% TaN_{bark}).

Leather Retanning Experiments. The skin was cut parallel and perpendicular to the backbone, and the strips were submitted to the complete tanning process using standard chrome-tanning salts. Wet-blue pieces were then retanned using laboratory drums. Four different essays were performed, as depicted in Table 1, aiming to compare the performance of bark extract of *E. globulus* (concentrated) with commercial chestnut extracts and synthetic tannins. In all the essays, the water/skin weight ratio was 2, and synthetic tannin was added to a final concentration of 1% w/w (skin). In runs 2 and 3, 1% and 3% of chestnut extract, respectively, was used, containing 70% of tannins. In the fourth run, the retanning agent was the concentrated *E. globulus*

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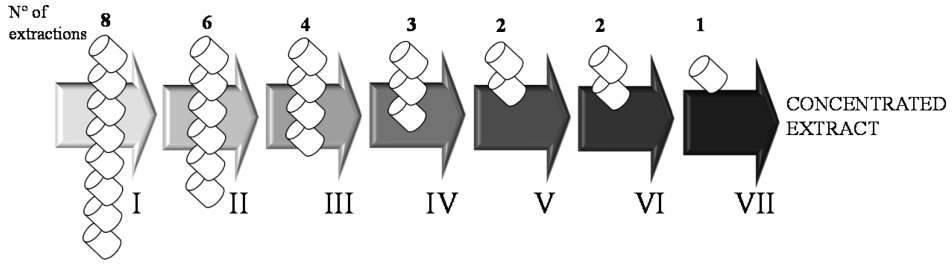

Figure 2. Stages of the concentration process based on bark extract recirculation.

Table 1. Percentage of Tannins Applied in Each Retanning Trial

	% w/w[a]		
trial	chestnut extract	*E. globulus* bark extract	synthetic tannin
1	0	0	1
2	0.70	0	1
3	2.1	0	1
4	0	0.74	1

[a]On the basis of dried weight of wet-blue material (referred also as "leather").

bark extract. The values presented in Table 1 refer to the tannin content in the extract per 100 g of wet-blue.

The final retanned materials obtained from each trial were characterized in terms of tear strength, tensile strength, and percent elongation at break using standard procedures described in the Official Methods of Analysis by the Society of Leather Technologists and Chemists.[27]

RESULTS AND DISCUSSION

Evaluation of Effect of Process Conditions in Extracts.

E. globulus bark extractions were carried with water and diluted alkaline solutions (0.1% and 0.5% of NaOH) at maximum temperatures of 80 , 120, and 140 °C. In the first stage, the aim was to evaluate the influence of time, temperature, and NaOH concentration in the extraction yield (based on total nonvolatile solids), and in the selectivity for TPC and for tannins (content on the o.d. extract) to subsequently select the best conditions to produce the extract for application in the retanning tests. The extraction yields for each condition are presented in Figure 3.

For both water and alkaline solutions, the increase in the extraction temperature (from 80 to 120 °C and from 120 to 140 °C, Figure 3) led to a notorious increment of the extraction yields due to the increasing solubility of the compounds and also probably to the improvement of mass transfer from bark matrix to the liquid. The highest effect of temperature on yield was obtained for water and 180 min, as depicted in Figure 3, from about 80 g/kg (120 °C) to 140 g/kg (140 °C). For extractions with NaOH solution, for each extraction temperature, the major difference is in the initial phase (20 min), showing that the increase in NaOH concentration considerably promotes the initial rate of the extraction. The effect of the NaOH concentration on initial yield is probably related with the swelling effect of alkali on the bark, turning easier the mass transfer from bark to the medium.

The final yield obtained for 0.1% NaOH at 120 °C (112 g/kg) (Figure 3.B) is higher than that obtained for extraction with water (at same time and temperature) but lower comparatively to that obtained with water extraction at 140 °C. Considering this result, water promotes an efficient extraction if the

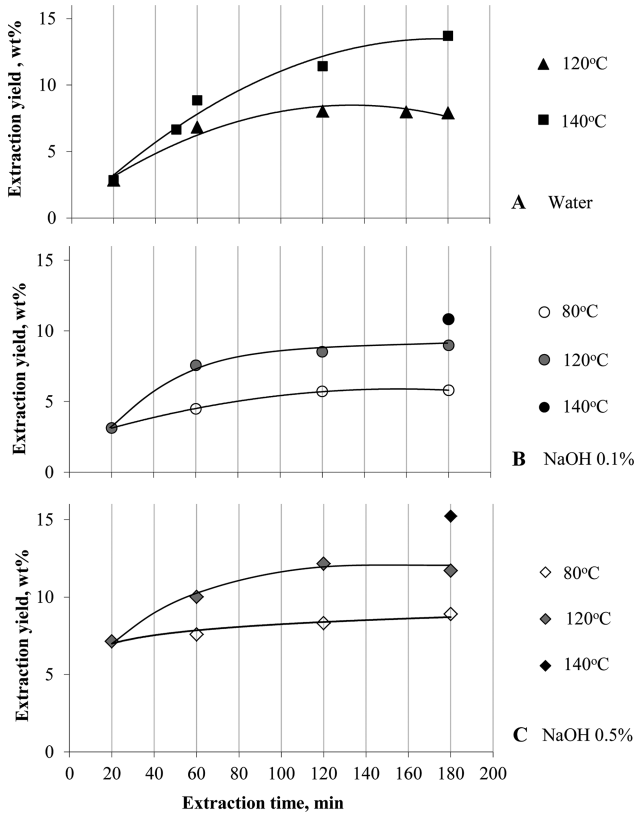

Figure 3. Evolution of the extraction yields (wt %) of *E. globulus* bark with extraction time for water (A) and for alkaline solutions: 0.1% NaOH (B) and 0.5% NaOH (C) at different temperatures.

combination of temperature and time is favorable. These two variables can be related through the so-called H-factor,[28] eq 1. This kinetic parameter is commonly used in the wood pulping process to combine time and temperature into a single variable to predict the lignin dissolution rate as a function of the time–temperature variable.[28] In the current work, this tool revealed to be very reliable because the merging of time and temperature in a single one allowed a more accurate evaluation of NaOH impact in the extracts parameters.

$$H = \int_0^t \frac{k_{T(t)}}{k_{373}} dt = \int_0^t e^{\left(43.181 - \frac{16113}{T(t)}\right)} dt \quad (1)$$

Indeed, extraction yield shows a noticeable correlation with the H-factor for each extraction media (Figure 4). With temperature and time combined into the H-factor, the effect of the extraction medium on the yield is clearly observed. The major difference between the alkaline solutions is reported for H-factor values bellow 22. As reference, this value corresponds to the following pairs: 180 min/120 °C and 120 min/140 °C.

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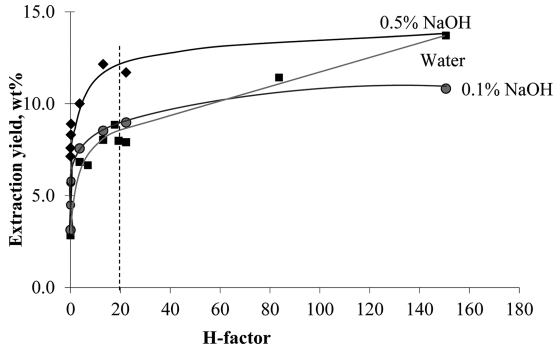

Figure 4. Extraction yields (wt %) of *E. globulus* bark in water, 0.1% NaOH, and 0.5% NaOH vs H-factor.

After that, the effect of alkalinity and H-factor on yield is residual, keeping higher values for 0.5% NaOH along the H-factor. For water extraction, an increase in yield with H-factor is observed. For an H-factor around 150, the extraction yield for water is similar to that of NaOH 0.5%.

Although the extraction yield is an indicator of the efficiency of extraction, considering the application of the extracts targeted in this work, i.e., leather retanning, the phenolic content is a key parameter for the selection of the extraction conditions for this objective.

The plot of TPC_{bark} as a function of H-factor is shown in Figure 5 for all the tested conditions. Considering these

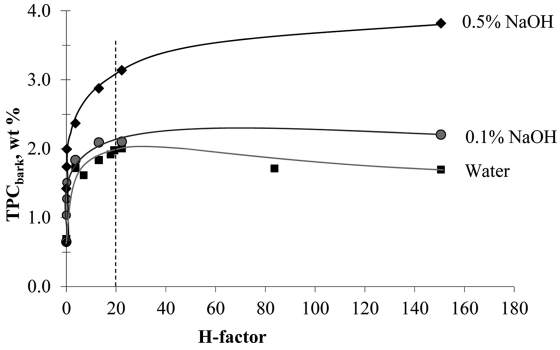

Figure 5. TPC_{bark} (wt %) obtained by the extraction of *E. globulus* bark in water, 0.1% NaOH, and 0.5% NaOH vs H-factor.

profiles, a clear effect of the extraction media is also noticeable with a favorable effect of the NaOH on TPC yield. In the case of NaOH 0.5%, the profile indicates a slight increase in TPC extraction with H-factor, while for water and NaOH 0.1%, no noteworthy change was noticed for an H-factor above 20 (Figure 5). On the basis of the TPC_{bark} and extraction yield obtained with water (Figure 4) where an increasing trend of extraction yield with H-factor was observed, it is possible to propose that higher extraction time and higher temperature lead to the preferential extraction of nonphenolic material, thus decreasing the selectivity of the process. This observation supports the importance of the evaluation of process selectivity.

Selectivity of Extractions. The selectivity of extraction processes, i.e., the yield on TPC compared to other components, and their dependence on operating conditions was evaluated. The plot of TPC_{bark} as a function of extraction yield (Figure 6) revealed a linear correlation between the two parameters until an extraction yield of around 8 wt %, corresponding to a maximum TPC of 2%. This means that for

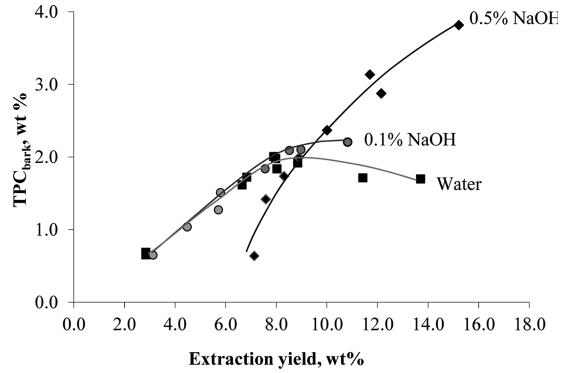

Figure 6. TPC_{bark} (wt %) vs extraction yield (wt %) of *E. globulus* bark in water and alkaline solutions.

each kilogram of bark, about 80 g of extract are obtained containing 20 g of phenolic material. The extraction yields in the range of 8−10% correspond to a maximum of selectivity for extraction with water and NaOH 0.1%. However, a different behavior was found for 0.5% NaOH: the increase in extraction yield is followed by a continuous increase in TPC_{bark} in the range of the conditions studied. This behavior is probably related to the dissolution of low molecular weight lignin in stronger alkaline solution, accounting for both TPC quantification and yield.

In view of the main objective of the present study, the tannin content was also evaluated for all the extracts. Figure 7 shows

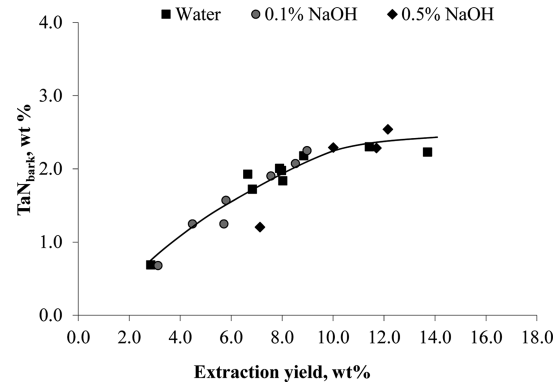

Figure 7. TaN_{bark} (wt %) vs extraction yield (wt %) of *E. globulus* bark in water and alkaline solutions.

the evolution of TaN_{bark} and its correlation with extraction yield. This representation shows an increase in both parameters until an extraction yield of 8−10% was reached and about 2% of TaN_{bark}. Moreover, there is a close correspondence between TPC_{bark} (Figure 6) and TaN_{bark} (Figure 7). From this point forward, the extraction yield increases with no variation of TaN_{bark}, indicating a decrease in extraction selectivity for compounds with tanning activity, as stated before (Figure 6). Finally, no correspondence was found between TaN_{bark} and the continuous increase in TPC_{bark} for NaOH 0.5%.

These results point out that the maximum phenolics/tannins that could be obtained by this extraction process is about 2.5 g/L, representing about 2% of the bark weight. At this point, the selectivity of the extraction is maximum for both TPC and tannins. Considering the softer conditions to obtain the bark extract with these characteristics, the choice was water as extraction medium and 140 °C of maximum temperature with a

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total time of 120 min, corresponding to an H-factor of 84. The extraction with alkaline solutions would require further neutralization processes for the application in retanning, thus introducing an additional step, with no advantage concerning yield and selectivity. This was an additional reason for the selection of water as extraction medium.

Concentration Process. The application of vegetal extracts on the retanning process requires higher tannin concentration than that obtained in a single extraction step. For example, the chestnut extract contains 70% tannins (information from suppliers), and the typical value of tannins in retanning experiments is about 10 g/L, although some variation would be possible depending on the target characteristics of the leather and operational conditions of the retanning process. Therefore, the aim in the present study is to get close to these values for *E. globulus* bark extracts. The conditions selected in the Selectivity of Extractions section were used to carry out consecutive extractions over fresh bark aiming to increase the concentration by 4−5 times. The values obtained for each step, from level I to level VII, are presented in Figure 8.

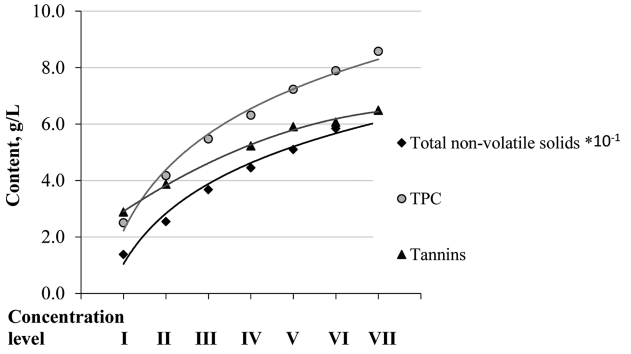

Figure 8. Cumulative content (g/L) of total nonvolatile solids, TPC, and tannins in the extract over recirculation at each concentration level (I−VII).

The recirculation process allowed obtaining a considerable increase in total solids, TPC, and tannins content in the liquid extract (Figure 8). For TPC, the first recirculation (I−II) allowed a concentration factor of 2. If this ratio could be maintained over all steps, it would lead to a final content of about 15 g/L. However, the extraction of TPC slightly decreased at each successive extraction leading to a cumulative final value of 8.6 g/L. The process selectivity for TPC (measured by $TPC_{extract}$) is not affected by the recirculation of the extraction media over fresh bark; the concentration factors (ratio VII/I) for total solids and TPC are very close, 4.6 and 4.3, respectively. Therefore, the content of $TPC_{extract}$ in the final extract is similar to the initial one. For tannins, the concentration in the final extract is 6.5 g/L. However, the selectivity decreased over the extraction steps, leading to a concentration factor of about 2.5, while for total solids the factor is 4.3; as a result, the $TaN_{extract}$ in the final extract is lower than in the initial extract. The tannin content was measured by a specific method used in leather technology, involving the reaction of these compounds with hide-powder. The method gives an assessment of the extent of the reaction between the components of the extract and the leather, which is related with both the amount and the nature of the components. Therefore, the lower $TaN_{extract}$ means that, during the recirculation, bark components with no tanning activity were preferentially extracted. These components could be of phenolic nature (as confirmed by TPC analysis). However, they do not interact with leather; hence, for this parameter, the recirculation was not as effective as for TPC.

Leather Retanning Essays. As stated in the previous section, the objective of the concentration process was to produce extracts with higher TPC and tannin content than in the initial extract, in order to apply them in leather retanning under conditions similar to those used for commercial tannins. After the concentration process, the extract presents 6.5 g/L of tannins and 8.6 g/L for TPC.

Figure 9 shows key physical properties of leather samples after retanning with the *E. globulus* bark extract, as well as for

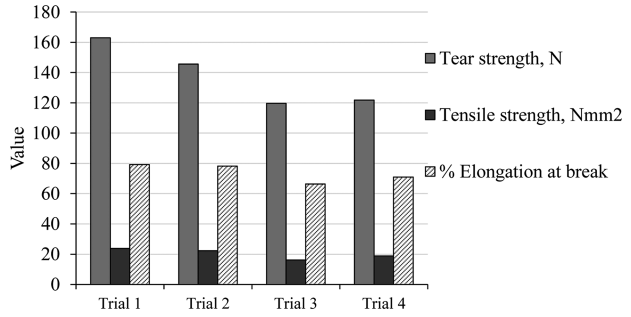

Figure 9. Results of leather physical tests after the retanning with only synthan (no vegetal extract) (trial 1), chestnut extract at 1% (trial 2), chestnut extract at 3% (trial 3), and *E. globulus* bark extract (trial 4).

the reference chestnut extract at three concentration levels: 0%, 1%, and 3% ($w_{extract}/w_{leather}$), trials 1, 2 and 3, respectively. Considering 70% the tannin content in chestnut extract, the concentration in trials 2 and 3 are 0.70% and 2.1% $w_{tannin}/w_{leather}$, respectively, as stated in Table 1. *E. globulus* bark extract was applied at 0.74% $w_{tannin}/w_{leather}$. In these conditions, it is possible to observe that the values of tear and tensile strengths, as well as elongation at break, provided by *E. globulus* bark extract are within the values obtained for the chestnut extract (Figure 9). The tearing resistance of retanned leather depends of both extract concentration and extract astringency. Higher astringent extracts are usually related with lower mechanical resistance and lower percentage elongation at break, but a certain degree of astringency of tannin extract is required to get leather fullness and roundness. Vegetable extracts are usually applied in the production of leather articles for high environmental resistance like box-calf and nubuck. The results obtained for the two vegetal extracts indicate that the adstringency of *E. globulus* bark extract is comparable to that of the chestnut extract, demonstrating that this is a possible application for the concentrated extract.

CONCLUSIONS

The water extraction process in a closed batch reactor with liquid-phase recirculation applying a temperature of 140 °C for around 120 min of total residence time revealed to be a feasible approach for the extraction of valuable phenolic compounds from *E. globulus* bark. The total solids yield was about 8 wt % o.d. bark, with a maximum of 2.5 g/L of TPC in the liquid extract. For the application envisaged, a concentration process based on extract recirculation over fresh bark was successfully performed, achieving a final extract with 8.6 g/L of TPC and 6.5 g/L of tannins.

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The application of *E. globulus* bark extracts in the retanning process has resulted in leather with high fullness, large grain, and less break pipiness, revealing good performance as vegetable retanning agents in the production of leather articles like box-calf and nubuck. The *E. globulus* bark tannins have considerable astringency, comparable to that of the chestnut commercial extract.

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Notes

The authors declare no competing financial interest.

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