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Evaluation of Potential Application for Guava Bark Extract in Leather Tanning

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Abstract

Using natural tanning materials is needed to reduce toxicity of leather tanning industry. This investigation was carried out to evaluate the efficiency of using guava bark extract; *Psidium guajava L.* in leather tanning. The collected guava bark was dried at 25°C for 5 days. Thereafter, the dried material was grounded for extraction using water at 90°C. Pickled pelts from 18 Barki rams aged 12-18 months were used and allocated randomly into 6 groups. The experimental groups were either guava extract separately or with using other re-tanning materials; chromium sulfate, aliphatic aldehyde, or phenol sulfonates. Extract characteristics, leather properties and scanning electron micrographs were determined. The results of extract characteristics showed the ability of using guava extract in leather tanning due to its values of extraction yield (54.24%), tannins content (21.36%), hide powder (31.12), and stiasny number (41.42). Although the properties of tanned leathers showed no preference in using the guava extract alone in tanning, but it could be more valuable when using as a re-tanning material to reduce chromium addition in mineral tanning or any other synthetic tanning materials to improve the quality of produced leathers.

Keywords: Extraction; Leather properties; Tannins.

1. Introduction

Leather is the major animal product for the manufacture of garments, shoes, bags, etc. and it gathers about 10 percent of the universal industrialization market [1]. During leather tanning process, raw hides or skins convert into leathers when collagen fibers react with tanning materials, which vary according to their sources [2]. Although, chrome tanning is the most widespread tanning material worldwide due to the high quality of its produced leather, vegetable tanning is still the most eco-friendly tanning material [3]. The effective material of vegetable tanning materials is tannins, which are water-soluble polyphenolic compounds, and thus it is rich in phenolic groups. Therefore, vegetable tannage is essentially a chemical combination of the positively charged $–NH_3^+$ groups in the collagen fibers of skins with the negatively charged tannin molecule of vegetable tanning material [4]. Due to the eco-friendly using of vegetable tanning is a demand, it is necessary to introduce alternative sources to bridge the gap between demand and production.

From previous investigations, there were many plant species containing variable concentrations of tannins. Some of these plants have been analyzed for using their tannins contents in different purposes such as pharmaceutical, adhesive, dyestuff, or tanning materials [5-7]. In vegetable tanning the quantitative method of extraction is more important than qualitative method because it produces high yield of extract. Since tannins are water soluble, water is the best used solvent in quantitative extraction method for reducing the production cost [4, 8, 9].

The most vegetable extracts used in leather tanning are quebracho, mimosa and chestnut extracts [4], while another various material need to evaluate for applying in leather tanning. Previous

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investigations were studied untraditional plant material such as sunt (*acacia nilotica*), Henna (*Lawsonia inermis*) and Pomegranate (*Puinca granatum L.*) [3, 6]. In this context, natural plant resources are preferred to achieve environmental and economic benefits in a manner that ensures sustainability [7].

Psidium guajava L. (guava) is considered one of the most edible plants, their leaves and barks contain polyphenolic compounds including tannins, which are used in traditional medicine [10, 11]. In 2019, world production of guavas was 55 million tonnes, led by India with 45%, whereas Egypt was ranked ninth with 1.5 million tons [12].

Therefore, this investigation aims to evaluate the potential application of using guava bark extract in leather tanning.

2. Materials and Methods

2.1. Raw material:

Guava bark was collected from Al-Maamoura agricultural area in Alexandria Governrate, which locates at the north of Egypt. The collected bark was dried at 25±3°C for five days in an open and shaded place without the use of any of thermal drying methods. Thereafter, dried guava bark was grounded by a 0.3 mm fineness grinder and stored in paper bags until being used.

2.2. Extraction and concentration:

Extraction was done in the Chemical Laboratory of Agriculture Biochemistry Department, Al-Azhar University, Cairo, Egypt. The extraction was carried out in a 2-L Pyrex glass reactor with mechanical stirring and automatic temperature control. Solid/ liquid ratio maintained constant at 1/10 (w/w). Water was used as extraction agent without any chemical additives. The extraction temperature was 90°C for 2 hours. Ground bark and water were mixed at room temperature, heated and once the selected temperature was attained, contact time begun to run. After one hour, the warm suspension was vacuum filtered. The solid residue was washed with water and the extract together. The liquid extract was dried using an oven at 60℃. The extraction yield was calculated as the percentage weight loss of the starting raw material [5].

2.3. Total phenol and tannins content:

Total phenols and tannins contents were determined by the Folin–Ciocalteu method using a spectrophotometer. The total phenols were estimated as tannic acid equivalent (TAE), while Polyvinylpolypyrrolidone (PVPP) was used to bind tannin-phenolics for measurement of tannins then non-tannins were determined and tannins were calculated [13].

2.4. Hide powder test:

Bark extract (400 mg) was dissolved in 100 ml of distilled water. Slightly chromated hide-powder (3 g) was added and the mixture was stirred for one hour at an ambient temperature. The suspension was then filtered through a sintered glass filter. The weight gain of the hide-powder was expressed as a percentage of weight of the starting material [5].

2.5. Stiasny number:

Bark extract (100 mg) was dissolved in 10 ml of distilled water. 1 ml of 10M HCl and 2 ml of formaldehyde (37%) were added and the mixture was heated under reflux for 30 minutes. The hot reaction mixture later was filtered through a sintered glass filter. The precipitate was washed 5 times with 10 ml hot water and finally dried. The yield of tannin was expressed as a percentage of the weight of the starting material [5].

2.6. Fourier Transform Infrared Spectrometry (FTIR):

The spectrophotometer (Bruker Varian 70 transform infrared using Platinium ATR unit) was used to analyze the chemical structure and the fingerprint extract. Small quantity of the extract in the solid phase was used and scanned directly on the instrument stage.

2.7. Tanning Sheep skins:

Sixteen slaughtered male Egyptian Barki sheep skins (12-18 months age) were cured by salting then transported El-Shafie tannery in the El-Max region in Alexandria, Egypt, and prepared for tanning with different treatments.

The skins were common in the first beamhouse steps which started from soaking to pickling. After then, the pelts were divided randomly into six groups (three pelts in each group). Table (1) shows the differences among experimental groups in tanning and re-tanning steps.

Table 1: Experimental tanning groups.

Experimental group	Tanning step	Re-tanning step
G1(Full vegetable)	40% Guava Extract	Not re-tanned
G2 (Combined tanning/*free-chrome*)	40% Guava Extract	3%Novalatan PF
G2 (Combined tanning *(free-chrome)*	40% Guava Extract	3%Novalatan PF + 3% Dolatan F
G4 (Combined tanning)	40% Guava Extract	3% Cr (33% basicity)
G5 (Combined tanning)	40% Guava Extract	6% Cr (33% basicity)
G5 (Full chrome)	9% Cr (33% basicity)	Not re-tanned

Novalatan PF is a synthetic re-tanning agent based on aliphatic aldehyde and Dolatan F is a synthetic re-tanning agent based on phenol sulfonates from Zschimmer & Schwarz company.

2.8. Leather properties determination:

All finished tanned leathers were taken for final testing and visual evaluation. Samples were obtained as per ASTM methods [14]. Specimens were conditioned at 20°C ± 2°C and 65% ± 4% R.H. over a period of 48 hours. Physical properties, namely; thickness, density, tensile strength, elongation percentage at break, split tear strength, static water absorption and shrinkage temperature were measured. Each value reported is an average of three samples. Chemical properties such as pH, moisture %, ash %, chromium content % have been carried out. Organoleptic properties were assessed for softness, grain smoothness, grain tightness, fullness, and general appearance by standard tangible evaluation technique. Five experienced tanners rated the leathers in a scale of 1-10 points for each functional property (higher points indicate a superior property). The average of the five tanners was recorded for each sample [15].

2.9. Scanning Electron Microscopy (SEM):

The leather specimens (1 cm^2) were cut from official sampling position according to ASTM-D2813 [14], subjected to sputter coating with gold ions using a JCF-1100E- JEOL and evaluated using a JEOL JSM-IT Series electron microscope. Three micrographs were depicted for each sample; the cross section at 40x, surface at 100x, and collagen bundles at 500x.

2.10. Color Measurement:

The reflectance of the tanned leather was measured from 400 to 700 nm (spectral interval 10 nm) with a portable SP62 Spectrophotometer from X-Rite which allows to obtain the CIE L*a*b* values.

2.11. Statistical Analysis:

Data were analyzed using GLM procedure of SAS [16] to evaluate the differences among produced leathers. The following model was used in the analysis:

$$Y_{ij} = \mu + T_i + e_{ij}$$

Where Y_{ij} is the observation taken on finished leather, μ is overall mean, T_i is a fixed effect of leather types and e_{ij} is the random error assumed to be normally distributed with mean = 0 and variance = $\sigma^2 e$.

Figure (1) summarizes all working steps of this study.

3. Results

3.1. Properties of guava bark extract:

Table (2) shows the extraction yield and extract properties for guava bark. The quantity parameters; yield, total phenol, total tannins, non-tannins and tannins/non-tannins values were 54.24%, 24.22%, 21.36%, 2.86% and 7.47, respectively. The previous investigations obtained vegetable extracts from other different vegetable materials whose quantitative properties are commercially feasible, were coincided with corresponding values from this study [3, 6, 17, 18].

From our point of view, the quality of obtained extract was positive for lead acetate and ferric chloride tests, which indicates the presence of hydrolysable tannins [19], whereas the stiasny number (41.42) confirmed the content of stable tannins, especially condensed tannins [5, 20].

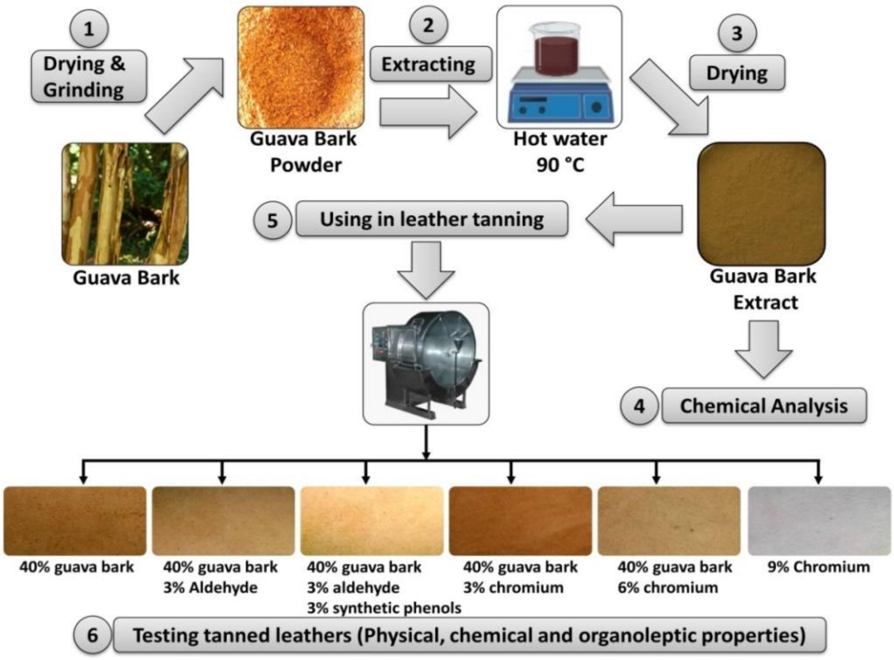

Figure 1: Schematic diagram for working steps.

Table 2: Chemical properties for guava bark extract.

Parameter	Value
Extraction yield	54.24 %
Total phenol	24.22 g TAE/100g extract*
Total tannins (T)	21.36 g TAE/100g extract*
Non-tannins (N)	2.86 g TAE/100g extract*
T/NT	7.47
Lead acetate	+
Ferric chloride	+
Hide powder	31.12
Stiasny number	41.42
pH	5.13
Color	Dark-Brown

** TAE: Tannic Acid Equivalent.*

Although the obtained value of staisny number is similarly with the extracts of some vegetable tanning material such as sunt pods, but it is still lower than the corresponding values of commercial quebracho and mimosa that used in tanneries [6].

Fourier transform infrared was used to study the molecular structure of each extract. The list assignment for the different IR bands of prepared guava extract and commercial quebracho and mimosa extracts are presented in Table (3). Figure (2) shows the infrared spectra of guava extract. The absorption bands for all regions are of medium or weak intensity, except regions (3650-3000 cm^{-1}) and (1695-1600 cm^{-1}) which are broad and strong. The 1695-1600 cm-1 absorption band was attributed to C=C stretching, which might be due to aromatic ring for tannins compounds in the extracts. Regarding to the previous investigations, all these regions were recorded for tannins extracts from other vegetable materials [6, 21-23].

3.2. Scanning electron micrographs for tanned leathers:

Scanned electron micrographs of the experimental tanned leathers are shown in Figure (3). The micrographs of guava tanned leather showed a clear swelling effect of the extract on the collagen fibers similar to vegetable tanning materials [4], and thus the cross section was the highest in compactness with lowest air gaps.

Table 3: Assignment of varying IR bands of different extracts.

Remarks		Absorption peak (cm^{-1})		
Bond	Absorption peak (cm^{-1})	Quebracho	Mimosa	Guava
OH stretching	3000-4000	3242	3244	3421
C=C stretching	1600-1695	1606	1605	1615
C-H bending	1330-1420	--	--	1384
Ester group	1175-1390	1368	1308	1193
		1279	1196	
C-O-C stretching	1000-1200	1158	1077	1123
		1111	1154	1099
		1033	1069	1036
Aromatic C-H out of plane bending	800-870	--	840	909
Ring deformation	700-780	773	--	753
C-S vibration of sulfonic group	600-680	643	622	658
				643
				601

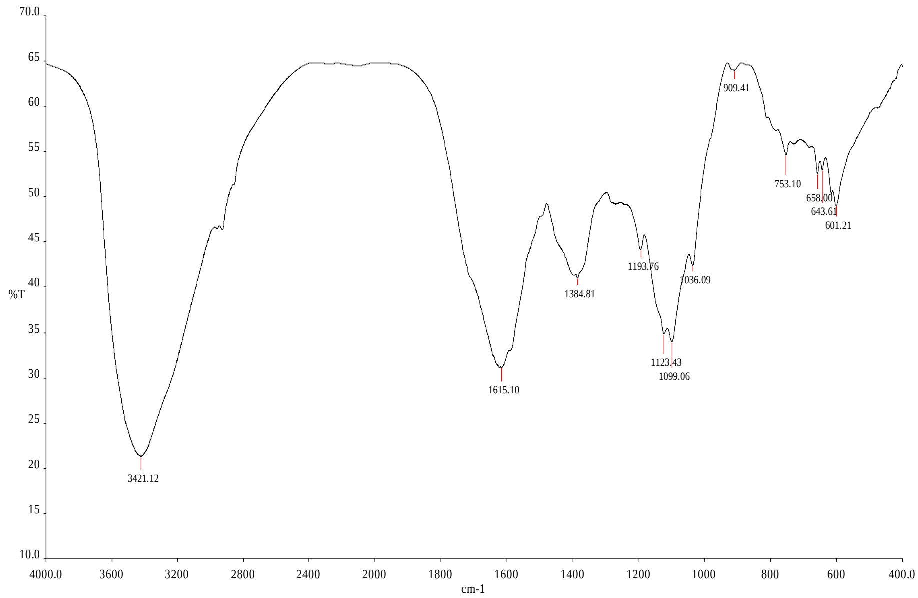

Figure 2: FTIR spectra for Guava bark extraction.

By re-tanning guava tanned leathers in other groups, the swelling effect decreased showing as less fullness of collagen fibers and an increment in the distances among them.

In re-tanned leathers with 3% Novalatan PF (aldehydes), cross section thickness started to increase due the increment in the distances among collagen fibers, whereas in re-tanned leathers with both 3% Novalatan PF and 3% Dolatan F (polyphenols), the cross section thickness showed the highest peak due to increasing of collagen fibers' fullness with medium distances in between.

Regarding to the cross section of re-tanned guava leathers with chromium sulfate, thickness increased by increment chromium content from 3% to 6% due to the wide distances among collagen fibers. As for fully tanned leathers (9% chromium sulfate), the collagen fiber bundles were compressed and intertwined with clear distances among them.

The grain surfaces of all groups showed non-fibrous surface with numerous pores but the distances among pores appeared curvier in re-tanned leathers, especially free chrome leathers.

3.3. Tanned leathers properties:

Physical and chemical properties are presented in Table (4), whereas Table (5) shows the organoleptic properties for the experimental tanned groups. Elongation, pH, grain tightness and grain smoothness were insignificant among tanned leathers, whereas other properties were significantly differed.

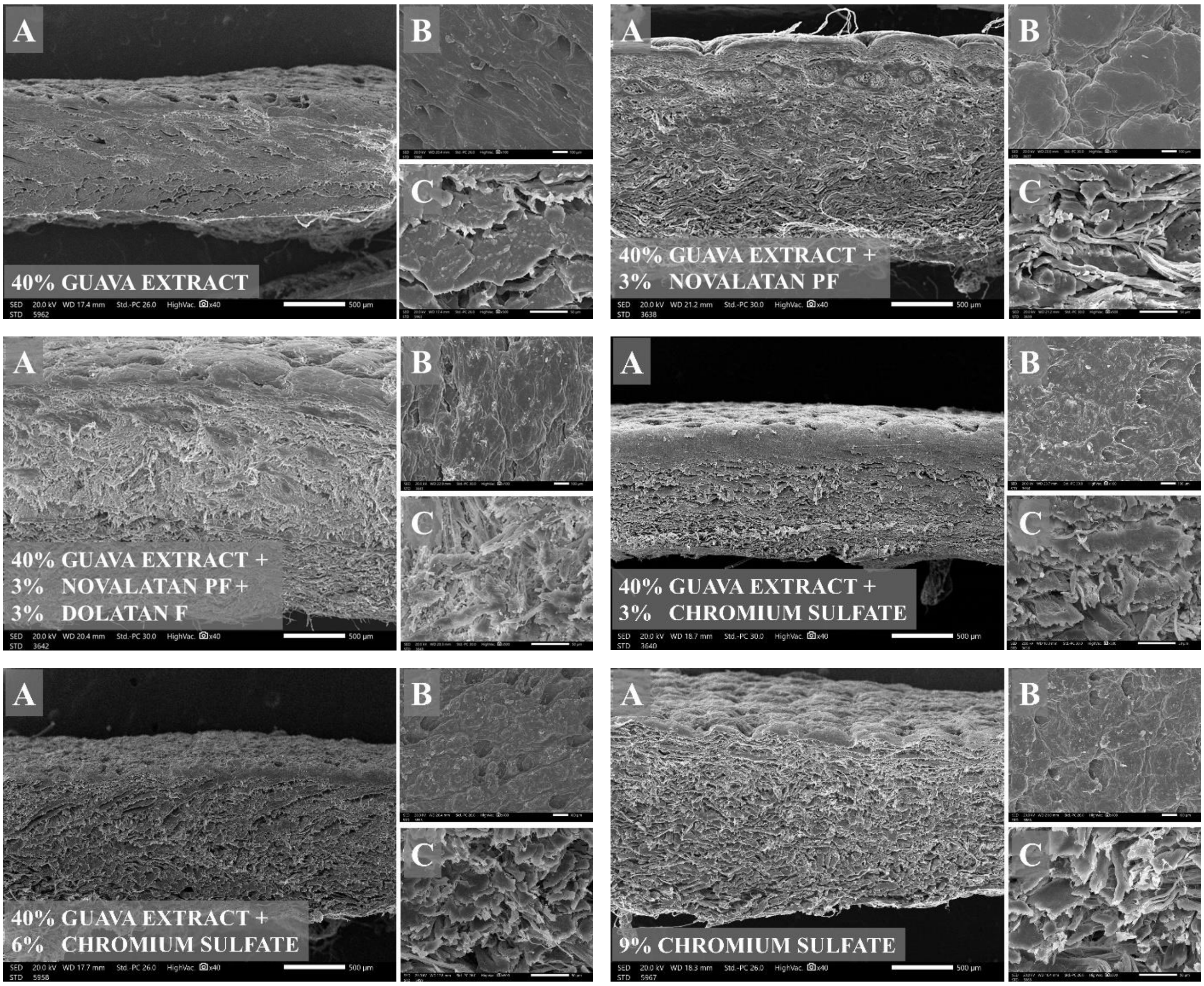

Figure 3: Scanning electron micrographs for all tanned leathers groups
A.Cross section depicted at 40x.
B.Grain surface depicted at 100x.
C. Collagen bundles depicted at 500x.

The re-tanned leathers in G2 and G3 showed the thickest and the highest density, which is normally due to the effect of vegetable tanning materials and synthetic polyphenols on collagen fibers [4, 8].

Chrome tanned leathers (G6) were lower in tensile strength than vegetable tanned leathers (G1), whereas tear strengths between the two groups were insignificantly different. This result may not be consistent with that pointed out by Ahmed *et al.* [24] but the higher values of other re-tanned groups were in agreement with that mentioned by Covington [4] and Musa *et al.* [25].

Although elongation values were insignificantly different, chrome tanned leathers tended to be the highest in elongation (70.98%). That is considered from the advantages of chrome tanned leather [24].

Regarding the water absorption property after 2 and 24 hours, G3 surpassed other groups and that may be due to increasing its thickness and density. The groups which were treated with chromium (G4, G5 and G6) showed lowest water absorption values without significant differences. This result is harmonized with Dutta [8] in water resistant characteristic of chrome tanned leathers.

The shrinkage temperature of G1 showed the lowest value (75°C). Covington [4] explained that when shrinkage temperature of vegetable tanned leather is <80°C, it is probably tanned with hydrolysable tannins. However, it is slightly higher than traditional shrinkage temperature for pickled pelts (68°C) as mentioned by BASF [2]. That gave an indication for the weak effect to produce fully tanned leathers, while other re-tanned groups have good values of shrinkage temperatures.

Table 4: Physical and chemical properties of different tanned leathers.

Property	Unit	G1	G2	G3	G4	G5	G6	Mean	SEM	Sig.
				Physical properties						
Thickness	mm	1.37^{b}	1.91^{a}	1.96^{a}	1.42^{b}	1.49^{b}	1.52^{b}	1.61	0.06	**
Density	gm/cm^3	0.49^{bc}	0.56^{ab}	0.62^{a}	0.51^{bc}	0.53^{bc}	0.45^{c}	0.53	0.02	**
Tensile strength	kg/cm^2	266.07^{a}	273.54^{a}	281.51^{a}	270.53^{a}	262.97^{a}	213.16^{b}	261.30	6.80	*
Elongation	%	64.56	60.18	60.94	60.45	68.05	70.98	64.19	1.42	ns
Tear strength	kg/cm	50.31^{c}	53.62^{c}	55.13^{bc}	63.01^{ab}	64.59^{a}	50.73^{c}	56.23	1.62	**
Water Absorption 2h	%	111.24^{b}	112.95^{b}	158.67^{a}	108.05^{b}	110.85^{b}	98.56^{b}	116.72	5.04	**
Water Absorption 24h	%	125.81^{bc}	133.78^{b}	166.67^{a}	112.68^{cd}	123.26^{bcd}	104.90^{d}	127.85	5.18	**
Shrinkage Temperature	°C	75.00^{c}	92.33^{b}	93.33^{b}	94.00^{b}	100.00^{ab}	105.67^{a}	93.39	2.59	**
				Chemical properties						
Moisture	%	14.31^{ab}	12.09^{c}	12.38^{bc}	16.20^{a}	16.10^{a}	14.99^{a}	14.35	0.46	**
Ash	%	2.17^{d}	2.50^{cd}	2.81^{c}	3.57^{b}	3.76^{b}	7.12^{a}	3.66	0.40	**
Chrome	%	0.00^{d}	0.00^{d}	0.00^{d}	1.35^{c}	2.69^{b}	3.22^{a}	1.21	0.32	**
pH	ml mol/L	4.00	4.08	4.39	4.79	4.96	4.86	4.51	0.12	ns

G1: leathers tanned with 40% guava extract, G2: leathers tanned with 40% guava extract and re-tanned with 3% NOVALATAN PF., G3: leathers tanned with 40% guava extract and re-tanned with 3% NOVALATAN PF and 3% DOLATAN F., G4: leathers tanned with 40% guava extract and re-tanned with 3% chromium sulfate., G5: leathers tanned with 40% guava extract and re-tanned with 6% chromium sulfate., G6: leathers tanned with 9% chromium sulfate.

SEM: standard error of the mean, ns: not significant, * significant at P<0.05, ** significant at P<0.01.

Means with different superscripts letter are significantly different (P<0.05).

Table 5: Organoleptic properties of different tanned leathers.

Property	G1	G2	G3	G4	G5	G6	Mean	SEM	Sig.
Fullness	7.20^{c}	8.80^{ab}	9.60^{a}	8.00^{bc}	8.40^{b}	8.20^{b}	8.37	0.18	**
Grain tightness	8.80	8.60	9.20	8.40	8.60	8.60	8.70	0.10	ns
Grain Smoothness	8.00	8.00	8.60	8.40	8.60	9.00	8.43	0.11	ns
Softness	7.80^{c}	8.00^{c}	8.00^{c}	8.00^{c}	8.60^{b}	9.20^{a}	8.27	0.11	**
General appearance	7.20^{c}	8.80^{bc}	9.60^{a}	8.00^{b}	8.40^{a}	8.20^{b}	8.37	0.10	**

G1: leathers tanned with 40% guava extract, G2: leathers tanned with 40% guava extract and re-tanned with 3% NOVALATAN PF., G3: leathers tanned with 40% guava extract and re-tanned with 3% NOVALATAN PF and 3% DOLATAN F., G4: leathers tanned with 40% guava extract and re-tanned with 3% chromium sulfate., G5: leathers tanned with 40% guava extract and re-tanned with 6% chromium sulfate., G6: leathers tanned with 9% chromium sulfate.

SEM: standard error of the mean, ns: not significant, * significant at P<0.05, ** significant at P<0.01.

Means with different superscripts letter are significantly different (P<0.05).

Table 6: CIE L*a*b* data of the tanned leathers.

Group	Color	L*	a*	b*
G1	Brown	49.86	13.82	56.68
G2	Light-Brown	74.96	13.34	64.32
G3	Beige	85.82	3.85	35.75
G4	Reddish-Brown	61.92	17.12	67.22
G5	Light-Brown	80.12	7.95	51.52
G6	Light-Blue	85.71	3.11	-20.12

G1: leathers tanned with 40% guava extract, G2: leathers tanned with 40% guava extract and re-tanned with 3% NOVALATAN PF., G3: leathers tanned with 40% guava extract and re-tanned with 3% NOVALATAN PF and 3% DOLATAN F., G4: leathers tanned with 40% guava extract and re-tanned with 3% chromium sulfate., G5: leathers tanned with 40% guava extract and re-tanned with 6% chromium sulfate., G6: leathers tanned with 9% chromium sulfate.

With respect to chemical properties of tanned leathers, free-chrome leathers (G1, G2 and G3) were the lower in moisture, this may be due to the increment of density property for these groups, as well as, decreasing the air spaces among fiber bundles (Figure 3). Additionally, the absence of chromium salt in free-chrome tanned leathers (G1, G2 and G3) led to decreasing their ash contents.

All leathers have been computed on a scale of 1–10 with 1 being the lowest for organoleptic properties. Guava bark tanned leathers (G1) showed the lowest values in all properties, contrarily to the re-tanned leathers with free-chrome tanning materials (G2 and G3), which showed the best in fullness and general appearance properties. On the other hand, fully chrome tanned leathers (G6) were the softest followed by the re-tanned leathers with 6% chromium sulfate (G5) and the other leathers were comparable in this property.

Using guava bark extract for producing full vegetable leathers (G1) produced leathers with brownish color, whereas using the re-tanning agents led to lightening the color for produced leathers (G2, G3, G4 and G5). Additionally, increasing the concentrations of re-tanning agent affected positively the color lightening (Table 6 and Figure 1).

Traditional quebracho and mimosa leathers are known for their colorfastness because it shows an approximately constant level of 17-27% reflectance from 400 nm to 500 nm, then increase to nearly 70% at 700 nm [6]. Therefore, guava bark tanned leathers are darker and more yellowish than the both of quebracho and mimosa leathers.

4. Discussions

From the properties of guava bark extract (Table 2), hot water extraction produced an extract of about half the raw material amount, which considered a good amount for commercial using [5, 20]. Additionally, the content of tannins is approximately one-fifth of the obtained extract, which was also detected by the results of lead acetate, ferric chloride, hide powder and stiasny number tests. Moreover, FTIR spectra (Figure 2 and Table 3) showed a fingerprint for phenolic compounds in similarity to those found in quebracho and mimosa extracts, which consist mainly of tannins [2, 4, 8].

The polyphenolic and tannins compounds in guava bark extract gave a good value of hide powder test and thus it is possible to be used it in leather tanning. However, the values of aforementioned extract characteristics are preferably used as a re-tanning agent or in combination tanning due to its lower tannins content, as well as the medium values for both hide powder and the stiasny number.

Furthermore, the presented data of tanned leathers properties (Tables 4 and 5) showed the acceptability of using the extract commercially in leather tanning. Guava bark extract has the swelling effect on collagen fibers same to traditional vegetable tanning materials that are traditionally used in tanning. Figure (3) clearly shows the swelled fibers in leathers (40% guava bark extract). It is obviously known that the vegetable tannins compounds are large in their molecular weights, in turn increasing the diameters of collagen fiber bundles [4, 8]. On the other hand, the physical properties of guava bark tanned leathers (Table 4) showed the lowest values in thickness and shrinkage temperatures, whereas all re-tanned leathers showed the superiority in quality than guava bark tanned leathers. This improvement is confirmed by more strengths, shrinkage temperatures and color lightening (Table 6). As the results of these effects, the scores for organoleptic properties of re-tanned leathers were improved (Table 5). From our point of view, this may be due to the positive effect for combination tanning, which increasing the crosslinks among collagen fibers and miscellaneous tanning materials.

BASF [2] and UNIDO [26] noted the acceptable range for leather manufacturing, the results of this investigation are within these ranges, showing remarkable values for strengths, elongation, and good value of water absorption. Nevertheless, using guava bark extract in combination tanning or as a re-tanning agent will give higher quality leathers.

5. Conclusions

The present study indicated that guava bark extract can be utilized as a source for tannins material in different industry purposes. Moreover, the study recommended for using in leather tanning in combination tannages with other tanning agent material or as a re-tanning agent material for improving the quality of produced leathers.

6. Conflicts of Interest

There are no conflicts to declare.

7. Acknowledgments

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