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Potential Application of Used Coffee Grounds in Leather Tanning

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ABSTRACT

Safety of environment and human health is an essential requirement of modern industrial techniques. Therefore, using natural agents in tanning industry may emerge as a trusted method to avoid the chemical contamination caused by using traditional chromium salts in tanning process. This study aimed to evaluate the hot water extract of used coffee grounds (UCGs) as a vegetable tanning agent. The collected UCGs were dried and extracted with hot water at 90 °C for 2h. The phytochemical screening properties of UCGs extract were determined. Sufficient amount of extract was prepared to be used in leather tanning. Three groups were tanned with UCGs extract solely at concentrations of 20, 30 or 40% of pelts' weight, while another three groups were tanned with the same concentrations and then re-tanned with 10% of a synthetic tanning agent "Phenol sulfonates". On tanned leathers, organoleptic, physical and chemical properties were determined; scanning electron micrographs were depicted to examine the leather surface and collagen fiber bundles. Analysis of UCGs extract revealed that it has good tanning properties, as it contained tannins (14.92%), tannins/non tannins ratio (2.06), hide powder (39.57) and Stiasny number (21.16). The results of leather properties showed that using UCGs extract alone at concentration of 40% achieved the best results for the vegetable tanning where the tanned leather had higher ($P<0.05$) tensile strength, tearing strength and shrinking temperature than that treated with the lower level of 20% UCGs extract. However, 40% of UCGs extract is highly recommended to be used to accomplish the required shrinkage temperature that should be ≥ 70 °C. UCGs extract could be successfully used as tanning agent in vegetable tanning to produce durable leathers with good fullness; it may be used for different manufacturing products, such as footwear and bags. Moreover, using a combination of UCGs extract at any of the used concentrations with phenol sulfonates 10% led to significant improvement in all studied traits as compared with using UCGs extract alone.

Keywords: leather properties, tannins, vegetable tanning.

INTRODUCTION

Leather tanning converts animal skins or hides as a material susceptible to biodegradation into leathers as a non-degradable material, stable thermally and resistant to abrasion that can be used in the manufacture of various leather products [Covington, 2009]. For decades, vegetable tanning was the only known tanning method. With development of the industry, other tanning methods had been developed, such as mineral tanning, which is currently prevalent in the world. Although chrome tanning has various advantages compared to vegetable tanning [BASF, 2007], solid and liquid wastes of this industry showed many negative effects on plants, animals and human's health [Erdem & Ozverdi, 2008; Jia, et al., 2016] that promoted a return to vegetable tanning again as an eco-friendly tanning method [Alim, et al., 2019].

Vegetable tanning is based on the use of natural plant extracts with high content of tannin compounds having small particles enough to penetrate, react and crosslink with collagen fibers in raw skins or hides. Both of condensed and hydrolysable tannins with high concentrations in some famous plants (e.g. wattle, mangrove, quebracho and hemlock, myrobalan and chestnut) are being currently used in leather tanning [BASF, 2007; Dutta, 2008; Covington, 2009].

As a result of the continuous need for vegetable tanning extracts, there is a large gap between the production and consumption of these extracts, causing an increment in tanning cost production. Therefore, the provision of new plant sources is important to bridge this gap [Falcão & Araújo, 2018; Guo, et al., 2020].

Extraction of tannins from plant sources is affected by different conditions including solvent type, extraction temperature and the solid to solvent ratio [Das, et al., 2020]. Using hot water was found to be the best method for extracting plant agents that are used in leather tanning, due to its simplicity, high content of tannins and lower cost of extraction process [Galvez, et al., 1997; Li & Maplesden, 1998; Vázquez, et al., 2008; Guo, et al., 2020].

Coffee is one of the most popular drinks around the world, and it is consumed in large quantities, amounting to about 11 million tons annually [FAOSTAT, 2020]. Coffee is usually prepared by extracting it in hot water to leave the used coffee grounds (UCGs) as a waste. The quantity of UCGs produced is estimated about 75% of the weight of the original coffee beans, so the quantity produced annually reaches 8 million tons [Choi & Koh, 2017].

Several studies indicated different organic components that can be exploited from UCGs for multiple purposes, such as making fertilizers, biodiesel and sorbent for metal removal instead of dumping into general waste and sent to landfill [Choi & Koh, 2017; Das, et al., 2020; Tran, et al., 2020]. Recently, the water extract of UCGs was chemically evaluated and gave promising results as a leather tanning agent [Mutuku, et al., 2022], but unfortunately, the application of UCGs extract in leather tanning has not been performed yet.

The current investigation aimed to estimate the possibility of using hot water extract from UCGs to be used in vegetable leather tanning.

MATERIALS AND METHODS

Sample collection

Wet UCGs are usually produced after preparing coffee using the Turkish method, in which ground coffee beans are mixed with water and then heated. As soon as the mixture begins to froth and before it boils, it is taken off the heat. Sufficient amount of wet UCGs were supplied from different cafés in Alexandria city, Egypt. The collected UCGs were mixed and dried at room temperature (25 ± 3 °C) and then stored in paper bags until being used.

Extraction

Extraction was performed using water without any chemical additives. UCGs were soaked in water with constant solid/ liquid ratio (1/10, w/w) for a day. The next day, the extraction was carried out in a 2-L Pyrex glass reactor with mechanical stirring and automatic temperature control. UCGs were heated and once the temperature reached 90 °C, extraction began to run for 2 hours. After extraction, the warm suspension was vacuum filtered. The liquid extract was dried in an oven at 60 °C till it is dried.

Phytochemical screening

Extraction yield

Total extraction yield was calculated as weight ratio between the dried extract and the initial dry weight of the raw material.

Total phenol and tannin contents

Total phenols and tannin contents were determined by the Folin–Ciocalteu method using a spectrophotometer. The total phenols were estimated as tannic acid equivalent (TAE), while Polyvinylpolypyrolidone (PVPP) was used to bind tannin-phenolics for measurement of tannins, then non-tannins were determined and tannins were calculated [Makkar, 2003].

Lead (II) acetate test

An amount of 0.5 ml of lead acetate solution (1%) was added to 10 mg of solid extract and the formation of precipitate indicates the presence of tannins and phenolic compounds [Ahmed, et al., 2018].

Ferric (III) chloride test

Five mg of the extract was taken and 0.5 ml of 5% ferric (III) chloride was added. The development of dark bluish black color indicated the presence of tannin compounds [Ahmed, et al., 2018].

Flavonoids test

Few drops of diluted NaOH solution were added to 5 ml of 10% extract solution. An intense yellow color was appeared in the test tube as the presence of flavonoids [Hossain, et al., 2013].

Hide powder test

UCGs 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. 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 [Vázquez, et al., 2008].

Stiasny number

UCGs extract (100 mg) was dissolved in 10 ml of distilled water. Then, 1 ml of 10M HCl and 2 ml of formaldehyde (37%) were added and the mixture was heated under reflux for 30 minutes. Later, the hot reaction mixture 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 [Vázquez, et al., 2008].

Fourier Transform Infrared Spectrometry (FTIR)

The spectrophotometer (Bruker Varian 70 transform infrared using Platinum 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.

Tanning sheep skins

Eighteen slaughtered male Egyptian Barki sheep skins were sent to El-Shafie tannery in El-Max region, Alexandria, Egypt. All skins were common in pre-tanning stage till pickling step. In tanning step, 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.

Tanned leather properties

Physical and chemical testing was applied on different samples of all finished leathers. Samples were obtained as per ASTM methods [ASTM, 2014]. The 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 tearing strength, static water absorption, permeability to water vapor and shrinkage temperature were measured. Every reported value was an average of three specimens. Chemical properties of pH, moisture % and ash % content were studied. The organoleptic properties of tanned leathers were assessed by five experienced tanners according to the standard tangible evaluation technique [Kasmudjiastuti & Murti, 2017]. The organoleptic properties included softness, grain smoothness, grain tightness, fullness, and general appearance on a scale of 1–10 points for each functional property (higher points indicate a superior property).

Scanning electron microscopy (SEM)

The leather specimens were cut from official sampling position according to ASTM- D2813, 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, grain surface at 100x, and collagen bundles at 150x.

Table 1. Experimental tanning groups

Experimental group	Tanning step	Re-tanning step
Group 1	20% UCGs extract	Not re-tanned
Group 2	30% UCGs extract	Not re-tanned
Group 3	40% UCGs extract	Not re-tanned
Group 4	20% UCGs extract	10% Dolatan F*
Group 5	30% UCGs extract	10% Dolatan F*
Group 6	40% UCGs extract	10% Dolatan F*

* **Note:** Dolatan F is a synthetic re-tanning agent based on phenol sulfonates from Zschimmer & Schwarz company.

Statistical analysis

The data were analyzed using GLM of SAS program [SAS, 2008] to evaluate the effect of tanning material, UCGs extract concentration and their interaction on the physical and chemical properties of finished leathers. The following model was used:

$$Y_{ijk} = \mu + T_i + C_j + TC_{ij} + e_{ijk} \quad (1)$$

where: Y_{ijk} – the observation taken on finished leather;
μ – overall mean;
T_i – a fixed effect of tanning material;
C_j – a fixed effect of UCGs extract concentration;
TC_{ij} – an interaction effect between tanning material and tanning concentration;
e_{ijk} – the random error assumed to be normally distributed with mean = 0 and variance = σ^2e.

Figure 1 summarizes all working steps of this study.

RESULTS AND DISCUSSION

Phytochemical screening of used coffee grounds extract

Table 2 shows the properties of UCGs extract. The extraction yield accounted for 42.43% and it was similar to that in a previous investigation [Low, et al., 2015].

The results of the preliminary phytochemicals screening were positive for ferric (III) chloride, lead (II) acetate and sodium hydroxide tests (Table 2 and Figure 2). This ensures that the UCGs extract contains tannins and flavonoids compounds. In addition, the results of total phenol, tannins, non-tannins and T/NT ratio confirmed the presence of phenolic compounds and agreed with the corresponding values obtained in another investigation [Mutuku, et al., 2022].

Table 2. Properties of used coffee grounds extract

Property	Value
Yield	42.43%
Total phenol	24.37 g TAE/100g extract*
Tannins	14.92 g TAE/100g extract*
Non-tannins	7.23 g TAE/100g extract*
T/NT ratio	2.06
Hide powder	39.57
Stiasny no	21.16
Ferric III chloride test for tannins	+
Lead(II) acetate test for tannins	+
Sodium hydroxide test for flavonoids	+
pH	5.21 mmol/l

* **Note:** TAE – tannic acid equivalent.

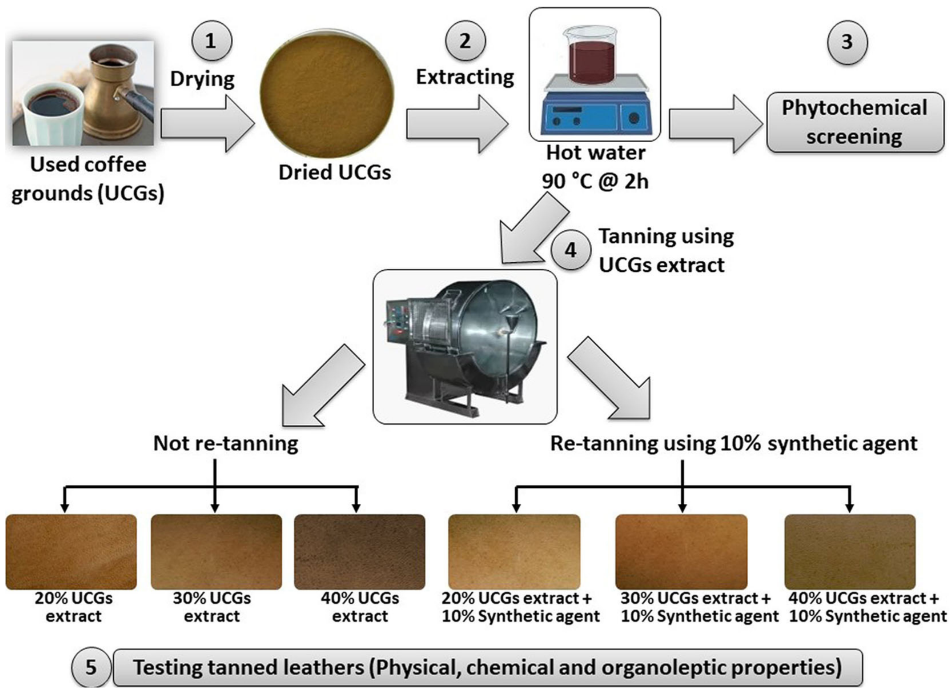

Figure 1. Schematic diagram for working steps

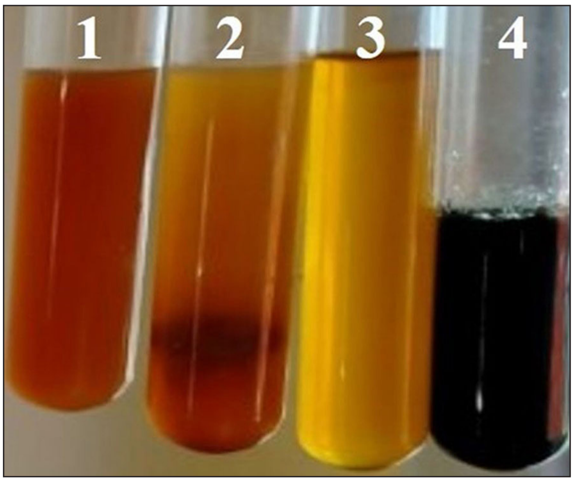

Figure 2. Changes in used coffee grounds extract by testing; (1) normal extract 10%, (2) lead (II) acetate test for tannins, (3) sodium hydroxide test for flavonoids, and (4) ferric (III) chloride test for tannins

As for the UCGs properties related to leather tanning, T/NT ratio that expresses the tanning strength of the extract was 2.06. This value indicated to superiority of UCGs extract over some commercial vegetable tanning extracts (pine bark and badan) and its similarity to some other extracts (tara, chestnut and sumac), while it is weaker than other extracts (quebracho and mimosa) [BASF, 2007]. Typically, the hide powder test informs about the proportion of tannins in the extract which bind with the skin [Dutta, 2008], whereas the Stiasny number indicates the condensed tannins content in the extract [Vázquez, et al., 2008]. In this study, the obtained values of hide powder (39.57) and Stiasny number (21.16) illustrated that UCGs extract contains sufficient amounts of tannins to react with collagen fibers in the skins [Covington, 2009]. The obtained pH value of UCGs extract was 5.21 mmol/l. This value was within the required pH range for interaction between tannins and skin fibers which ranges between 2 and 8 mmol/l, where the change in the isoelectric point of collagen fibers allows it to bind with tannins compounds [Combalia, et al., 2016].

The bands shown in the FTIR spectrum of UCGs extract indicated the presence of tannins compound (Figure 3). The band at 3343 cm^{-1} refers to the vibrations of hydroxyl groups and its broadening indicates strong vibrations. This indicates the presence of many functional groups of phenolic compounds, such as condensed tannins. Additionally, the 1636 cm^{-1} band indicates the stretching of the C-C bonds of aromatic rings in the structures of phenolic compounds. Moreover, the bands at 1051 and 995 cm^{-1} refer to C-H absorption [Nasr, et al., 2017; Falcão & Araújo, 2018; Marques, et al., 2021].

Tanned leathers properties

The effects of tanning material, UCGs extract concentration and the interaction between them on the physical properties of tanned leathers are shown in Table 3.

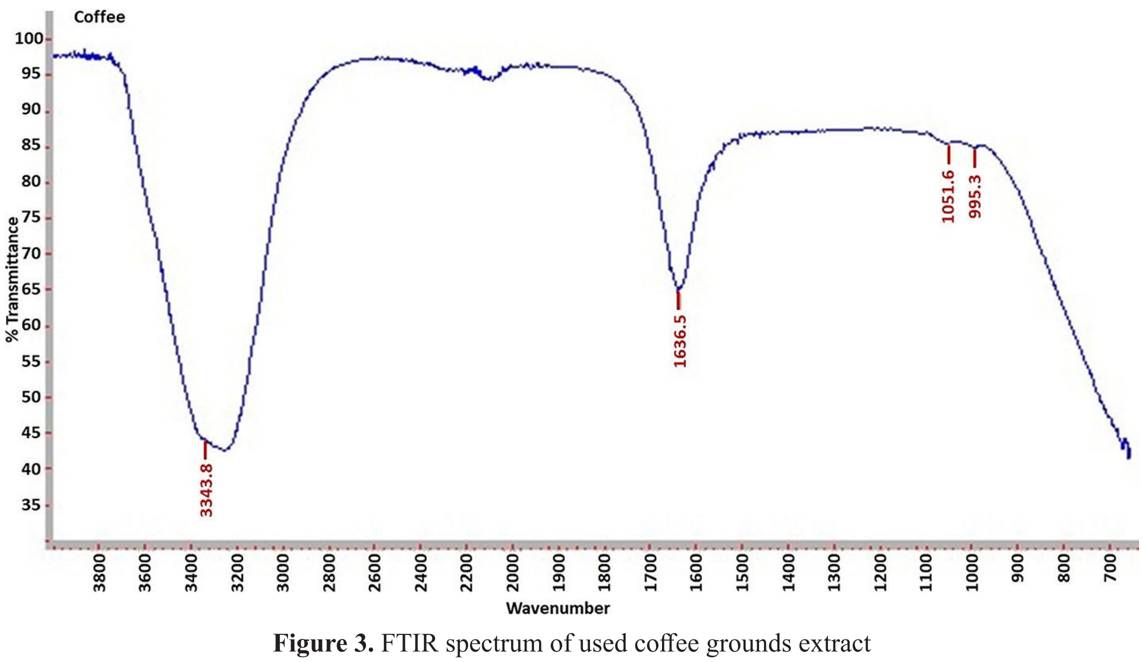

Figure 3. FTIR spectrum of used coffee grounds extract

Table 3. Physical properties of tanned leathers as affected by tanning material, UCGs extract concentration and their interaction

Property		Thickness	Density	Tensile strength	Tearing strength	Elongation	Shrinkage temperature	PWV	Water Absorption
Unit		mm	gm/cm^3	Kg/cm^2	Kg/cm	%	^{o}C	mg/cm^2/hr	%
ASTM		D1813	D2346	D2209	D4704	D2211	D6076	D5052	D1815
Effect of tanning material (T)									
UCGs extract		1.67	0.80^a	149.89^b	47.97	53.49	67.44^b	1.68	246.03
UCGs extract + synthetic agent		1.56	0.68^b	233.55^a	49.50	46.90	81.78^a	1.65	249.06
Significance		ns	**	*	Ns	ns	**	ns	ns
Effect of UCGs extract concentration (C)									
20%		1.43^b	0.69	123.52^b	35.89^c	49.81	72.33	1.68	255.47
30%		1.62^{ab}	0.74	194.52^{ab}	46.63^b	47.65	74.67	1.70	251.51
40%		1.79^a	0.79	257.12^a	63.70^a	53.12	76.83	1.62	235.65
Significance		*	ns	*	**	ns	ns	ns	ns
Interaction effect (T × C)									
UCGs extract	20%	1.38^b	0.72^{bc}	100.94^c	36.21^d	48.85	63.67^e	1.71	249.61
	30%	1.70^{ab}	0.79^{ab}	159.61^{bc}	49.49^{bc}	51.19	68.33^d	1.65	256.98
	40%	1.93^a	0.88^a	189.11^{bc}	58.22^b	60.42	70.33^c	1.69	231.50
UCGs extract + 10% synthetic agent	20%	1.47^b	0.65^c	146.10^{bc}	43.77^{cd}	50.77	81.00^a	1.65	261.33
	30%	1.54^b	0.69^{bc}	229.42^b	69.17^a	44.11	81.00^a	1.74	246.05
	40%	1.66^{ab}	0.70^{bc}	325.13^a	35.55^d	45.81	83.33^a	1.56	239.81
Significance		*	*	**	**	ns	**	ns	ns
Overall of means		1.61	0.74	191.72	48.73	50.19	74.61	1.67	247.55
Standard error of mean		0.06	0.02	19.59	3.09	1.79	1.82	0.03	3.65

Note: UCGs used coffee grounds. ns – not significant, * significant at $p<0.05$, ** significant at $p<0.01$.
Means in the same column with different superscripts letter are significantly different ($p<0.05$).

Physical properties

The effect of tanning material was obvious on the lower density ($P<0.01$) besides the higher tensile strength ($P<0.05$) and shrinkage temperature ($P<0.01$) of UCGs tanned leathers than those re-tanned by a synthetic tanning agent. The microscopic images in Figure (4) showed that using UCGs extract alone facilitated swelling of collagen bundles, whereas re-tanning leathers improved coherence and reduced swelling in fiber bundles. These results indicated higher efficiency of using the mixture of UCGs extract and the synthetic tanning agent rather than using UCGs extract solely. In agreement, various studies clarified that miscellaneous tanning usually produces higher quality leathers than those tanned with only one tanning materials, due to the diversity of active groups in different tanning agents and hence more bonds and crosslinks with collagen fibers in skins that improves strengths and shrinkage temperature in tanned leathers [BASF, 2007; Dutta, 2008; Covington, 2009].

Regarding the effect of UCGs extract concentration, a proportional increment in leather thickness ($P<0.05$), tensile strength ($P<0.01$) and tearing strength ($P<0.01$) was accompanied to the increased concentration of UCGs extract from 20 to 40%. Cross-sectional depictions by electron microscopy emphasized the UCGs extract concentration effects on density and thickness of leather specimens (Figure 4). The variation in density might be attributed to the engagement between the fiber bundles and tannins that increase the mass and volume as well, but in different ratios leading to higher density when higher concentrations were applied. This may explain the variation in thickness, as shown in Figure 4. The other explanation may be due to the presence of other substances in the extract, such as sugars that may cause fermentation and thus increase the spacing among the fiber bundles [Covington, 2009]. This gave an indication of a clear fermentation as a result of the tannins present in the UCGs extract, compared with re-tanning leathers with a synthetic tanning agent.

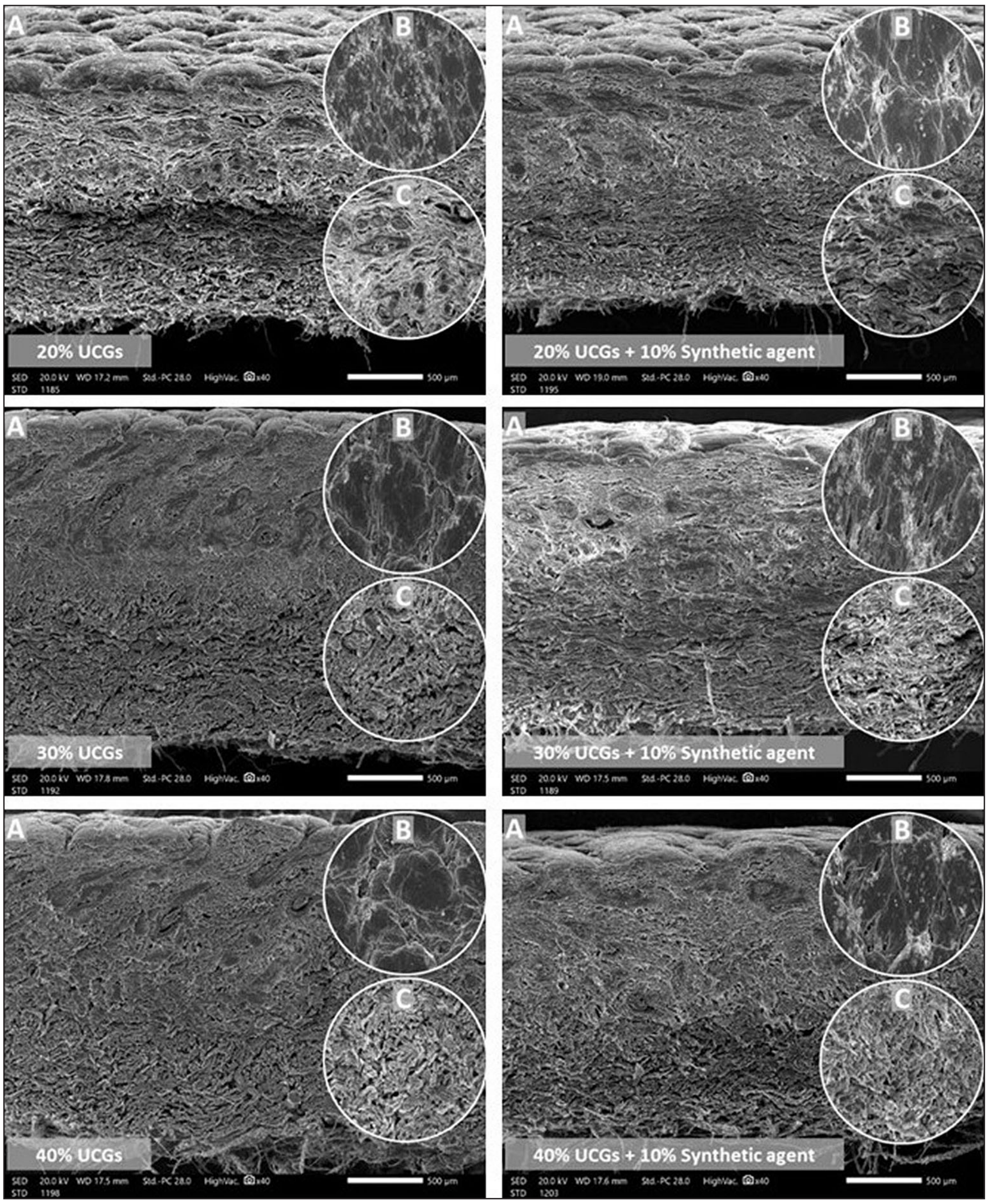

Figure 4. Scanning electron micrographs for all tanned leathers groups with used coffee grounds (UCGs); (A) cross section depicted at x40, (B) grain surface depicted at 100x, and (C) collagen bundles depicted at 150x

With respect to leathers durability properties, the tensile and tearing strengths of tanned leathers were improved by increasing of the UCGs extract concentration. This improvement might be referred to at least one of two explanations or both; the first explanation might be due to the increased crosslinks formed among collagen fibers that strengthened adhesion and cohesion (Figure 4), and made them more resistant to loads. The other prospected explanation might be due to the inverse mathematical relationship between leather thickness and either tensile or tearing strengths [Abdelsalam, et al., 1998].

The interaction between the effects of tanning material and UCGs extract concentration showed significant differences. The effect was significant ($P<0.05$) with both thickness and density and highly significant ($P<0.01$) with tensile strength, tearing strength and shrinkage temperature. The results of shrinkage temperature showed that using UCGs extract alone in tanning with concentrations less than 40% produced the leathers with a shrinkage temperature of less than 70 degrees, which is the lowest allowed shrinkage temperature in vegetable tanning [BASF, 2007; Dutta, 2008; Covington, 2009]. Additionally, the other results of interaction effect showed that increasing the concentration of UCGs extract improved the quality of tanned leathers, as well as the properties were further enhanced when re-tanning with a synthetic tanning agent. Consequently, a concentration of 40% UCGs extract was found to be the minimum limit when using UCGs solely or it can be used with any concentration in miscellaneous tanning to produce leathers suitable for the purposes of manufacturing footwear and bags, according to the recommended quality requirements of different leather types [UNIDO, 1994; BASF, 2007].

Chemical properties

Regarding the chemical properties of tanned leathers (Table 4), the ash content of tanned leathers with UCGs extract was higher ($P<0.01$) than the corresponding re-tanned leathers, as a result of the addition of the synthetic tanning agent.

Organoleptic properties

Re-tanning leathers in this study with a synthetic tanning material improved their organoleptic properties (Table 5). The improvement in leathers fullness and softness related with increasing leather thickness, as well as enhancing both tensile and tearing strength (Table 3). Additionally, narrow pores and light wrinkles on the surfaces of re-tanned leathers (Figure 4) explained the improvement in grain tightness, grain smoothness and general appearance.

Table 4. Chemical properties of tanned leathers as affected by tanning material, UCGs extract concentration and their interaction

Property		Moisture	Ash	pH
Unit		%	%	mmol/L
ASTM		D6403	D2617	D2810
Effect of tanning material (T)				
UCGs extract		13.21	1.25^{b}	4.43
UCGs extract + synthetic agent		13.19	2.60^{a}	4.59
Significance		ns	**	ns
Effect of UCGs extract concentration (C)				
20%		13.26	1.53	4.62
30%		13.14	1.95	4.57
40%		13.21	2.29	4.35
Significance		ns	ns	ns
Interaction effect (T × C)				
UCGs extract	20%	13.27	0.91^{d}	4.30
	30%	13.14	1.33^{cd}	4.43
	40%	13.22	1.52^{c}	4.57
UCGs extract + synthetic agent	20%	13.24	2.17^{b}	4.93
	30%	13.13	2.57^{ab}	4.70
	40%	13.20	3.07^{a}	4.13
Significance		ns	**	ns
Overall of means		13.20	1.93	4.51
Standard error of mean		0.04	0.19	0.12

Note: UCGs used coffee grounds. ns – not significant, ** significant at $P<0.01$. Means in the same column with different superscripts letter are significantly different ($P<0.05$).

Table 5. Organoleptic properties of different tanned leather

Group	Fullness	Grain tightness	Grain smoothness	Softness	General appearance
20% UCGs extract	4.6	5	5.8	5.8	6.4
30% UCGs extract	8	7.2	7.8	7.6	7.6
40% UCGs extract	9	7.4	7.8	7.8	8.2
20% UCGs extract + 10% synthetic agent	5.8	6	7.2	7.4	8.4
30% UCGs extract + 10% synthetic agent	8.4	7.4	8.4	8.2	9.2
40% UCGs extract + 10% synthetic agent	9.6	7.8	8.8	8.4	9.4

Note: UCGs used coffee grounds.

CONCLUSIONS

UCGs extract contains tannins with good tanning strength. The concentration 40% of UCGs extract is highly recommended for use to accomplish the required shrinkage temperature that should be ≥ 70 °C. UCGs extract could be successfully used as tanning agent in vegetable tanning to produce durable leathers with good fullness; it could be used in manufacturing different products, such as footwear and bags. Moreover, using a combination of UCGs extract at any of the used concentrations with phenol sulfonates 10% led to significant improvement in leather properties as compared with using UCGs extract solely.

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