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Research Article

Utilization of Improved Indigenous Tannins of "Garad" In Semi Chrome Tannage

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Abstract

New tanning mixture was investigated to improve the performance of indigenous tanning materials. Many experiments were conducted in National Leather Technology Centre, Sudan using a blend of 80% *Acacia nilotica pods*'Garad' and 20% *Azadirachtaindica* 'Neem' barks. The spray-dried powder from a mixture of *Acacia nilotica pods* and *Azadirachtaindica* 'Neem' was applied for semi-chrome tanning to produce shoe upper leathers. The physico-mechanical properties of the semi-chrome tanned leather were compared with conventionally tanned leather. The pretannage and semi-chrome tannage were preceded using accustomed method in NLTC, Sudan while physio-mechanical analyses of the leather were performed using AOAC (1996). Parameters of the tanned leather were tensile strength (22.0 N/Cm_2), tear strength (5.2 N/cm), stitch tear strength (11.8 N/cm), elongation (57%), distension and strength of grain (10.6 mm) and shrinkage temperature (100°C). The results showed that the 'Garad - Neem' blend significantly enhanced the quality of tanned leather to almost double the level of the leather tanned by conventional pure Acacia nilotica pods 'Garad' power.

Keywords: Leather; *Acacia Nilotica*; *AzadirachtaIndica*; Pretannage; Semi-Chrome Tannage; Mechanical; Physicochemical Properties.

Introduction

Dried mature pods of *A. Nilotica* was used in local tanneries in Sudan as indigenous materials to produce a pinkish white leather of good quality, thus Ibrahim (2001) examined the tannins content of *Acacia Nilotica pods* and the results identified the tannins content of garad pods to befairly high [1] where as Fagg & James (2013) reported that the tannin content of grand powder of *A. nilotica* was 16% in India and 23% in Sudan [2]. Thus dependence to Slaats (1999) and Simon (2003) studies which are suggested that the best alternative to chroming is tanning with synthetic and vegetable tannins because it is so friendly to the environment than chromium tanning although it is cheaper and can easily be applied for various sorts of pelts. On the other hand, chrome method leads to the formation of hazardous waste. Besides, finished products, leather, after exploitation becomes unwelcoming waste by environmental point of view, thus attempt was done to utilize the tannins of A. nilotica pod in modern tannage [3,4], Haj Ali (2007) utilized the spray dried powder which is produced from A. nilotica pods to produce full vegetable tanned leather and the result showed the leather had good mechanical properties whereas it had low shrinkage temperature compared to chrome tanned leather which confirmed [5] Gold Farb (1999) comparison study between the thermal stability of vegetable tanned leather and chrome tanned leather using types of vegetable tannin materials, mimosa, quebracho and wattle. The results found that the vegetable tanned leathers showed lower thermal stability but they exhibited lower water swelling and can be colored using direct dyes [6]. Thus many attempts to improve the thermal stability of *A. nilotica pods* tanned leather was done, Musa and Gasmelseed (2013a) studied the eco-friend combination tanning system using 20% *A. nilotica pods* and 4% oxazolidine to produce upper shoes leather. The results showed that the eco-friend tanned provided a shrinkage temperature of 102ºC and the characteristic of the leather indicated that the system provides leather with good organoleptic properties [7], also Haroun et al. (2009) studied the free chrome combination tannage system involving 10 % A. nilotica pods and 2% aluminum sulphate. The produced leathers exhibited shrinkage temperature of ~125ºC, elongation at break 65.6%, tensile strength 38 N/mm^2 and tear strength 98N/mm, the chemical properties of the leather are found to be quite normal [8] whereas Musa and Gasmelseed

(2013b) were carried out method which improved Sudanese rural garad tanned crust leathers for the production of semi-chrome shoe upper leathers. The results explained that the leathers produced are full, soft, and flexible with high tensile strength. However, the stripped rural garad tanned leathers retained with 8% basic chromium sulphate showed high thermal stability (104ºC) and good organoleptic and strength properties [9], thus for more application and improvement of tanning technical the study was building using eco-friendly processes to reduce the pollution load of tannage and produce high quality leather, improve the physical properties, shrinkage temperature, tensile strength and fullness to the produced leather and reduction of the cost and replacement of the imported tanning materials utilizing modified tannins of *A. nilotica pods.*

Materials and Methods

Source of materials

A. nilotica pods were brought from Sinnar State, Sudan. Goat pelts were obtained from slaughterhouse of ELKadaro, Khartoum North. Sudan. Chemicals used for the experiment and analysis were of analytical grade.

Preparation of indigenous tannins material

Spray dried powder was prepared using blending of 80% of Acacia nilotica pods powder with 20% of *Azadirachtaindica* bark powder. The blended powder was bleached with 5% of Hibiscus sabdariffabark powder and then leached using rotary system then 3% of sodium chloride was added. The leaching was spray dried at inlet temperature of 175°C and outlet temperature of 100°C and 1 atm pressure. The dried sprayed powder was kept in polyethylene bag for further processes.

Experimental design:

The experimental design was outlined in randomized complete design with two treatments; t1 indigenous method; 100% *Acacia nilotica pods*; and t2 modified method; 80% *Acacia nilotica pods* and 20% *Azadirachtaindica* barks; replicated three times.

Tanning trails methods

Pretannage: Four pieces of goat pelts; 4kg; were weighed and soaked in experimental drum for 30 minutes with 4 liters of water. The pelts were re-soaked in a pit using 6 liters of water and then left overnight. In the second day the pelts were placed back into the drum and washed for 10 minutes. The hairs were removed by painting unhearing method using a mixture of 80 g of sodium supplied and 40 g of lime in paste formed of 12.6 pH and 20° Bk. The pelts were covered with polyethylene and left for 30 hours then scudded manually using scudding knifes and washed in drum for 15 minutes. Then transfer to the drum for reliming with 80g of fresh lime and 4 liters of water and after that washed. Then pelts were replaced into the drum and washed again followed by delimed with 60g of sodium format and 4 liters of water for one hour followed by drain and washed for 10 minutes. The pH of pelts was adjusted to a pH 8.0 followed by bated at 37ºC for 30 minutes in a drum with 20 g of orboron and 4 liters of water then drained and after that washed for 5 minutes. Four hundred grams of sodium chloride were dissolved in 4 liter of water and then the pelts were run for 30 minutes followed by addition of 40 g of formic acid diluted (1:10) added to the pelts in the experimental drum and run for 40 minutes. The pH was adjusted to 2.5 using formic acid. The pelts remove and covered by polyethylene and horsed up. Thickness of the pelts was adjusted using shaving machine to 0.8 mm.

Semi chrome tannage: Two pieces weighing 2.0 kg as dry weight of deliming pelt were transferred to the excremental drumcontent 1 liter of above pickle water. 40 g of basic chrome sulphate was added and drummed for 40 minutes. The content was left to stand for 4 hours during which the content was rotated for 5minutes each hour. Twenty gram of sodium formate was added and drummed further for 10 minutes, drained, and washed with tape water.

40 g of local sulphonated oil and 80 g of garad spray powder were drummed for 30 minutes. Then the concentration of bath was raised by adding 100 g of garad spray powder and drumming was continued for 30 minutes, then additional 100 g of garad powder were added into the bath and drummed for 30 minutes. 60 g of oil was added and drummed for 50 minutes. The penetration was checked and it was found to be all through. 30 g of formic acid were added and drummed for 15 minutes then washed, horsed up, tied by polyethylene, left over night, and toggled.

The recipe was repeated using the spray dried powder and the obtained leather was prepared to physical and chemical tested.

The mechanical and physico- chemical properties of leather: The samples were prepared according to SLP1&2 then specimens subjected conditioning according to SLP3. Thickness, tensile strength and elongation, tear strength and distension were measured using (SLP 4,6,7 and 9) [10] and strength of grain, stitch tearing strength and tong tears strength were measured using (ASTM D.2261 and 4705) [11,12]where sampling and physico-chemical properties of leather, moisture, fat, total soluble solid, ash and chrome contents were measured using (SLC 1,2,3,4,5,9 and 8) [10].

Statically Analysis

The data analysis of variance performed for comparison was conducted by using a computer program equipped with SPSS statistical analysis method at a significant level $p \leq 0.05$

Result and Discussion

Mechanical properties of leathers which produced using semi chrome and either indigenous or modified tannins

Thickness of semi chrome and either indigenous or improved tanned leathers: The thickness of the goat leather treated with semi chrome and either indigenous *Acacia nilotica pods* as the control or spray dried of blending of 20% *Azadirachtaindica* and 80% *Acacia nilotica* was shown in (Figure1).

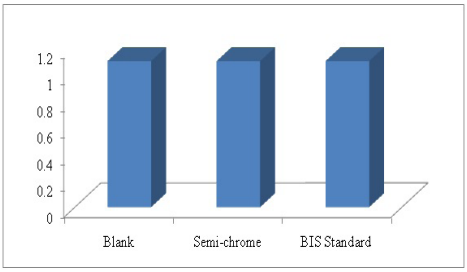

Figure 1: Thickness of semi chrome and either indigenous or improved tanned leathers and BIS standard.

The results showed that thickness of semi chromed leather treated with either unmodified and modified spray-dried materials characterized with an excellent cross-section and fullness compared to the standard of shoe upper leather and it felt in recommended range, IS, (2003) and SS, (2003)[13,14].

Although of high strength of semi chrome tanned leather but there are some disadvantages of such as lack of fullness, filling and softening; therefore, indigenous tanning materials as retanning agents were developed to improve the chrome tanned leather properties and the results suggested that modified 'Garad – Neem' materials increased the homogenous interaction of strength, fullness and fellness that recommended for good leather. These agreed with Nilay et al. 2014 vegetable tannins are opted in leather industry for their mechanical properties they gain to the leathers such as fullness, filling and softening [15].

The strengths of (tensile,tear, and stitch tear) of semi chrome and either indigenous or improved tanned leathers

The results of tensile, tear and stitch tear strengths values of the goat leather treated by either *Acacia nilotica pods* or blending; 20% *Azadirachtaindica* and 80% *Acacia nilotica*; were shown in (Figures 2,3,4).

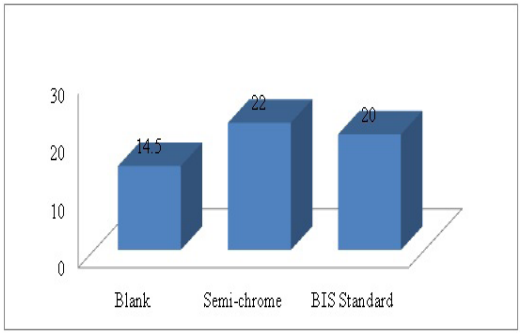

Figure 2: Tensile strength of semi chrome and either indigenous or both improved tanned leathers and BIS standard.

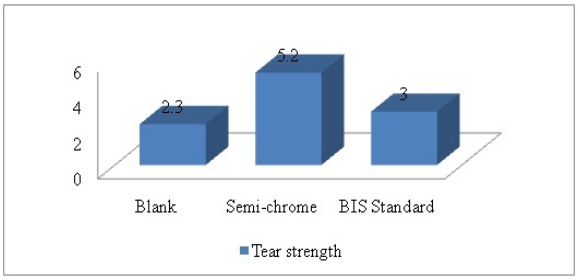

Figure 3: Tear strength of semi chrome and either indigenous or both improved tanned leathers and BIS standard.

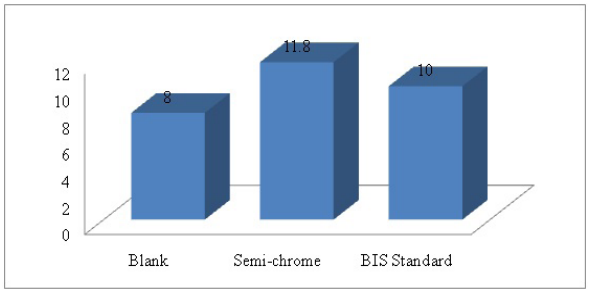

Figure 4: Stitch tears strength of semi chrome and either indigenous or improved tanned leather and BIS standard.

The leathers treated with the semi chrome and improved tanning materials showed highest strength than those treated with indigenous 'Garad' and better in compared with the standard of shoe upper leather which closed in agreement with standard, IS, (2003) and SS, (2003) [13,14]. The strengths values of goat tanned leathers increase by applying a blend of 20% *Azadirachtaindica* and 80% *Acacia nilotica*.

These results suggested that the presence of 20% of *Azadirachtaindica* modified the tannin conduct and raised the tannage power of *Acacia Nilotica* to almost double its normal power.

This could be attributed to the existence of considerable amounts of condensed tannins in *Azadirachta Indica* bark which seem to be very important to strengthen the leather beside the customary benefits of hydrolysable tannin in *Acacia Nilotica* required for fullness and color. These agree with who reported that *AzadirachtaIndica* bark contains considerable amounts of condensed tannins [16]. Therefore, it is quite understandable that the types and contents of tannins together are quite essential to strengthen the fibres of the leather. Generally collective actions of the power quality of the leather 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 condensed tannins. Condensed tannins penetrate rapidly and aggregate more readily in the pelt fibres deposited a very large molecules that cross-linking through hydrogen bond to the peptide groups of the collagen. While chrome tan cross-links with polypeptide chains by principle valences through coordination bonds with the acidic amino acid side chains of the collagen

cross-links induce strengthens properties that give the chrome tanned leathers its high quality. This agree with Srearam and Ramasami, (2004) which reported that the cross-links induce physical and mechanical properties that give the chrome tanned leathers its high quality chrome tanned leathers which are characterized by their light weight and high strength [17] and disapproves to Roig et al. 2012 conception that the trivalent chromium salts interact by chemical bonding with the carboxylic groups of collagen in the skin, giving to the leather its strength and stability properties [18]. This process gives the leathers with excellent physical properties and high stability for the footwear manufacturing processes this agree to Sykes and Cater. (1982) who report that the metal retannage involved the formation of extended tannin-metal complexes that effectively crosslink the system rather than the induction of the formation of covalent bonds between the tannin and collagen or within the collagen polymer [19].

Elongation and distension and strength of grain of semi chrome and either indigenous or improved tanned leathers and BIS standard: The elongationand distension and strength of grain of the goat leather tanned usingsemi chrome and either 100% of *Acacia nilotica pods* as the control or spray dried of blending; 20% *Azadirachtaindica* and 80% *Acacia nilotica*; were shown in (Figures 5 and 6).

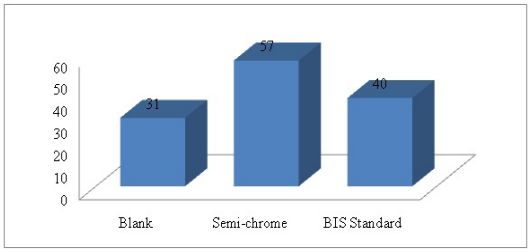

Figure 5: Elongation of semi chrome and either indigenous or both improved tanned leathers and BIS standard.

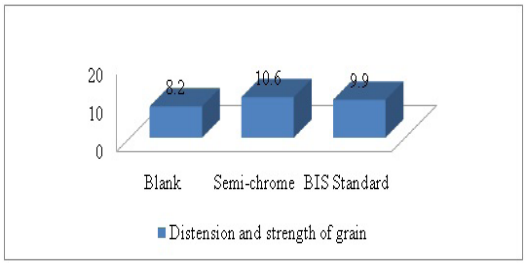

Figure 6: Distention and strength of grain of semi chrome and either indigenous or improved tanned leathers and BIS standard.

The result showed better elasticity, softness and flexibility of indigenous and blended tanned leather is fairly differ, it is agree with the standard of shoe upper leather and felt in recommended range, IS, (2003) and SS, (2003) [13,14]. These results assume that the nature of indigenous tannin was changed since addition 20% 'Neem' it raised tannage power of 'Garad' and reduced consumption of tannin to the half than using 'Garad' alone. *Acacianilotica* contain consider amount of hydrolysable tannin which undergo hydrolysis releasing non-tannins molecules which reduced the tannin liquor acidity causes an osmotic effect collagen swell, likely plumps, that accelerates the penetration and fixation of the tannin producing very firm leather thus it is essential to control the pH of thetanning liquor using blending method, 'Garad – Neem' and natural salt, which organized the pelts swelling/ plumping and developed physical properties such as softness, flexibility, strength and thermal stability of yielded leather. This result confirm that increase in acid swelling/ plumping ruptures stabilizing cross-links in the fiber structure, short links, and releases additional hydrogen bond sites, peptides groups, for tannin fixation, this is coincided with Looney, (2002) who mentioned that final pH values of 3.5-4.0 produce flexible leather where decreasing of the pH below than 3.0 produce very firm leather [20]. Also the results assume that there are another reason to discuss achieved percentage of elongation, at break, values it is increase as a function of the amount of chromium present in the leather matrix this agree to Ravichanadran and Natchimuthu, (2005) conception [21].

The shrinkage temperature of semi chrome and either indigenous or improved tanned leathers

The hydrothermal stability of the goat leathers tanned usingsemi chrome andeither100% of *Acacia nilotica* pods control or spray dried of blending of 20% *Azadirachtaindica* and 80% *Acacia nilotica* were shown in (Figure 7).

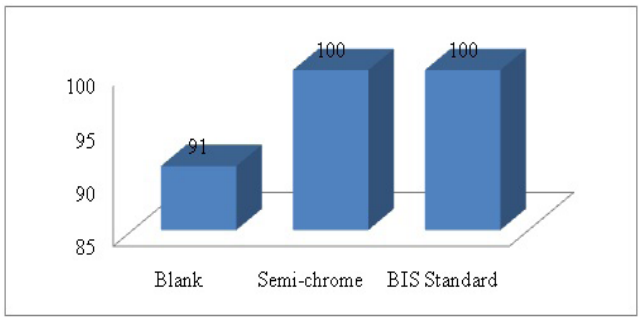

Figure 7: Shrinkage temperatures of semi chrome and either indigenous or improved tanned leather and BIS standard.

These results proposed that 20% of *Azadirachtaindic*a modify the tannin nature and modified 'Garad' tannage power and reduced amount of consumption tannin to half. *Azadirachtaindica* bark wealthy in condensed tannin which acts as strength agent of the tanned leather while *Acacia Nilotica* contain high hydrolysable tannin which is reduced thermal stability. Shrinkage temperature assesses the amount of tannin and can enhance the deposition through the cross-section of tanned leather, ended with better elasticity, softness and flexibility of leather.

The results show that, the shrinkage temperature of the semi chrome/ modified tanned leather is higher degrees than that of semi chrome/ indigenous tanned leather one. Thus, the incorporation of

the condensed into leather increases the thermal stability of the chrome/improved leather over that of the semi chrome/ indigenous tanned leather. This improvement in thermal stability can be attributed to the formation of condensed–collagen composite. Which can be explained by brought about multiple weak hydrogen bonding between the numerous hydroxyl groups (-OH) of the polyphenols and the countless hydrogen atoms of (-NH) peptide groups, which support of the junction between the grain and corium. These results indicate that condensed filling up the empty parts of leather and tightness the leather fibers. This is consistent with Covington et al, postulation who concluded thermal stability of leather depends on the kinetic stability of the interaction between the tanning molecules and the protein side chains. Musa et al. (2013) reported that typical shrinkage temperature for new leather tanned with vegetable tannins/ semi chrome is 104°C [7].

Physico-chemical properties of leathers which produced using semi chrome and either indigenous or modified tannins

Moisture and fat contents of semi chrome and either indigenous or improved tanned leathers: The moisture and free fat content of the goat leather tanned using semi chrome and either100% of *Acacia nilotica* pods or spray dried blended 20% *Azadirachtaindica* and 80% *Acacia Nilotica* were shown in (Figure 8).

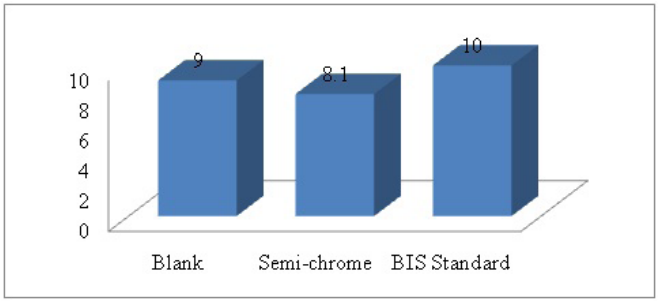

Figure 8a: Moisture content of semi chrome and either indigenous or improved tanned leathers.

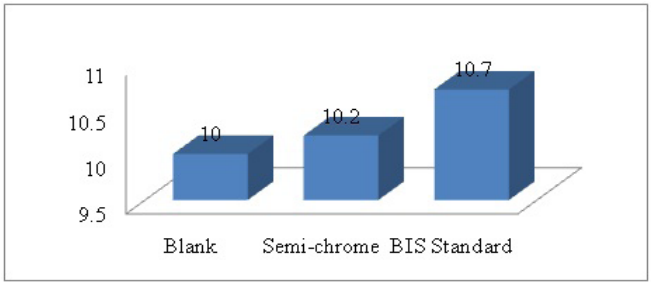

Figure 8b: Fat content of semi chrome or either indigenous or improved tanned leather.

and 4.34). The results showed that elasticity and flexibility of leather agree with the standard of shoe upper leather, IS, (2003) and SS, (2003) [13,14].

Mentioned results suggested that both moisture and fat increase the fiber strengthens and flexibility of leather for a certain limit, firstly, strength is depend on angle of the fiber and their splitting value so low angle and high splitting value yielding high tensile strength. The amount of flexibility is estimated using elongation, distension and strength of grain values which indicate if the amounts of moisture and fat content were reasonable in the fibers or not.

This coincided with Bitlisli et al. (2004) who reported that both physico-chemical properties changed according to amount of the fat content of the leather which increased with the increase of its fat content and then decreased after a certain limit. In generally the moisture and fats values present in both indigenous and improved tanned leather are comparable to those of normal standard values [22].

Total Soluble of semi chrome and either indigenous or improved tanned leathers: Total soluble matter of the goat leather treated using semi chrome and either 100% of *Acacia Nilotica pods* or blended 20% *AzadirachtaIndica* and 80% *Acacia Nilotica* were shown in (Figure 9).

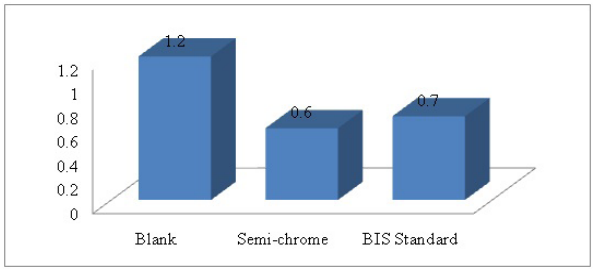

Figure 9: Total soluble content of semi chrome and either indigenous or both improved tanned leathers and BIS standard.

The results showed that both total soluble and degree of tannageexposed the fixation of tannin particles on the collagen fibers and the stability of leather. Semi chrome leather treated with the blended 'Garad–Neem' powder showed high stability due to fixation and low soluble matter of leather compared to semi chrome leather treated with traditional 'Garad' and agrees with the recommended standard of shoe upper leather, IS, (2003) and SS, (2003) [13,14]. These results suggested that semi chrome tanning developed the optimal condition of the formation of tanning matrix including the amount of tanning agents, outside and inside conditions of collagen and the reaction order with collagen. Where blended 'Garad–Neem' improved the tanning power of indigenous 'Garad' tannin and decreased amount of spending tannin to half. Condensed tannins, 'Neem' is more stable to hydrolysis and microbial attack than indigenous 'Garad' tannins, contain consider amount of hydrolysable tannins, this due to strong co-valent bonding between individual carbon atoms and the absence of ester links. Indigenous 'Garad' tannins hydrolysis decomposed the tannin and

released sugar and organic acid that increased the soluble matter and decreased the degree of tannage, where condensed tannins are deposit large molecules size of the polyphenol, Reds, contained high numbers of –OH groups which deposit into the pelts fibre and cross-link through large amount of hydrogen bonds to peptide groups in collagen. As reported by Rao, (2001) these phenol-peptide strong interactions improve the leather stability [23].

Ash content of semi chrome and either indigenous or improved tanned leather

Ash of the goat leather treated using semi chrome andeither100% of *Acacia nilotica pods* or blended 20% *Azadirachtaindica* and 80% *Acacia nilotica* were shown in (Figure 10).

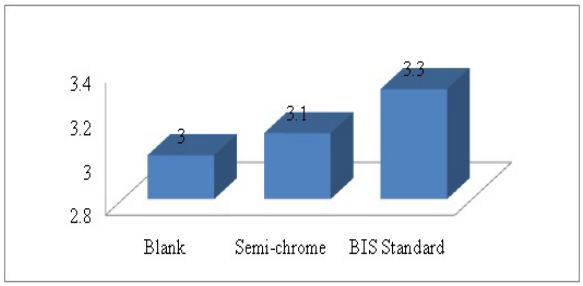

Figure 10: Ash content of semi chrome and either indigenous or both improved tanned leathers and BIS standard.

The resultsshowed that ash content represented the inorganic content on the collagen fibers which is agree with the standard of shoe upper leather, IS, (2003) and SS, (2003) [13,14].

Chrome content of semi chrome and either indigenous or improved tanned leathers: Chrome content of the goat leather treated using semi chrome and either100% of *Acacia nilotica pods* or blended 20% *Azadirachtaindica* and 80% *Acacia nilotica* were shown in (Figure 11).

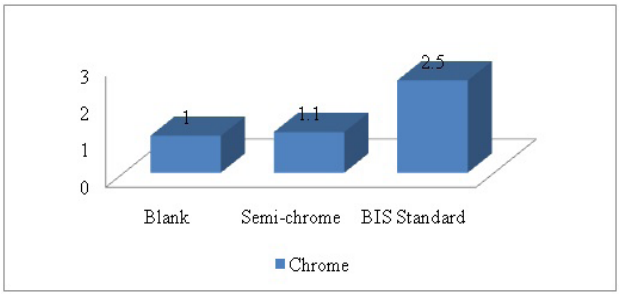

Figure 11: Chrome content of semi chrome and either indigenous or improved tanned leather

The results showed that there were in significant differences in chrome content represented between these michrome and either indigenous or improved tanned leathers and it is lower than standard.

Statistical assessment of semi chrome and either indigenous or improved tanned leathers: Statistical data of SPSS analysis shows that there are significant differences of mechanical and physico-chemical properties of produced leathers using both improved tannins comparing indigenous tanned leathers (Table 1).

No	Description	Mean	Std	Sig. 0.05
1	Thickness	1.1	0.0087	1.00
2	Tensile strength	18.8	3.36	0.00
3	Elongation	42.66	12.18	0.00
4	Tear strength	3.56	1.388	0.00
5	Stitch tear strength	9.9	1.76	0.00
6	Distension and strength of grain	9.53	1.13	0.00
7	Shrinkage temperature	97	4.5	0.00
8	Moisture	8.886	0.818	0.00
9	Fat	10.25	0.291	0.00
10	Total soluble matter	0.8667	0.265	0.001
11	Chrome content	1.399	0.680	0.08

Table 1: Anova test for mechanical and physicochemical properties of tanned leathers using either improved or indigenous tannins.

Showed statistical analysis at $P < 0.05$ level as described by Gomez and Gomez (1984) to evaluate the significant differences between the treatments [24].

Conclusion

Mechanical and physio-chemical characteristics of semi-chrome/ blended 'Garad–Neem'tanned leathers were examined and the results compared to control leathers explained that the experimental process results leathers with good thermal stability and organoleptic properties that is important for commercial viability of the tanning system. Large collective actions of the power quality of the leather increase with homogenous interaction on hydrothermal stability are recommended for good leather. The physical properties of the leathers prepared compiled quite well with the standard requirements. As far as the physical and technical properties of the crust leather concerned; the experimental trial revealed the best performance in terms of softness, fullness, grain stability and general appearance. This sequence, besides the good properties of the final leather is also easily applicable from an industrial point of view.

Recommendations

It is highly recommended that scientific methods must be adopted in harvesting and storage of *Acacia Nilotica pods*; because it is seasonal crop contains high tannin content that susceptible to microbial damage when harvested and stored in wet climate conditions.

Research's to be conducted to utilize the blended national tanning materials in recommended having eco-friendly tannage with better

properties with different plants and concentrations. Phytochemical investigation of tannins in Sudanese plants is recommended.

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