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Research Article

Innovation an Eco Friendly Technology: Tanning System using Semi Chrome and Improved Indigenous Tannins (*Acacia Nilotica* Pods)

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Abstract

Semi-chrome tanned leathers were obtained using spray dried powder which were carried out using leaching of 70% crushed 'Garad' and 30% 'Neem' barks mixture to develop the fulfillment of 'Garad' tanning power. Tanning system was conducted in industrial research consultancies center, Sudan. Mechanical and physio-chemical analyses of the leather were executed using SLTC. Mechanical properties of the produced leather were compared with traditional tanned leather and the strengths, of tensile, one edge tear and two edges tear, of semi chrome tanned leather were: (200 kg/cm^2, 52 and 100 kg/cm) respectively where the distension and strength of grain was (10 mm) and the thermal stability (100°C). The experimental explain that the blending 'Garad-Neem' significantly enhanced the quality of tannins powder and tanned leather.

Keywords: Leather; Acacia Nilotica; Azadirachta Indica; Pre-tannage; Semi-Chrome Tannage; Mechanical; Physicochemical Properties

1. Introduction

Throughout the world the tanneries are looking for alternative tanning of chroming using synthetic and vegetable tannins because it is as friendly to the environment and to given close correlation between chrome tanning and to the environmental impact of leather processing, auditing the efficiency of processing operations takes on prime

importance whereas a great deal of chrome containing solid wastes such as splitting and shavings are produced, which is certainly difficult to be degraded and harmful on the environment if discharged directly [1, 2]. On this pattern Alim et al. utilized 'Garad' from *Acacia Nilotica* to produce chrome free tanned leather with good mechanical properties whereas it had low shrinkage temperature compared to chrome tanned leather [3] which confirmed with Gold Farb in comparison study between the thermal properties of chrome free tanned leather using mimosa, quebracho and wattle and chrome tanned leather [4]. The industry currently uses certain standards based on the physical characteristics of intermediate and final product such as shrinkage, shrinkage temperature and thermal stability thus many attempts to improve the thermal properties of free chrome leather was done demonstrated that using oxazolidine [5] or resorcinol tanning agents combined with other (vegetable or synthetic agents) allows for the obtaining of quality leathers that can be used by footwear and upholstery industries [6]. Whereas Hassan et al. carried out a methods using Sudanese rural garad for the production of semi-chrome shoe upper leathers. The results explained that the chemical properties of leathers in all trials are found to be quite normal. The shrinkage temperature of experimental leathers for all trials found above 85.4°C and the tensile strength above 103.00 Kg/cm^2 [7]. Whereas *Acacia nilotica* (Sunt) is a member of sub-family *Mimosoideae* of *leguminous* trees. It is of multiple uses in Sudan, Africa and many Arabian countries [8]. Three subspecies of *Acacia Nilotica* dominated in Sudan. The first one is *Tomentosa* with the pods necklace-like narrowly and regularly constricted between the seeds and grows throughout Sudan. The second subspecies is *Nilotica*, in which glabrous pods are strongly constricted between the seeds and grows along the White Nile. The third subspecies is *Adansonii*, in which the pods are only slightly constricted between the seeds and grows in Western Sudan [9, 10]. The *Acacia Nilotica* tannins were applied in Sudan particularly pods of the subspecies *Nilotica* which has been known and used for tannage since long time ago [11]. Which is contain considerable amount of tannins whereas the grand powder of *Acacia nilotica* pods contain 23% in Sudan and 16% in India [12]. Musa and Gasm elseed reported that 'Garad' tannins had a behavior like pyrogallol and catechol tannins hence 'Garad' is a mixture of pyrogallol/ catechol [13]. The chemical composition of 'Garad' pods tannin suggested being a mixture of di/tri gallic acid, which consists of five tannins $C_{20}H_{19}O_{10}$, $C_{20}H_{20}O_{10}$, $C_{21}H_{18}O_{10}$, $C_{21}H_{19}O_{10}$, and $C_{22}H_{19}O_{10}$. These oligo-gallic acids hydrolyze to yield gallic acid, ellagic acid and phlobaphenes $C_{14}H_{18}O_4$ [14]. Whereas Rao and Orwa et al. reported that the *Azadirachta Indica* bark contains ~12 % condensed tannins and some chemicals which were required by leather industry [15, 16]. Therefore for more application and improvement of tanning techniques, the current study is prepared to produce high quality leather, improve the physical properties such as shrinkage temperature, tensile strength and fullness, reduction the cost and replacement of the imported tanning materials utilizing blending of 'garad-neem' in eco-friendly processes to reduce the pollution load of tannage.

2. Materials and Methods

2.1 Source of materials

The tannin materials Garad were brought from blue Nile State, Sudan. Goat pelts were obtained from warehouse in Omdurman, Khartoum. Sudan. Reagents used for the experiment and analysis were of analytical grade. Preparation of tannins powder was conducted using mixture of 70:30% of Garad to Neem respectively. The eques mixture was

dried at inlet temperature of 175°C and outlet temperature of 100°C and 1 atm pressure using spray drying instrument.

2.2 Experimental design

The experimental design was outlined in randomized complete design with two treatments; T1 traditional tanned method; and T2 improved method; 'Garad-Neem'; replicated three times.

2.3 Tanning methods

Grain goat pelts have been used for semi chrome and 'Garad-Neem' spray dried powders tanning are shown in table 1, the experimental was repeated using origin 'garad' spray dried powder instate of blend as a control, the amount of chrome sulphate used for the tanning trails has been 2% Cr_2 (SO_4) in both experimental processes and the obtained leather was prepared to mechanical and physico-chemical tests.

Process	**%**	**Product**	**Time**	**Remarks**	**Ph**		**Real Time**
					Skin	**Float**	
Washing	200	Water at 28°C	30'	-	-	-	-
Drain			-	-	-	-	-
Unhairing	150	Water at 28°C	-	-	-	-	-
	6	lime	60	-	-	-	-
	3	Sodium sulphide	60'	Overnight and run 10'/h	-	pH=12.5	-
Next Morning		Run	10'	-	-	-	-
Drain/Wash/ Drain	200	Water at 28°C	10'	-	-	-	-
Reliming	100	Water at 28°C	-	-	-	-	-
	2	lime	30'	-	-	pH=12.5	-
Drain/Wash/ Drain	200	Water at 28°C	30'	-	-	-	-
Drain/Wash/ Drain	200	Water at 28°C	10'	-	-	-	-
Neutralization	100	Water at 28°C	-	-	-	-	-
	1.5	Sodium formate	60	-	-	pH=8	-
Drain/Wash/ Drain	100	Water at 28°C	20'	-	-	-	-
Batting	80	Water at 30°C	-	-	-	-	-
	1.0	Orbon	30'	Check FFT	OK	pH=7,0/7, 2	
Drain/Wash/ Drain	200	Water at 28°C	10'	-	-	-	-

Drain/Wash/ Drain	200	Water at 28°C	10'	-	-	-	-
Pickling	60	Water at 28°C	-	-	-	-	-
	10	Salt	10'	bring to Be=6	-	-	-
	1	Formic Acid (1:5)	30'+30'	-	-	-	-
	0.4	Sulphuric Acid (1:10)	30'+30'	STOP Overnight	-	-	-
Next Morning		RUN	10'	-	bcg=yellow	pH=3,0/3,1	-
Tannage	2	Chrome 26/33	240'	-	-	-	-
	1	Sod. Formate	30'	-	-	-	-
	0.1	Fungicide	-	-	-	-	-
	50	Water at 28°C	-	STOP Overnight	-	-	-
Next Morning	0.6	Sod. Bicarbonate	30'+30'	(add in 2 times)	BCG= Blue	pH=4.5-5	-
Drain/Wash/ Drain	50	Water at 45°C	40'	-	-	-	-
Drain	-	-	-	-	-	-	-
Mechanical Operations		**Pile Up/Sammy/Shave/Re-Tannage**					
Retan	100	Water at 28°C	-	-	-	-	-
	2	Fat liquor	-	-	-	-	-
	4	Garad-Neem powder	60'	-	-	-	-
	4	Garad-Neem powder	60'	-	-	-	-
	4	Garad-Neem powder	60'	Check FP	-	-	-
	2	Fat liquor	40'	-	-	-	-
	1.5	Formic Acid	15'	-	-	-	-
Drain/Wash/Drain	50	Water at 28°C	10'	-	-	-	-
		Horsed up, tied by polyethylene sheet, left over night, and toggled.					

Table 1: Formulation of semi chrome- 'garad'/ 'garad-neem' tanning system for grain goat pelts.

2.4 The mechanical, physico-chemicals tests and hand evaluation of leathers

Samples for various physical tests from experimental crust leathers have been obtained as per (SLTC) [17]. Specimens have been conditioned at 20 ± 2°C and relative humidity 65% ± 2% during 48 hours before use in a test. Physical properties such as thickness, tensile strength, percentage elongation at break and Shrinkage temperature have been measured as per standard procedures [17] where distention and strength of grain (bally flexometer), stitch tearing strength and tong tears strength were measured according to (ASTM D.2261 and 4705) [18, 19]. Experimental crust leathers have been assessed for softness, fullness, grain smoothness and general appearance by hand. For physic-chemical analysis, leather of all kinds must be ground in a cutter mill according to SLTC [17]. The ground material obtained was used to determined the moisture%, fat%, total soluble solid%, total ash content%, and chrome content% according to standard procedures (SLC 1, 2, 3, 4, 5, 9 and 8) [17].

2.5 Statistical analysis

The data mechanical, physicochemical analyzed using the statistical package for science (SPSS) at a significant level p=0.05 using (ANOVA) [20].

3. Result and Discussion

No	Description	T1	T2	BIS	Mean	Std	Sig. 0.05
1	Thickness/mm	1.1	1.1	1.0	1.067	0.0485	1.00
2	Tensile strength N/cm^2	18.5	22	20	20.6	1.456	0.00
3	Elongation%	31	52	40	41.00	8.2247	0.00
4	Tear strength N/cm	2.3	4.8	3	3.367	1.0691	0.00
5	Stitch tear strength N/cm	8.9	10.3	10	9.733	0.61229	0.00
6	Distension and strength of grain/mm	8.2	10.3	9.9	9.4667	0.9233	0.00
7	Shrinkage temperature°C	91	100	100	97	4.304	0.00
8	Moisture content%	9	8.7	10	9.2	0.5697	0.00
9	Ash content%	3	3.1	4.5	0.3.53	0.694	0.08
10	Fat content%	10	10.2	10.7	10.3	0.2987	0.00
11	Total soluble matter content%	1.2	0.6	0.7	0.833	0.266	0.001
12	Chrome content%	1.0	1.1	2.5	1.5333	0.6945	0.08

Table 2: Mechanical and Physico-chemical properties of leathers which produced using semi chrome retanned by the blend.

Tannage is a chemical process that converts animal skins and hides into leather by involving additional cross-links to collagen. The efficiency of tanning depends on the binding activity of the tanning agents to the functional groups in collagen and between them [21]. It also depends on the pre-tannage and the thickness of the animal skins or hides. Thus utilizing 2% of chrome sulphate accelerate both garad/ garad-neem tannins to penetrate through cross-section

of pelts and lead to uniform distribution of these agents and satisfactory tanning thus leathers showed a good cross-section, fullness, smoothness and general appearance, therefore results table 2 showed that there are no significant difference in thickness compared to standard requirement of shoe upper leather, BIS, and SS [22, 23].

The chrome tanning improve the strength properties of the leather such as tensile, tear and stitch tear, strengths, whereas tensile strength was measured as the force required to rupture a leather specimen of unit cross sectional area. The tensile strength was thus the combined breaking strength of all the fibers which are taking part to fight against the applied load therefore represent the maximum applied stress for ultimate tensile strength [24]. Thus according to that the tensile strength table 2 of this semi metal/ 'garad-neem' tanning gave competitive results to produce shoe upper leather than those tanned with semi metal/ 'garad' powder and they comply with the standards required for high quality upper leather, IS, and SS [22, 23]. Retanning is a key operation in leather making with the purpose of it is to obtain leathers with some special characteristics [25]. The strengths were significantly affected by the types and content of tannins however condensed tannins penetrate rapidly and aggregate more readily in the cross-section deposited very large molecules than hydrolysable types, so that in current study blends garad which contain considerable amount of hydrolysable tannins [26] and neem bark contain existence of considerable amounts of condensed tannins [27] to improve the tannins properties and raised the tanning power of blending tannins and introduction of blend tannins into the semi chrome tanning system produces a definitive improvement in the strength properties of the leather. This due to the fact that the fibre bundles are well separated in the case of chrome/garad tanned leather; while chrome/ garad-neem tanned leather shows cemented fibres bundles and this would lead to that the chrome/ garad-neem tanned leather would exhibit high tensile strength and tear with good softness where as chrome/garad tanned leather would exhibit low strength with normal softness Generally collective actions of the leather quality increase with homogenous interaction of tensile; tear and stitch tear strengths that recommended for good leather. Hence good strengths leather due to the behavior of chrome and garad-neem tannins.

The elasticity, softness characteristics and flexibility of both experimental and control leathers are observed to be quite normal. Indigenous garad tannins are known to produce hard/ durable leathers and are generally employed for producing firm leathers for out sole, pelts, etc. Hence, it is important to evaluate the extent of softness contributed by neem tannins on the final leathers. The experimental leathers garad-neem exhibited better softness compared to the garad control leathers. The trend in the object assessment of softness values are in accordance with the data shown in table 2. The obtained values of the grain crack and grain break in this study are normal and indicate good strength of the leather produced. Whereas the flexibility after 100,000 flexes for the experimental leathers compared with the grey scale indicates good flexibility and the semi chrome leathers produced could be accepted for shoe upper leather manufacture, IS, and SS [22, 23].

garad hydrolyzable tannins undergoes hydrolyzis releasing nontannins such as chebulinic acid, gallic acid, etc., which drops the pH of the tannins liquor and causes unlikely collagen swell/ plumping, producing very firm leather, thus the method of blend 'Garad-Neem' and used natural salt was adopted to control the pH of the tanning liquor and organized swelling/ plumping of the pelts and developed softness, flexibility, strength and thermal stability of

produced leather. This is coincided with Looney, who mentioned that pH values of 3.5-4.0 produce flexible leather whereas dropping of pH below than 3.0 produce very firm leather [28]. The shrinkage temperature of both control and experimental leathers were shown in table 2 the thermal stability of collagen is an important property for the assessment of the quality of skin, as it indirectly indicates any structural destabilization of the skin matrix due to microbial attack. The thermal stability of chrome tanned leathers is well known to be greater than 100°C, [21] where the vegetable tanned is much less than chrome. The hydrolysable tanned leather recorded rang of 70 ± 6°C and condensed tanned leather over 80°C [8]. It is seen from the table 2 that just by the utilize 30% of neem in blending of garad in semi chrome tanning exhibited about 10°C increase in shrinkage temperature compared to semi chrome/ garad control leathers. his due to an increase in the amount of tannin fixed in the presence of condensed tannins and increased exhaustion of garad observed can be semi-quantitatively related to the increase in shrinkage temperature of semi tanning systems, and which attribute to the bonding between condensed-collagen-chrome and condensed-chrome-collagen composite which can be explained by bring about countless weak hydrogen bonding between the numerous hydroxyl groups (-OH) of the polyphenols and the countless of ($-NH_3^+$) peptide groups, which support of the junction of leather fiber.

The chemical analysis values of experimental leathers (semi chrome/ garad-neem) and control (semi chrome/ garad) are given in Table 2. The chemical analysis data for the experimental leathers is comparable to that of control leathers, however the water soluble matters for the control leathers is more compared to the experimental leathers.
ANOVA analysis data Table 2 confirmed that there are significant differences of (tensile, tear, stitch tear) strengths, shrinkage temperature and total soluble mater of semi metal/ blend tanned leather compared to semi metal/ garad control tanned leathers.

4. Conclusion

quality parameters of semi-chrome/ ‘garad-neem’ tanned leathers were measured and compared to measured mechanical and physio-chemical properties of semi-chrome/ ‘garad’ tanned leathers as control and the requirements of shoe upper leather Sudanese standard. The experimental recipe result of semi metal/ ‘Garad-Neem’ in leathers proved acceptable properties of strength, hydro-thermal stability, softness and flexibility which act an important viability for the ‘Garad-Neem’ spray dried powder in commercial tanning. The mechanical and physio-chemical properties of the leathers prepared compiled quite well with the standard requirements, the leather concerned revealed the best performance in terms general appearance when used the blend tannins which granted homogeneous interaction and hydrothermal stability of leather compared to garad. This the semi-metal/ blend recipe, besides the acceptable properties of the produced leather is also easily applicable from an industrial point of view.

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