

# Tara Tannin Extract Improvement

## I. Extraction and Concentration Through Membrenary Filtration Techniques

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*The paper presents the results of original research on improving tara tannin extract for ecologic tanning methods in the context of the newest global ecology concepts on reducing carbon consumption by using tannin resources that do not imply deforestation. The paper proposes processing tara tannin through extraction and concentration using microfiltration, ultrafiltration and reverse osmosis membranes, determining a reduction in the concentration of insoluble matter and an increase in the tannin concentration, without modifying tannin through hydrolysis. In the first part of the paper we present the optimal filtration parameters using filtration membranes and the characteristics of concentrated tanning extracts, compared to the initial products.*

*Keywords: tara tannin, tannin concentration, membrenary techniques, vegetable tannin*

The most general definition of tannins is that which separates these phenolic compounds from other secondary phenolic products of plants and which are set apart by their chemical reactivity and biological activity [1]; the most important reaction is precipitation of protein, which underlies natural leather tanning processes. Vegetable tanning agents are some of the oldest materials used for leather processing; the term *tannin* is of celtic origin [2], meaning oak, and certifies the origin of these materials. The largest amounts of natural tannins are extracted from tree bark (mimosa, *Acacia mollissima*) and/or wood (quebracho, *Schinopsis lorentzii* and chestnut, *Castanea sativa*), which implies deforestation, and, as a result, the greenhouse effect. Bearing in mind the principle of using ecologic materials, our research investigates the possibility of extending the use of tannins from vegetable sources that do not imply deforestation, namely from the pods of tara shrub (*Caesalpinia spinosa*). Tannin extracted from these pods is known as a hydrolysable tannin from the class of gallotannins, mainly made up [3] of the ester of polygallic acid with the quinic acid (fig. 1), which gives leather the lightest colour, fastness to light and superior mechanical properties, compared to other types of tanning agents.

What sets the tara tannin apart from other commercial tannins is the fact that it is not an extract, but a finely ground powder from tara pods. Therefore, tara tanning agent has

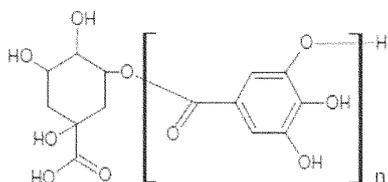


Fig. 1. The main structure of gallotannin in tara

a low tannin content, a high amount of insoluble substances and its use involves loading effluents with significant amounts of organic matter. Recent studies report the possibility of using ultrasound to improve extraction yields of valonea tannin, a hydrolysable tannin obtained from fruits of acorn cups of *Quercus* species [4]. Other papers research the possibilities of improving tara tannin by solubilisation in water or by sulphitation [5], by grinding and sieving until obtaining a powder having particle size of 50 $\mu$ m [6]. These research studies show that the size of tara tannin particle influences the content of tannin extracted in solution and allows increasing the tannin content by 4%, with positive effects on reducing chemical oxygen demand in effluents from leather tanning. Other research studies propose to combine tara tannin with synthetic tannins with dispersing and tanning properties in order to optimize the consumption of tara tannin [7]. Techniques of concentrating tannin through filtration membranes have been approached only for residual solutions [8, 9] and have proven the possibility of separating tannin and reusing it in the tanning process. This paper proposes a technology based on filtration membranes to concentrate tannin from tara extract and improve properties, compared to the classic technique of evaporation applied to condensed tanning agents (catechic) and to the commercial tanning agent.

### Experimental part

#### Materials and methods

Vegetable tara tannin from Leather Quimica was used as powder with volatile matter content 8.6%, total soluble 53.8%, tannin content 39%, non tannin 15%, insoluble matters 35% and pH= 3.7.

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### Tara tannin extraction and processing

In order to prepare the concentration of tara tannin, an extract of the vegetable tannin powder was dissolved in distilled water, in vegetable tannin : water ratios of 1:4 and 1:2 and the solution was heated to 70°C, for 1 h with magnetic stirring. Other two extraction variants were prepared by dissolving the vegetable tannin in water and ultrasounding the solution for 2-4 h in the ultrasound bath (Ema S15kHz Elmasonic) at a temperature of 70°C. The influence of ultrasound time was studied by characterising the tara tannin solutions after 1, 2, 3 and 4 h of ultrasound. After extraction, solutions were cooled and centrifuged for 15 min using the Sigma centrifuge (UK) with 5000 rpm.

To optimize centrifugation time, we studied the influence of centrifugation time on tannin properties after 5, 10, 15 and 20 min.

In order to identify advantages of membrane concentration, a solution of tara tannin extract, obtained by dissolving in distilled water in a vegetable tannin : water ratio of 1:2, heating at 70°C for 1 h, was subject to concentration by evaporation. For this purpose, the solution with 28% concentration was slowly evaporated in an oven set to 45°C, until the volume was reduced to half.

### Tara tannin characterisation

Chemical characteristics of tara tanning solutions were analysed according to standards SR 1883:2008 and ISO 14088:2011. The main characteristics specific to tanning materials were: dry substance, tannin content, total soluble matter, non tannin, insoluble matter, sediments, fixing power with slightly tanned leather powder and the pH. As tara tannin is easily hydrolysable, the concentration of free gallic acid was determined in order to assess the influence of concentration treatments on the hydrolysis of tannin and to select the optimal process to improve tara tannin. Free gallic acid was determined using the rhodanine method and by reading absorbance at 520 nm [1].

### Tara tannin concentration by filtration membranes

In order to concentrate tara tannin from obtained extracts, the KMS Cell CF-1 Module (Koch Membrane

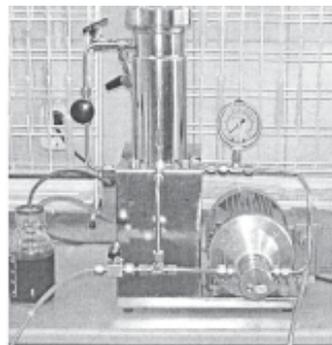


Fig. 2 . KMS Cell CF-1 Module (Koch Membrane Systems Inc)

Systems Inc, UK) was used, with the following characteristics: active membrane surface: 28cm<sup>2</sup>; liquid flow: tangential, variable rate; engine speed: 0-6000 rpm; useful volume of tank: 500mL; working pressure: 0-10 bar (fig. 2). The laboratory module used is recognized as one of the most advanced for elaboration of pilot separation and concentration technologies using filtration membranes for bioactive compounds [10] and for recoverable materials from effluents [11].

During tests of tara tannin concentration from tara extract solutions, 2 concentration technologies, one based on microfiltration membranes (MF) and ultrafiltration membranes (UF), labeled MF/UF, and the other based on microfiltration and reverse osmosis, labeled MF/RO were elaborated and tested. The membranes used were: MF membrane of cellulose acetate with 0.45 mm pores (Sartorius); UF membrane of cellulose regenerated with cut-off of 5000 Da (Millipore) and RO membrane of nitrocellulose, with 0.025 µm pores (Millipore).

Establishing working technologies involved experiments on types of membranes, liquid flow regimes or work pressure. The technological flowchart for tara tannin concentration was created as a result of experiments involving the following work stages: equipping the filtration module with suitable membranes; prefiltration of extract; microfiltration of extract in order to clarify and retain large components; concentration of the microfiltration permeate, by ultrafiltration or reverse osmosis. In order to

Sample symbol	Description
Tara pd	Tara tanning material in powder form, milled tara pods, grading: 95% in mesh 100 (149µm).
CB1 CB2	Tara solution obtained by dissolving powder tannin in distilled water in a ratio of 1:5 (CB1) and 1:2 (CB2), heated at 70°C, for 1 hour with stirring, centrifuged for 15 minutes.
2CBE-Evap	Tara solution obtained by dissolving powder tannin in distilled water in a ratio of 1:2, heated at 70°C, for 1 hour, centrifuged for 15 minutes and concentrated by evaporation at 45°C, until the volume is reduced to half.
TUS2	Tara solution obtained by dissolving powder tannin in a ratio of 1:5 and ultrasound at 70°C, for 2 hours, centrifuged for 15 minutes.
TUS4	Tara solution obtained by dissolving powder tannin in a ratio of 1:5 and ultrasound at 70°C, for 4 hours, centrifuged for 15 minutes.
MF/UF	Tara solution obtained by heating or ultrasound and concentrated by microfiltration and ultrafiltration.
MF/RO	Tara solution obtained by heating or ultrasound and concentrated by microfiltration and reverse osmosis.

**Table 1**  
DESCRIPTION OF TARA TANNIN  
SAMPLES TESTED

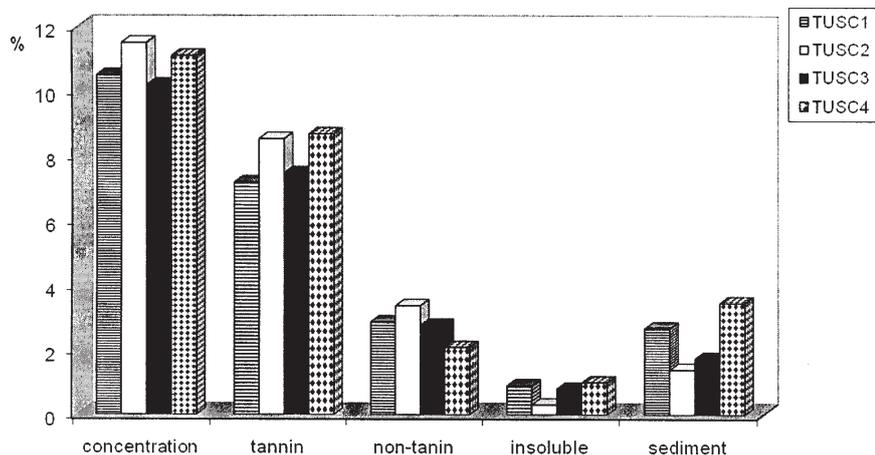


Fig. 3. Influence of ultrasound time on characteristics of tara extracts

establish the optimal mode of operation for ultrafiltration and reverse osmosis techniques, several modes of operation were tested, and then the variation of the liquid flow was drawn depending on the filtering pressure for the two types of membranes.

The description and codes of tested tara samples are presented in table 1.

### Results and discussions

Experiments regarding the optimal conditions of tara tannin extraction by ultrasound and centrifugation have enabled the selection of variants which provide the most favourable composition for subsequent concentration through filtration membranes.

Studying the influence of ultrasound time on the quality of tara tannin led to the selection of ultrasounded variants 2 h (TUSC2) and 4 h (TUSC4) as those which enable higher concentration in dry substance and tannin, compared to the other variants, ultrasounded 1 (TUSC1) and 3 (TUSC3) hours (fig. 3).

The influence of centrifugation time of tara extract solutions obtained by heating and/or ultrasound was monitored by centrifugation for 5, 10, 15 and 20 min (C5, C10, C15 and C20) and then by chemical analysis of tannin concentration, insoluble-matter content, sediment or fixing ability on slightly chrome-tanned leather powder.

Figure 4 shows that centrifugation for 15 min enables to obtain the maximum amount of tannin, the minimum amount of insoluble matter and sediment and maximum fixing ability on leather powder.

Tara extract solutions obtained by heating and/or ultrasound for 2 and 4 h and centrifuged for 15 min were processed by prefiltration, microfiltration and ultrafiltration or reverse osmosis.

The optimal permeability regime of filtration membranes was established as a result of experiments on variation of liquid flow depending on pressure. Figure 5 shows a linear variation of liquid flow depending on pressure and optimal pressure at 6 bar for UF membranes and at 10 bar for RO membranes.

Technologies for tara tannin concentration from vegetable extracts using filtration membranes are presented in figure 6.

The appearance of filtration membranes (fig. 7) indicates a higher degree of retention of tanning components on the RO membrane, the membrane with the finest pores. Tannin retention on reverse osmosis filtration membranes was confirmed by the chemical analysis of the concentrated tara solution which, although more concentrated in dry substance, the tannin content is lower than in the case of solutions concentrated by ultrafiltration.

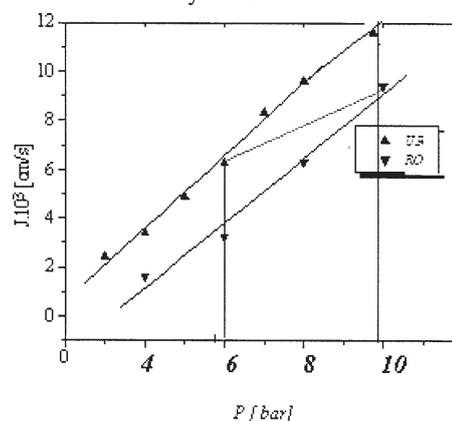


Fig. 5. Variation of liquid flow depending on pressure for UF (▲) and RO (▼) membranes

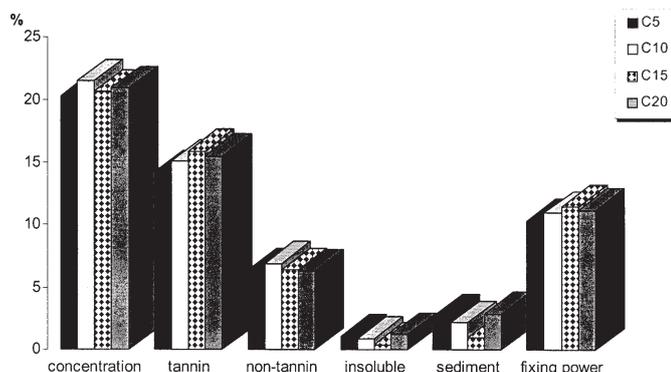


Fig. 4. Influence of centrifugation time on characteristics of tara extract

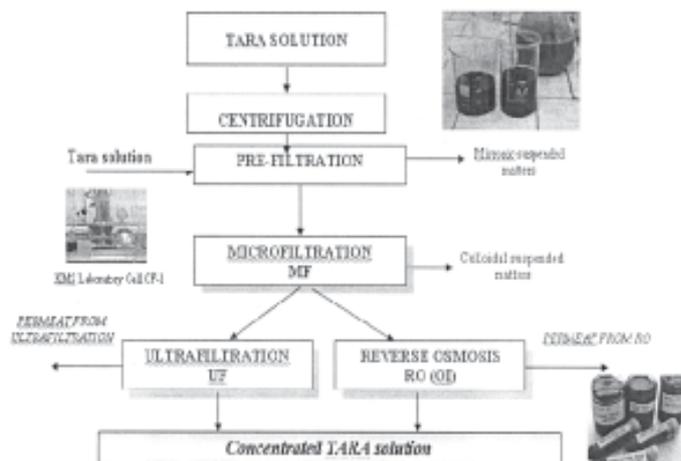


Fig. 6. Technological flowchart for tara tannin concentration by MF/UF and MF/RO

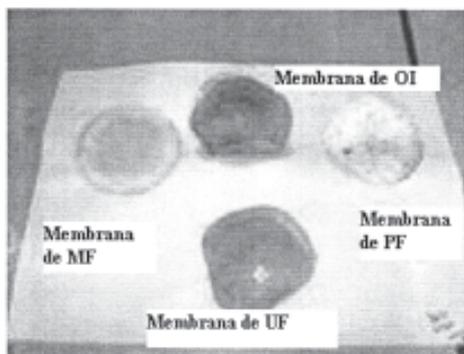


Fig. 7. Pre-filtration (PF), microfiltration (MF), ultrafiltration (UF) and reverse osmosis (RO) membranes after tara solution concentration

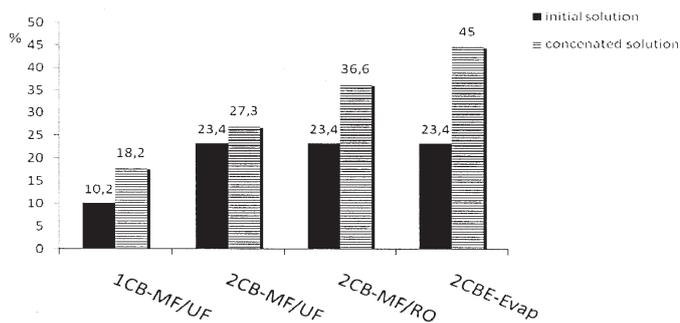


Fig. 8. Concentration of initial and final tara solutions obtained by MF/UF, MF/RO and by evaporation from diluted (1:5) and concentrated (1:2) solutions.

Results of chemical analyses of initial and concentrated solutions indicate different performance in improving the degree of concentration in dry substance and tannin for the 2 variants of membranary technologies. Thus, the most concentrated solutions are those filtered by MF/RO, slightly inferior to the solution concentrated by evaporation (fig. 8).

It can also be noticed that by MF/UF concentration, higher concentrations are obtained in the case of processing more diluted solutions (1:5), than in the case of concentrated ones (1:2).

Regarding tannin concentration, increases of 2.8-24.3% occur; the MF/UF process applied to more diluted tara solutions led to a maximum tannin concentration, compared to all the other processes (fig. 9). The slight reduction of tannin concentration in the solution concentrated by evaporation leads to the conclusion that the concentration regime favoured tannin hydrolysis with release of gallic acid.

The influence of the type of extraction and concentration technology on the integrity of hydrolysable tara tannin was assessed by determining free gallic acid (fig. 10).

Membrane techniques provide the best preservation of tara tannin, with the lowest free gallic acid concentration, compared to the solution obtained from tara powder, from the solution concentrated by evaporation or from the extract obtained by ultrasound.

Other advantages of extraction and concentration techniques used lie in the reduction of insoluble matter from 35.6% in tara powder to 0.4-3.5% in tara concentrates; reduction of sediments from 39.8% in tara powder to 1.87-6.6% in concentrated solutions. The concentration technique using membranes enabled an increase in the tannin/non-tannin ratio from 2.6 in the case of powder tannin to 3.2 for MF/UF and 3.0 for MF/RO.

The second part of research approaches properties of concentrated tara solutions in terms of particle size, stability,

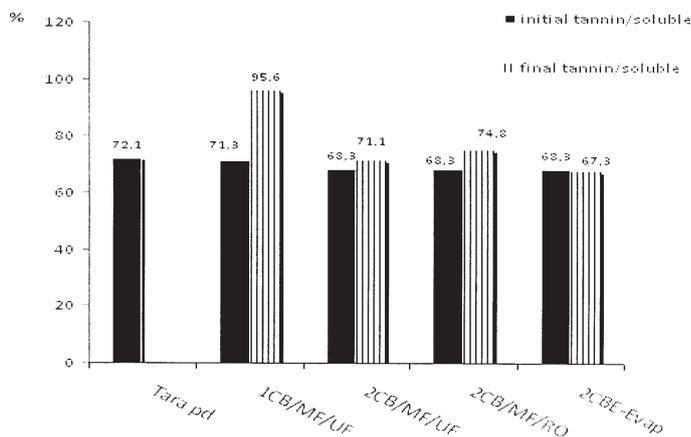


Fig. 9. Tara tannin concentration in initial and concentrated solution, compared to powder tara tannin.

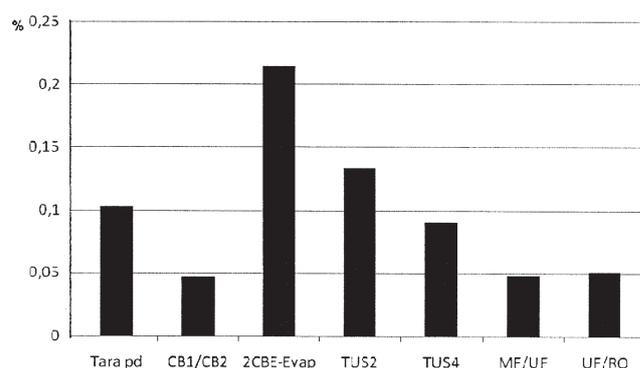


Fig. 10. Free gallic acid content in concentrated tara solutions by membrane techniques, compared to the extracted solution by heating, ultrasounded or obtained from tara powder dissolution

penetration ability and tanning ability for bovine leather, and reduction of effluent pollution.

## Conclusions

Original research has proven the possibility of concentrating tara tannin, a hydrolysable, ecologic tannin, by membranary filtration techniques. Experiments have led to the elaboration of optimal concentration parameters using filtration membranes: the type of membranes, sequence of filtration processes, optimal pressure for which permeability is maximum. The best results were obtained for more diluted tannin extract solutions, obtained by heating, without ultrasound and centrifugation for 15 min. Tara tannin solutions were obtained, with higher tannin concentrations by 24.3% compared to the commercial tannin, without increasing free gallic acid concentration, with significantly low concentrations of insoluble matter and non tannin substances.

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