Effect of Ultrasound on Watery Dissolutions of Vegetable Extracts used in Leather Tanning

by

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Abstract

This paper analyses the effect of ultrasound on the aqueous dissolutions of vegetable extracts. This effect has been compared with that of a drum, which is the type of reactor used in leather tanning nowadays. The results indicate that the studied effects have similarities and that there is the possibility of using ultrasound during leather tanning with vegetable extracts. This may result in improvements in the quality of the leathers obtained.

Resumen

Esta publicación analiza el efecto del ultrasonido sobre las soluciones acuosas de extractos vegetales. Este efecto ha sido comparado con el de un fulón, el cual es el tipo de reactor utilizado en la curtición de hoy en día. Los resultados indican que los efectos estudiados tienen similitudes y que existe la posibilidad de utilizar ultrasonido durante la curtición al tanino con extractos vegetales. Esto podría resultar en mejorías en la calidad de los cueros obtenidos.

Introduction

Sound waves with frequency above the human audible range of 16 kHz are called ultrasound. Ultrasound may be broadly classified as power ultrasound and diagnostic ultrasound. Power ultrasound (hence forth ultrasound) having a frequency range of 20-100 kHz is commonly employed for enhancing physical processes and for accelerating chemical reactions.
The application of ultrasound to different operations of the tanning process has been the aim of research since the 1950s. Several researchers designed beamhouse processes by applying ultrasounds and found that these favored the penetration of chemicals in the hides[1-4].

In chrome tanning researchers found that ultrasound accelerate the reactions of chrome hydrolysis, olification and oxalation[5]. It also increases the speed of chrome penetration and its absorption by the skin [3,6-9] In dyeing and fatliquoring the use of ultrasound contributes to better exhaustion baths and an improved distribution of the dyeing stuffs [8,10-16] and the grease [8,15-21]. A recent study[22] also examined the chemical, physical and mechanical effects of ultrasonic treatment on collagen from bovine hides. This study demonstrated that collagen molecules could withstand sonification in the low frequency, high power range typically used for industrial processing.

Results from these studies have generally been satisfactory. However, such results have only been obtained at a laboratory scale as the ultrasonic power employed would have been too high for replication in industrial practice.

The use of ultrasound may be important in the operation of vegetable tannage. Nowadays, tannage with vegetable extracts can be accomplished in less than 24 hours. The use of the drum makes this possible as it provides the necessary mechanical effect. However, this process has a shortcoming. Sometimes, the hides are damaged when they hit against the pivots of the drum. When this occurs, the leathers show scratches and in turn their commercial value decreases. In fact, up to an 50% devaluation of the final product may result from such a flaw. Damage to the grain of the leather can be prevented by using pits instead of drums, although the process is excessively long. Several researchers[3,8,16,23-26] have provided evidence to support the fact that ultrasound accelerate the penetration of vegetable extracts into the skin or hide. These researchers concluded that the depolymerising action of ultrasound on the structure of tannins facilitates the penetration of the tanning agent into the pelt. Hence, the use of ultrasound may reduce the time of tannage while damage to the grain is avoided.

In order to be able to apply the ultrasound to leather tanning with vegetable extracts in industrial practice, it is first necessary to determine the extent to which those variables related to that type of tannage (type of extract, concentration of de dissolution of vegetable extract and working temperature) may be influential.

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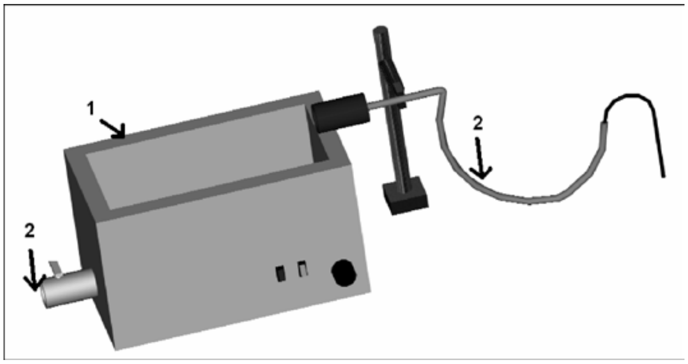

Figure 1: Ultrasound tank (1) with a system of water circulation (2) in order to control the temperature

This study looks into the effect that the ultrasound may have on the size of those particles present in aqueous dissolutions of different types of vegetable extracts. The variables commonly associated with the tannage which are analysed in this study are concentration of the dissolution and its temperature.

EXPERIMENTAL

Tested extracts

Four different types of vegetable extracts were tested in the study. One type is classified into the group of hydrolysable or pyrogallic tans (e.g. chestnut), whereas the other types belong to the group of condensed or catechin tans (e.g. gambier, mimosa and quebracho).
The tested extracts were as follows:

"N" chestnut, provided by Silvachimica, S.R.L., Santa Croce, Italy.
"CM" gambier, provided by Silvachimica, S.R.L., Santa Croce, Italy.
"Clarotan" mimosa, provided by Tanac, S.A., Montenegro, Brazil.
"Indusol ATO" quebracho provided by Silvachimica, S.R.L., Santa Croce,

Although gambier "CM" is not one of the most commonly used extracts in the industry, it was selected as one of the extracts for the trial due to its low solubility. We inferred that this characteristic would make it easier for us to detect the difference in extract performance in an aqueous dissolution with or without applying any mechanical effect compared to the other extracts being used on the trial,.

Equipment

The following instruments were used:

a) Tank with a built-in ultrasound generator, TC-8 model, Estmon Ultrasonidos brand, Cerdanyola, Spain. Working frequency: 32 kHz. Capacity: 8 litres. Power of ultrasound: 525 W. Power of heater: 750 W. A system allowing the addition of cold water was built in so as to control the working temperature (Fig. 1).
b) Meter for measuring the diameter of particles through laser diffraction, LS230 model, Beckman Coulter España brand, Madrid, Spain.
c) Stainless steel laboratory drums, "Inoxvic, S.A." brand, Vich, Spain. Measurements: 150 mm in width x 300 mm in diameter. Speed: 36 rpm. The temperature is controlled by resistors which are attached to the wall of the drum.

Variables in the study

The variation in diameter of the polymers in the aqueous dissolutions of the vegetable extracts described in Section 2.1 of this present paper was studied. These were formed by the molecules of the different compounds which are part of the four vegetable extracts mentioned. These polymers were (i) not subject to any kind of agitation, (ii) subject to the mechanical effect produced by a drum, and (iii) subject to the effect of the ultrasound.
The study was carried out taking into account the effect of the following variables on the particle size:

- Temperature. The working temperatures were 27°C and 40°C.
- Concentration of the dissolution of vegetable extract. The working concentrations were 30% and 60% (weight/volume).

Methodology

Previous dissolution of the vegetable extracts

Vegetable extracts do not dissolve readily in water at the different temperature conditions held throughout the experiment. It may be difficult as a result to interpret the results obtained. Therefore, the dissolution of the vegetable extracts was not considered in the experiment. Hence, the first measurement of the diameter of the particles was made once the dissolution of the vegetable extracts in water was the most complete possible. As far as the tests carried out in a drum are concerned, the dissolution was considered complete after running the vegetable extract and the dissolution in the drum for thirty minutes. As for both the tests with no agitation and with ultrasound, the following procedures were followed: both the vegetable extract and the water were mixed together and sealed tightly inside a plastic bag; the plastic bag was immersed in the ultrasound tank; the ultrasound were applied for a period of thirty minutes. After this, the dissolution was considered to be as complete as the one that had been achieved with the drum.
Although the plastic materials are not the most appropriate ultrasonic transmitters, the consistence of the results obtained in this case indicated that the power used was more than enough to carry out the experiment successfully.

Tests carried out with no agitation

Aqueous dissolutions of the extracts of chestnut, mimosa and quebracho were prepared at 30% and 60% concentration and were maintained with no mechanical effect at 27°C and 40°C, depending on the test. The dissolutions were removed from the ultrasound tank after the previous dissolution and were left to stand. Samples from each of the dissolutions were obtained periodically, and the diameter of the resulting polymers was measured. The total length of time for each of the tests was four hours and thirty minutes. The test with the extract of gambier could not be carried out since it is very insoluble and it precipitates.

TABLE I
Conditions for obtaining the minimum diameter of particle: Precipitate vessels

Extract	50% Volume				75% Volume				90% Volume			
	Conc. (%)		T (ºC)		Conc. (%)		T (ºC)		Conc. (%)		T (ºC)	
	30	60	27	40	30	60	27	40	30	60	27	40
Chestnut	2.5	4.5	3.2	3.7	11.0	13.0	14.4	9.4	13.0	17.0	19.0	12.0
Mimosa	4.5	3.0	2.4	5.0	9.0	8.0	6.4	11.0	15.0	18.0	14.0	19.0
Quebracho	11.5	4.5	7.6	8.2	20.0	11.0	14.4	16.6	39.0	21.0	29.0	31.0

TABLE II
Conditions for obtaining the minimum diameter of particle: Ultrasounds

Extract	50% Volume				75% Volume				90% Volume			
	Conc. (%)		T (ºC)		Conc. (%)		T (ºC)		Conc. (%)		T (ºC)	
	30	60	27	40	30	60	27	40	30	60	27	40
Chestnut	2.3	2.1	2.5	2.0	5.5	6.0	7.5	4.0	11.0	11.0	13.0	19.5
Gambier	6.8	8.1	8.6	6.3	16.0	19.5	20.5	15.0	23.0	28.5	31.0	22.0
Mimosa	4.1	3.2	4.0	3.5	10.0	14	13.0	11.0	16.0	25.0	23.0	17.0
Quebracho	5.0	4.2	4.5	6.0	12.0	12.5	11.0	14.0	19.0	17.5	18.0	18.5

TABLE III
Conditions for obtaining the minimum diameter of particle: Drum

Extract	50% Volume				75% Volume				90% Volume			
	Conc. (%)		T (ºC)		Conc. (%)		T (ºC)		Conc. (%)		T (ºC)	
	30	60	27	40	30	60	27	40	30	60	27	40
Chestnut	6.0	3.5	4.0	5.5	9.0	10.0	9.0	10.0	19.0	15.0	14.0	20.0
Gambier	18.5	15.5	14.0	19.0	33.0	32.0	28.0	37.0	42.0	44.0	38.0	47.0
Mimosa	4.0	4.0	5.5	2.5	10.0	9.0	14.0	4.0	13.0	12.0	20.0	6.0
Quebracho	6.0	2.0	4.0	4.0	9.0	4.0	7.0	6.0	12.0	10.0	12.0	10.0

Tests carried out in the ultrasound tank

Aqueous dissolutions of the extracts of gambier, chestnut, mimosa and quebracho were prepared at 30% and 60% concentration and were kept in the ultrasound tank in operation at the chosen temperature once the dissolution was considered almost complete. The temperature was checked periodically and samples from each of the dissolutions of vegetable extracts were taken in order to measure the diameter of the particle. The total length of exposure of each of the dissolutions to the ultrasound was five hours and thirty minutes.

Tests carried out in the drum

Aqueous dissolutions of the extracts of gambier, chestnut, mimosa and quebracho were prepared in accordance with the given concentration. The temperature was controlled through a heating system which is fitted to the drum. The temperature was checked periodically and samples from the dissolution of the vegetable extract were taken in order to measure the diameter of the particle. The total length of time devoted to each of the tests was five hours and thirty minutes. In sum, 48 tests were conducted in duplicate.

RESULTS AND DISCUSSION

The software which is part of the Coulter Counter Particle Size Analyser calculates a number of statistical quantities to characterize the particle size distribution. The statistics are calculated as they would be for a frequency distribution, with the volume percent in a certain size channel being analogous to the frequency of occurrence of a certain value.

In relation to the present study, this allows the behaviour of the vegetable extract aggregates to be distinguished with regard to their size. As the percentage of volume of a given sample increases, the behaviour of those aggregates with a bigger size has a greater effect on the final result.

This is important because the vegetable extracts are formed from chemical components of various natures and their degree

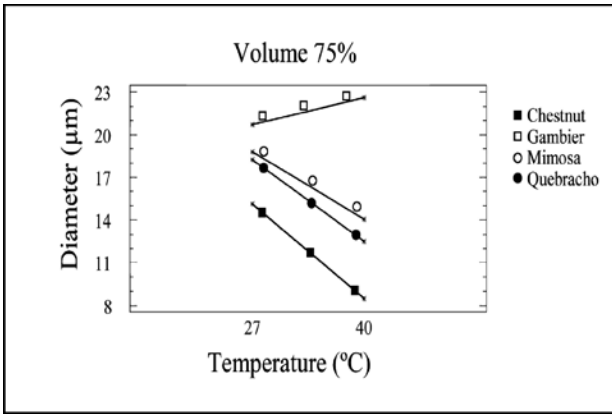

Figure 2: Graph representing one of the analyses conducted

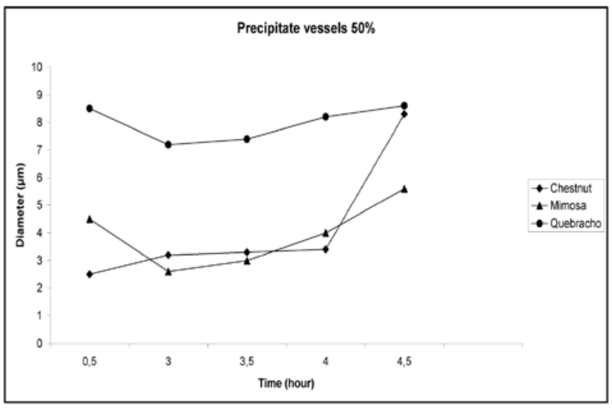

Figure 3: Variation in diameter of the chemical elements in the watery dissolutions at rest of the different vegetable extracts in relation to time. Volume given: 50%.

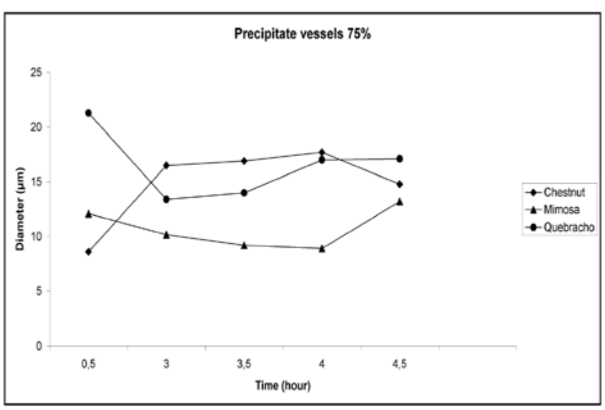

Figure 4: Variation in diameter of the chemical elements in the watery dissolutions at rest of the different vegetable extracts in relation to time. Volume given: 75%.

of polymerisation in a aqueous dissolution is not the same. It was considered in this case that three different readings of each of the samples would suffice to obtain data leading to strong conclusions.

The results which corresponded to the 50%, 75% and 90% of the volume of each of the samples were analysed. These

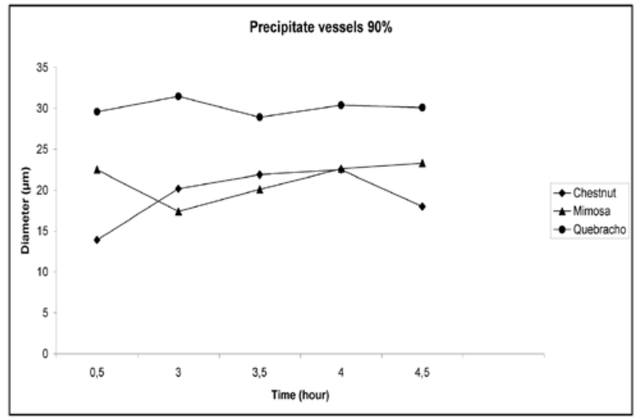

Figure 5: Variation in diameter of the chemical elements in the watery dissolutions at rest of the different vegetable extracts in relation to time. Volume given: 90%.

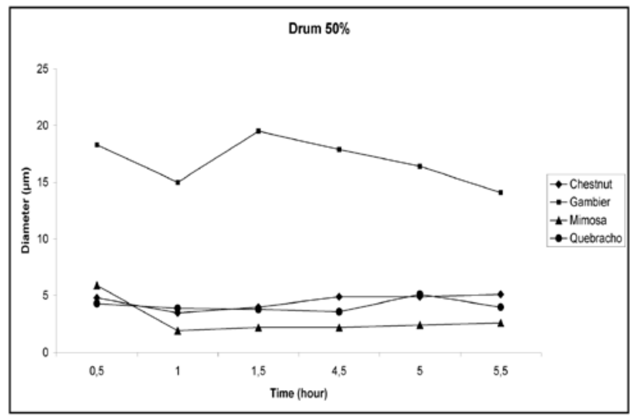

Figure 6: Variation in diameter of the chemical elements in the watery dissolutions of the different vegetable extracts subjected to the mechanical effect of the drum in relation to time. Volume given: 50%.

analyses indicated the variables which were influential and the extent to which these variables had an effect on the size of the aggregates formed by each of the vegetable extracts tested.

It must be born in mind that the results obtained have to be interpreted from a qualitative perspective and that they basically speak for different tendencies. Any change in the working conditions would be likely to cause a shift in the values obtained from the measurements. This being the case, the tendencies should still be the same. Figure 2 shows the results obtained for the four vegetable extracts in accordance with the different working temperatures. This Figure shows all the results of the measurements obtained with 75% volume in the tests using ultrasound. The graph of the diameters of particle seems to indicate that the diameters of the chestnut, mimosa and quebracho are reduced when the temperature is increased, whereas the gambier has the opposite behaviour. The graph also indicates that there is less influence of the temperature in the case of the gambier (a less acute slope), whereas the three remaining vegetable extracts followed a different pattern.

The mimosa, quebracho and gambier fall into the same chemical category within the group of tans. They belong to the group of condensed or catechin tans. The chestnut belongs to the group

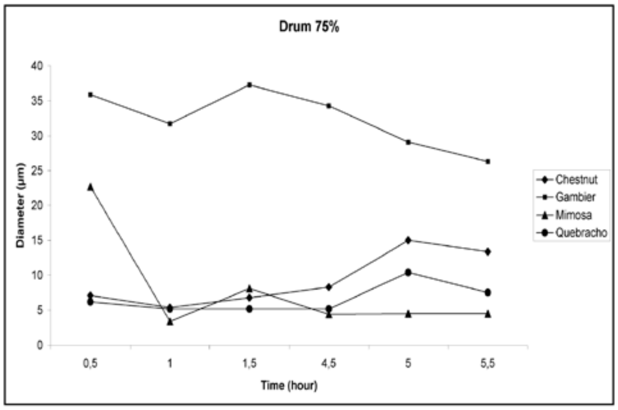

Figure 7: Variation in diameter of the chemical elements in the watery dissolutions of the different vegetable extracts subjected to the mechanical effect of the drum in relation to time. Volume given: 75%.

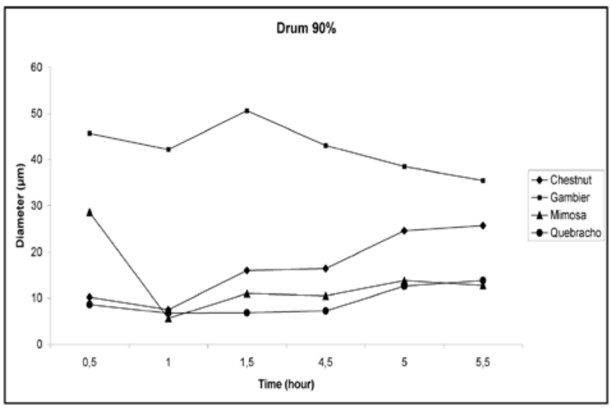

Figure 8: Variation in diameter of the chemical elements in the watery dissolutions of the different vegetable extracts subjected to the mechanical effect of the drum in relation to time. Volume given: 90%.

of hydrolysable or pyrogallic tans. However, this classification is based on the chemical composition of the vegetable extract prior to its chemical modification. Thus, in view of the results obtained in this example provided here, the modifications the vegetable extract is subjected to before its commercialization should be taken into account if one intends to predict the effect of the ultrasound on an aqueous dissolution of the extract under different working conditions. The complete process of chemical modification is usually considered a commercial secret by the manufacturer of vegetable extracts and they only give away part of the information to the customer. Thus, and despite the fact that a qualitative reading of the results obtained in this work leads to very clear conclusions, the quantitative results are only valid for those vegetable extracts tested here.

The working conditions in which the shortest diameters of particle were obtained are represented in Tables I, II and III. Each table corresponds to one of the three different systems (i.e. precipitate vessels, ultrasound and drum) which have been tested. The numbers in each box indicate the diameter of particle in µm. Such a number is the mean of all the measurements made throughout the experiment.

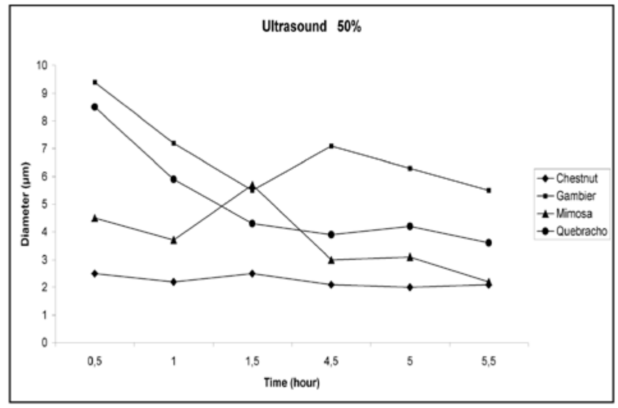

Figure 9: Variation in diameter of the chemical elements in the watery dissolutions subjected to the effect of ultrasound on the different vegetable extracts in relation to time. Volume given: 50%.

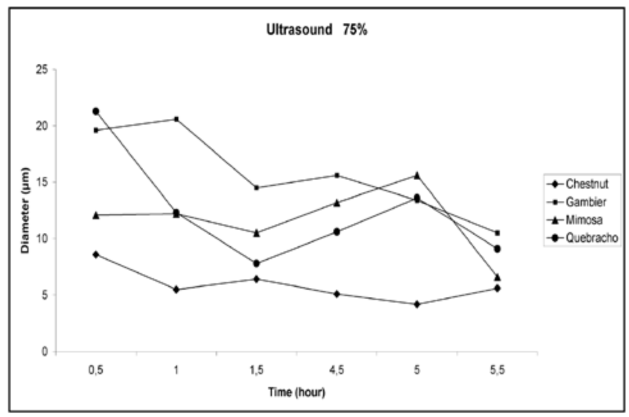

Figure 10: Variation in diameter of the chemical elements in the watery dissolutions subjected to the effect of ultrasound on the different vegetable extracts in relation to time. Volume given: 75%.

An analysis of the results obtained indicates that, with regard to each of the agitation systems used, the vegetable extracts tested differ in behaviour from one another. In addition, each of the vegetable extracts tested behaves differently as regards the agitation system employed.

The analysis also indicates that the influence of the variables under study (i.e. concentration and temperature) may vary depending on the size of the given aggregates.

Finally, and most importantly for practical purposes, the minimum particle diameters obtained using the ultrasound are shorter in three of the vegetable extracts tested (i.e. chestnut, gambier and mimosa) than those obtained using the drum.

This seems to indicate that the disaggregating effect of the drum can also be obtained by means of applying the ultrasound.

The effect of processing time on the solution of extracts has also been analysed. It was observed that the diameter of particle in those dissolutions which were at rest increased over time (Figs. 3, 4 and 5). This effect is more acute on the aggregates with lower diameter (50% of the volume).

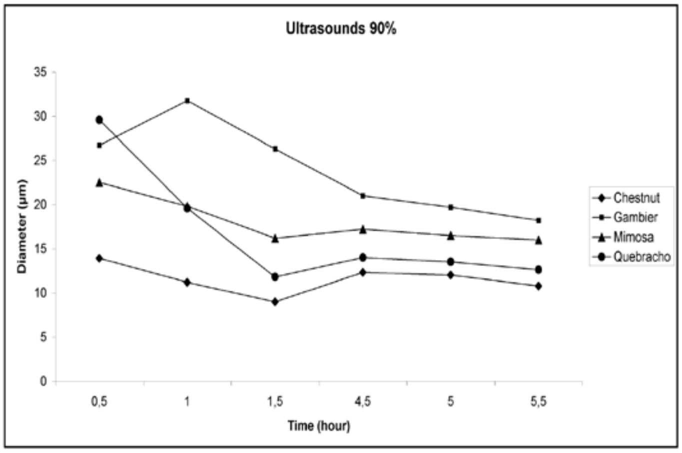

Figure 11: Variation in diameter of the chemical elements in the watery dissolutions subjected to the effect of ultrasound on the different vegetable extracts in relation to time. Volume given: 90%.

As for the tests carried out in the drum (Figs. 6, 7 and 8), there was an increase of diameter over time in the aggregates with a greater diameter (75 and 90% of the volume). The gambier, however, behaves in an opposite way to the other three vegetable extracts. This effect of polymerisation is weaker than in the previous case.

As far as the tests carried out in the ultrasound tank is concerned (Figs. 9, 10 and 11), the ultrasound generally showed a steady diameter of particle throughout the experiment. It was also observed that the average diameters of particle were generally slightly lower than those carried out in the drum. The average diameters of particle in the tests carried out without agitation on the dissolutions of extract were clearly higher than those obtained from the remaining tests.

It can easily be inferred from the analysis of the results that the behaviour of each of the extracts is different and that it probably depends on their composition. The values of diameter of particle obtained from the chestnut, mimosa and quebracho for each of the tests carried out are similar on the whole, whereas those obtained from the gambier are always significantly higher. It is worth reminding at this point that we work with vegetable extracts that are marketable, and that they are not pure. Thus, these extracts are often treated chemically in order to increase their solubility. This implies, for instance, that the behaviour of two extracts of chestnut from two different brands may be different.

However, the results obtained from the tests and their analyses indicate that the effect of the ultrasound on the diameter of particle of the vegetable extracts in a aqueous dissolution is similar to that of the drum. The comparison with the aqueous solutions of vegetable extracts that are at on stand demonstrates that both the effect of the ultrasound and the effect of the drum influence the vegetable extracts, either constraining or preventing their molecular aggregation. It can be inferred from this that the action of the ultrasound may facilitate the penetration of the vegetable extracts into the hide. This would help to reduce the size of the particles involved in the tanning process to a similar extent or more than that resulting from tanning in the drum.

Conclusions

It has been demonstrated that the polymerisation of the particles that are part of different vegetable extracts is prevented by subjecting their aqueous dissolutions to the effect of ultrasound. Consequently, the particle size of the different polymers present in the vegetable extracts is reduced. This reduction can be compared to what occurs when the same dissolutions are subjected to the mechanical action of a drum. This reduction enhances the penetration of the vegetable extract into the hide. Therefore, the use of ultrasound may come to substitute the drum in the tanning process and damage to the hides would therefore be prevented. This would entail, from an economical point of view, an increase in the value of the leathers obtained and the possibility to enhance competitiveness within the tanning industry.

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