TEKSTİL VE KONFEKSİYON

VOL: 32, NO. 3
DOI: 10.32710/tekstilvekonfeksiyon.1066811

Application of Indigenous Plant-Based Vegetable Tanning Agent Extracted from *Xylocarpus granatum* in Semi-Chrome and Chrome Retanned Leather Production

Raju Kumar Das[1] 0000-0002-3071-1925
Al Mizan[2,3] 0000-0001-8577-9356
Fatema-Tuj-Zohra[1] 0000-0002-2298-9978
Bahri Basaran[3] 0000-0002-0893-6300
Sobur Ahmed[1] 0000-0001-9331-038X

[1]Institute of Leather Engineering and Technology (ILET), University of Dhaka, Dhaka-1000, Bangladesh
[2]Department of Leather Engineering, Khulna University of Engineering & Technology (KUET), Khulna-9203, Bangladesh
[3]Department of Leather Engineering, Faculty of Engineering, Ege University, Bornova, Izmir 35100, Türkiye

Corresponding Author: Sobur Ahmed, soburahmed@du.ac.bd

ABSTRACT

Environmental issues are nowadays the prime concern worldwide for leather industries due to chrome containing solid and liquid wastes generated from the tannery. Therefore, experts are being encouraged in exploring alternative tanning agents. This study aimed at applying a novel vegetable tanning agent extracted from *Xylocarpus granatum* barks for the production of semi-chrome (SC) and chrome retanned (CR) leathers to reduce chromium use. Characterization of the SC and CR leathers was performed by Fourier Transform Infrared (FTIR) spectroscopy which revealed prominent tanning activity of the extracted tannins. The tanned leathers exhibited shrinkage temperatures of 112˚C for SC and 103˚C for CR leathers. The physicomechanical properties were found as tensile strength >230 kg/cm^2, tear strength >30 kg/cm, grain cracking load >20 kg, distention at grain crack >7 mm, ball bursting load >38 kg, and distention at ball bursting >12mm that was comparatively acceptable according to UNIDO standard for shoe upper leathers.

ARTICLE HISTORY
Received: 01.02.2022
Accepted: 07.07.2022

KEYWORDS

Vegetable tanning, FTIR, shrinkage temperature, physico-mechanical properties, strength properties

1. INTRODUCTION

The leather industry is under pressure due to worldwide concerns environmentally as it releases huge amounts of effluents to the environment, particularly during the tanning process. Putrescible raw hides and skins, a by-product of the meat industry, are turned to be imputrescible through the tanning process. The transformation of raw hides and skins into leather involves several steps, i.e. pre-tanning, tanning, and post-tanning [1]. In tanning processes, tanning materials with various substances having crosslinking ability react with the moieties being isolated and activated of fibrous protein in which a series of complex preliminary attempts are executed to enhance the tanning reactions. Hence, leather making is a lengthy process and involves the use of many different mechanical and chemical processes *viz.*, soaking, liming, de-liming, pickling, tanning, post tanning, and finishing operations using several chemicals e.g., sodium hydroxide, lime, chlorides, sulfuric acid, formic acid, chromium, ammonium salts, metallic salt, different organic chemicals, enzyme etc. [2]. Among the processes, tanning is considered one of the important and unavoidable processes that protect the leather against microbial degradation. It influences the properties of the end product by stabilizing the raw skin collagen proteins with different tanning agents, e.g. mineral, vegetable, aldehyde, syntan, resin, and oil tannage [3]. Among the varieties of tanning agents, basic chromium sulphate accounts for 88-90% of total tannage consumption which provides excellent heat stability and strength properties to the leather [1,4]. However, environmental pollution is the only key concern for the use of chromium in

To cite this article: Das RK, Mizan A, Zohra FT, Basaran B, Ahmed S. 2022. Application of ındigenous plant-based vegetable tanning agent extracted from xylocarpus granatum in semi-chrome and chrome retanned leather production. *Tekstil ve Konfeksiyon* 32(3), 258-264.

leather tanning, because only about 54-57% of chromium is consumed by pelt in the tanning and retanning process [3], and the remaining must be treated before being released into the environment. Alteration of Cr(III) to Cr(VI) by various environmental influences could be harmful and carcinogenic for human health and possibly is of a detrimental effect on the ecosystem. During the manufacturing and finishing process of the leather and leather products, the application of heat and UV radiation to the chrome tanned leather could convert chromium (III) to chromium (VI) [5, 6]. Furthermore, the human health risks associated with chromium-rich solid waste could impact respiratory, skin, and bone damage, renal problems, liver damage, kidney failure, infertility, cancer, and even birth defects [6-8]. Although chrome tanning has gained importance in leather manufacture, its advantage is overshadowed by its negative impact on the environment. Chromium wastes are released from tannery effluent to the environment due to low uptake by pelt; thereby, accumulating in the soil where it was discharged. However, vegetable tanning is an eco-friendly method as compared to the chemical tanning process like chrome tanning and also discharges minimum amounts of pollutants to the environment. Therefore, the total or partial substitution of chromium in leather production is an environmental demand that can outperform the advantages of chromium in leather manufacture.

Semi-chrome tanning and chrome re-tanning processes are the methods where the properties of leather could be approached to that of chromium leather by supplementation for lackings. Mimosa, quebracho, sumac, tara, valonea, divi-divi, oak, and chestnut etc. are the most widely used tannins in re-tanning and pre-tanning processes for semi-chrome and chrome re-tanned leather at present [9, 10]. Several researchers have previously investigated novel vegetable tanning systems based on tannins derived from alternative plant sources such as acacia seyal bark [1], acacia nilotica fruit [11, 12], acacia xanthoploea bark [12], hogenia abyssinica bark [12], acacia senegal bark [13, 14], henna extract [3], longan bark [15]. These vegetable tanning materials exhibited promising results; however, they are not practiced commercially.

Xylocarpus granatum (Family: Meliaceae) known as "Dhundul" in Bangladesh is generally found in low-lying, salt-tolerant forest and muddy areas of the Sundarban mangrove forest [16]. It's also found in East Africa, Polynesia, Thailand, Indonesia, Myanmar, Malaysia, India, China, and Australia's tropical regions [17, 18]. The bark of *X. granatum* has never been used as a new source of vegetable tanning material in pre-tanning and re-tanning. According to research published for dye extraction from this plant's bark, *Xylocarpus granatum* barks from mature plants may include tannin content and reddish-brown dye on a dry matter basis [18]. Also, this is a mangrove plant that has yet to be evaluated and classified as a tanning material. Several studies have indicated that the bark of several mangrove plants contains 16-48% tannin [19].

The objectives of this study were i) to evaluate *X. granatum* bark extract as a vegetable tannage substitute in the manufacture of semi-chrome and chrome retanned leather, ii) to examine and analyze the tanning properties of the semi-chrome and chrome-retanned leather processed by *X. granatum* bark whether it meets the tanning requirements, and iii) to analyze the strength properties, e.g. tensile strength, tear strength, grain cracking load, shrinkage temperature, and distention at grain crack of leather tanned with the combination of extracted tanning materials and chromium, and to verify them with the concerned recommended values of United Nations Industrial Development Organization (UNIDO).

2. MATERIAL AND METHOD

2.1 Material

Xylocarpus granatum, also known as "Dhundul," was collected from the Sundarban, the world's largest mangrove forest, along the Malancha River, situated 16 kilometers south of Shyamnagar, Satkhira, Khulna, Bangladesh. The Sundarban covers 6017 square kilometers in Bangladesh's southern region [20, 21]. The bark of *X. granatum* was collected from three different matured plants and mixed thoroughly for identical sample preparation. Wet salted 06 pcs mature goat skins with approximately 6-7 square feet each were taken for the leather processing. These wet salted goat skins were collected from the Posta hides/skins market, Dhaka, Bangladesh. Leather processing chemicals were collected from the local market of Bangladesh other than standards.

2.2 Methods

2.2.1 Application of extracted tanning materials (*X. granatum* bark) in semi-chrome and chrome retanning processes

Extract of *X. granatum* bark (vegetable tanning agent) was prepared using 100% methanol by rotary evaporator in a previous study of the same author and found 31.22% extraction efficiency of tannin [22]. The extracted tannin was found to be a condensed type of tannin whereas the *Xylocarpus granatum* bark tannin contained 48% of condensed tannin [22]. It was applied in leather to produce semi-chrome and chrome retanned leather for evaluating their necessary properties.

The soaking to pickling process (a common series of steps) of leather processing was carried out in this study maintaining the conventional process. The pre-tanning process was done for both conventional with chrome tanning and experimental with developed tannin respectively following the recipe depicted in Table 1.

After aging (pile-up for 8 days) of the leather, re-tanning and post-tanning processes were carried out for both chrome re-tanned and semi-chrome leather respectively by following the recipe shown in table 2 and table 3. The wetback and fatliquoring processes were done according to the conventional procedure, thus not mentioned in the table.

Table 1. Pre-tanning with chrome and vegetable tannin agent (developed) of goat skin

Wet blue process			
Percentage	Chemicals	Duration (min)	Observation
In the pickle liquor at pH 2.8			
4	Basic chromium sulfate (33%)	30	
1 0.20	Chrome stable fat (Remsol OCS) Fungicide	30	
4	Basic chromium sulfate (33%)	60	Penetration 100%
1.50	Sodium formate	30	
0.40	Sodium bicarbonate	3 steps after 20 min with 2 hours additional run	pH 4.0
0.10	Fungicide	45	pH 4.0
Drained and piled up			
Vegetable pre-tanning (Developed Tannin)			
Percentage	Chemicals	Duration (min)	Observation
Pelt in pickle bath at pH 2.8			
1.50	Sodium formate	30	pH 3.5-4.0
0.10 0.10 0.20	Fungicides (Busan 30L) Polyphosphate (RW) Sequestering agent (Trilon B)	30	
1	Hypo	30	
3	Developed tannin	2 steps 60 min and 30 min	
0.5-0.8	Sodium bicarbonate (1:20)	3 steps 20 min and 120 min	
0.10	Fungicide (Busan 30L)	35	pH 3.8-3.9
Drained and piled up			

Table 2. Tanning, and post tanning process of goat skin for chrome retanned leather

Neutralization and retanning			
Percentage	Chemicals	Duration (min)	Observation
Wet blue leathers were taken and prepared for neutralization			
150 3 2	Water at 45ºC Neutralizing syntan (Naphthalene syntan) Sodium formate	50	pH 5
4	Acrylic resin	20	
1 6 4 3 0.50	Sequestering agent (Trilon B) Developed tanning agent Replacement syntan (Dihydroxydiphenyl sulphonic acid) Phenolic replacement (Phenol sulphonic acid) syntan Synthetic fat (Lanoline based)	60	
6 3 3 1	Developed tanning agent Replacement syntan (Dihydroxydiphenyl sulphonic acid) Phenolic replacement syntan (Phenol sulphonic acid) syntan Dispersing agent	60	
6 3 3 1	Developed tanning agent Replacement syntan (Dihydroxydiphenyl sulphonic acid) Phenolic replacement syntan (Phenol sulphonic acid) Fatliquor (Lanoline based)	60	
Left overnight			
0.50	Formic acid	2 steps after 15 min interval	
Drained and washed well			

Table 3. Tanning and post tanning process of goat skins for semi-chrome leather

Acid wash and rechroming			
Percentage	Chemicals	Duration (min)	Observation
150 0.40	Water Formic acid	25	pH 3
6 2 1 1	Basic chromium sulfate (33%) Chrome syntan Sodium formate Chrome stable fat (Remsol OCS)	60	
1 1.50 2	Sodium formate Neutralizing syntan (Naphthalene syntan) *X. granatum* bark tannin (Developed tannin)	40	
Left overnight, run 20 min next day, drained and washed well			
Neutralization			
150 2 0.50 0.50	Water at 45ºC Neutralization syntan (Naphthalene syntan) Sodium formate Synthetic fat (Lanoline based)	45	pH 5
Drained and washed well			
Re-tanning			
150 3	Water at 45ºC Acrylic resin	20	
0.50 6 3 3 1 1	Sequestering agent (Trilon B) Develop tanning agent Replacement syntan (Dihydroxy diphenyl sulphonic acid) Phenolic replacement (Phenol sulphonic acid) syntan Dispersing agent Synthetic fat (Lanoline based)	65	
100	Water at 45ºC	Left overnight	
The next day run 20 min, drained, and washed well			

2.2.2 Determination of hydrothermal stability

The shrinkage temperature (T_s) of pre-tanned and re-tanned leather was measured to determine its hydrothermal stability. The leather samples were cut (50mm×12mm) across the backbone and carried out the test following the standard method IUP-16 [23]. For this analysis, three replicates were examined, and the mean with standard deviation was reported in this study.

2.2.3 Determination of the phenolic compound in tanned leather using FT-IR

The functional groups and other polyphenolic compounds were identified using Fourier Transform Infrared (FT-IR) spectroscopy such as -OH group, aromatic C-H stretch, -CO group, C-H bending, and carbon-carbon double bond stretch present in the tanned leather. The FT-IR spectra were examined using IRPrestige 21, Shimadzu (Japan) in the range of 4000–400 cm^{-1}.

2.2.4 Determination of physico-mechanical properties of tanned leather

The tanned leather (semi-chrome and chrome re-tanned) was cut for sampling into specific measurements for a specific test done in this study and conditioned the cut sample maintaining temperature 25±2˚C, relative humidity 65±2%, and 48 hours by following the ISO-2419 standard method [24]. Tensile strength, percentage of elongation, tear strength, resistance to grain cracking, and distension at grain crack, ball bursting strength, and distension at ball burst were carried out to assess the mechanical and physical characteristics of semi-chrome and chrome re-tanned leather [25-27]. In this study, all experiments were checked three times for both parallel and perpendicular to the backbone and represented as the mean with standard deviation.

3. RESULTS AND DISCUSSION

3.1 Hydrothermal stability

The shrinkage temperature (T_s) of the leather sample represents the hydrothermal stability of the leather and table 4 describes the T_s values of pickle pelt, wet blue, pre-tanned (developed tannin), semi chrome, and chrome retanned crust leather for both semi-chrome and chrome re-tanned leather. The T_s for wet blue and experimental wet-tanned leather were found at 100.67 °C and 78.67 °C respectively shown in table 4. The statistics reported previously for shrinkage temperature on pre-tanning with chromium sulfate ranges up to 120 °C [9, 28]. The shrinkage temperature of the pickled pelt was around 58°C and increased to 79 °C after tanning (tanned with *X. granatum* extract) which might be due to the cross-linking between reactive moieties of collagen and polyphenolic compounds of *X. granatum*. The T_s of semi-chrome leather was 103.34°C and chrome re-tanned leather was found at 112.34°C which suggests that the extracted tanning material from *X. granatum* could substitute conventional mimosa and quebracho vegetable tannins with chrome in terms of increasing hydrothermal stability. The size of polyphenol molecules and the number of -OH groups determine the rise in shrinkage temperature. The kinetic stability of linkages between the tanning agent molecules and the protein's side-chain determines the shrinkage temperature [29]. In semi-chrome leather, pre-tanning with developed tannin and the addition of chromium to the re-tanning process could increase the cross-linking between polyphenol and collagen, resulting in a stable complex matrix where chromium acts as a ligand [29]. As a result, the hydrothermal stability of the tanned leather showed an elevated level.

Table 4. Shrinkage temperature (T_s) of pickle, wet blue, and leather tanned by developed tannin (mean ± standard deviation)

Samples	Shrinkage Temperature °C
Pickle pelt	58.67 ± 1.15
Wet blue	100.67 ± 1.52
Experimental wet-tanned leather (Extracted *X. granatum* tannin)	78.67 ± 1.15
Chrome re-tanned leather	112.34 ± 1.53
Semi-chrome leather	103.34 ± 2.05

3.2 Analysis of the phenolic compound in tanned leather using FT-IR

FTIR Spectra of the pickle pelt, semi-chrome, and chrome re-tanned leather are shown in figure 1. The tanned leather sample showed the presence of O-H stretching, C=O stretching, aromatic C-H stretching, C=C ring stretching, C-H bending, C-O stretching, Out-of-plane C-H bending compared with pickle pelt. FTIR spectrum of chrome re-tanned and semi-chrome leather showed respectively a relatively broadband at 3325 cm^{-1}, and 3425 cm^{-1} representing the presence of –OH groups of polyphenols such as tannin and flavonoids which is in congruence with the other studies [30-33]. On the other hand, the pickle pelt showed a relatively spike-type band at 3383 cm^{-1} representing the presence of the amino group of the protein collagen. Besides, a medium band was found at 2935 $cm^{-1}$for both semi-chrome and chrome re-tanned leather that indicates the presence of aromatic C-H stretching in these leather samples whereas pickle pelt showed no band at this region. Again for both leather samples strong peak at 1716 cm^{-1} and 1612 cm^{-1} was noticed while the pelt showed peaks at 1643 cm^{-1} that indicate the presence of C=O stretching and C=C ring stretching with a substituted benzene ring. In this study, peak(s) at 1519 cm^{-1} and 1516 cm^{-1} was found for both leather samples which stipulate the presence of catechin and its near derivatives (e.g., epicatechin) in the sample. Therefore, the leather tanned with the extracted *Xylocarpus granatum* bark tannins showed vegetable tanning material-rich compounds in it because it confirmed the presence of several polyphenolic groups in its chain.

3.3 Physico-mechanical properties of tanned leather

Table 5 shows the physico-mechanical characteristics of leathers investigated in this study. The tensile strength of experimental chrome re-tanned and semi-chrome leather was 243 kg/cm^2 and 364 kg/cm^2 respectively, which is much greater than the acceptable quality levels declared by United Nations Industrial Development Organization's (UNIDO). Similar investigations on indigenous crossbred sheepskin done in Ethiopia and Turkey revealed average tensile strengths of combination tanned leather of 249 kg/cm^2 and 218 kg/cm^2 respectively [3, 34]. Further, the experimental semi-chrome leather had a very high percentage of elongation (41.12%), which is considerably above the chrome re-tanned leather (35.47%) and is a well-accepted value suggested by UNIDO (Table 5). Therefore, the experimental leather could stretch and may hold more loads without breaking. As a mangrove plant, *X. granatum* bark tannin contains flavonoid chemicals (e.g., catechin hydrate, epicatechin, etc.) and phenolic hydroxyl groups, which may react with collagen via numerous hydrogen bonding and quinoid processes, which potentially increase leather strength. The variation of tensile strength varies on the composition of the tanning agents, type of tannin, quantity of tannin, the control of beam-house operations, pre-tanning, tanning, post-tanning and /or methods of tanning [12]. The higher strength properties of the experimental leather could be due to the high content of condensed tannin (48%).

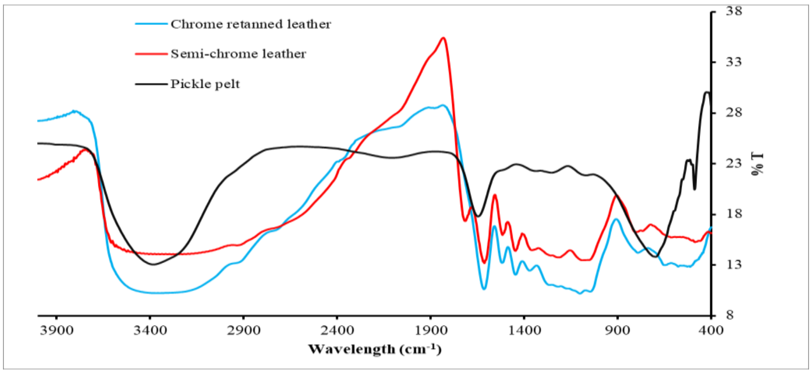

Figure 1. FTIR spectra of pickle pelt, semi-chrome, and chrome retanned leather

Table 5. Physico-mechanical properties of semi-chrome and chrome retanned leathers (mean± standard deviation)

Parameters	Chrome re-tanned leather	Semi-chrome leather	Acceptable values [35]
Tensile strength (kg/cm^2)	243.46 ± 12.76	364.71 ± 19.52	≥ 230
Elongation (%)	35.47 ± 4.15	41.12 ± 1.28	30 – 45
Tear strength (kg/cm)	31.34 ± 3.01	46.92 ± 4.06	≥ 30
Grain crack load (kg)	28 ± 1.00	35 ± 3.60	≥ 20
Distension at grain crack (mm)	12.71 ± 0.46	13.57 ± 0.98	≥ 7
Ball burst load (kg)	38.67 ± 1.15	44.67 ± 2.31	-
Distension at ball burst (mm)	14.89 ± 0.98	15.98 ± 1.94	-

In this study, for tearing strength, the chrome re-tanned leather showed 31.34 kg/cm and 46.92 kg/cm for semi-chrome leather. Other research has shown tear strength of 39.79 kg/cm when using 20% nilotica L. pods tannin [34] which is similar to this study. Also, the type of the tannin and the regulation of beam-house activities seem to be highly influencing parameters for leather tearing strength [12, 36].

The lastometer test which measures the real cracking and bursting load with distension is another essential physical test for evaluating the overall quality and strength of the leather. Grain cracking and ball bursting loads were found to be 28 kg and 38.67 kg for chrome re-tanned leather and 35 kg and 44.67 kg for semi-chrome leather respectively. Also, the distention at grain crack and ball burst for chrome re-tanned leather were 12.71 mm and 14.89 mm respectively whereas semi-chrome leather showed 13.57 mm and 15.98 mm respectively (Table 5) which are far beyond the minimum recommended value set by UNIDO for distention at grain crack (6.5 mm) and distention at ball burst (7.0 mm) respectively for all types of leather. For various sheep leathers, several researchers reported distention at grain fracture 6.74 mm/9.9 mm and distention at ball burst 7.72 mm/ 10 mm [37]. The types of tannin ingredients, pre-tanning procedures, tanning, and post-tanning processes are considered to be the influencing factors of the grain cracking load and ball-bursting load of leather [12].

4. CONCLUSION

The experimental semi-chrome and chrome retanned leathers exhibited excellent strength properties, hydrothermal stability, and smoothness. The high shrinkage temperature obtained in this study which is greater than 102 ℃ made the leathers usable parallel to conventional leather and provided an opportunity to be utilized as well alternative to the conventional SC and CR leathers. In addition, tensile strengths over 243 kg/cm^2 with 35-41% elongation provided the produced leathers better strength with proper flexibility for shoe uppers. Further, the main fact is that *Xylocarpus granatum* naturally grown in the southern part of Bangladesh (Sundarban region) could be regarded as a renewable material because it regenerates bark (after a few months of being peeled off). Hence, its utilization in tanning could pave the way for sustainable leather processing. Apart from our findings, as an indigenous source, cheaper sale price than that of commercial mimosa and quebracho, with greater extraction efficiency, and environmentally safe characteristics could make this material a potential tanning agent for future use. It is possible to conclude that *Xylocarpus granatum* bark extracts can be utilized as pre-tanning and retanning agents in leather tanning.

ACKNOWLEDGMENT

The authors wish to express their gratitude to Prof. Dr. Mohammed Mizanur Rahman, Director, Institute of Leather Engineering and Technology, University of Dhaka, Prof. Dr. Md. Zahangir Alam and Prof. Dr. Mohammad Nurnabi, Department of Applied Chemistry and Chemical Engineering, University of Dhaka, for their laboratory support. This work was partially funded by the Ministry of Science and Technology, Bangladesh under the National Science and Technology (NST) fellowship (Group: Physical Science, Reg. No: 317).

REFERENCES

1. Hussein SA. 2017. Utilization of tannins extracts of acacia seyal bark (taleh) in tannage of leather. *Journal of Chemical Engineering and Process Technology* 8, 334-342.
2. Ahmed S, Fatema-Tuj-Zohra, Mahdi MM, Nurnabi M, Alam MZ, Choudhury TR. 2022. Health risk assessment for heavy metal accumulation in leafy vegetables grown on tannery effluent contaminated soil. *Toxicology Reports* 9, 346-355.
3. Adiguzel-Zengin AC, Zengin G, Kilicarislan-Ozkan C, Dandar U, Kilic E. 2017. Characterization and application of acacia nilotica l. as an alternative vegetable tanning agent for leather processing. *Fresenius Environmental Bulletin* 26(12), 7319-7326.
4. Mahdi H, Palmina K, Gurashi AG, Covington D. 2009. Potential of vegetable tanning materials and basic aluminum sulphate in sudanese leather industry. *Journal of Engineering Science and Technology* 4, 20-31.
5. Basaran B, Ulas M, Bitlisli BO, Aslan A. 2008. Distribution of Cr (III) and Cr (VI) in chrome tanned leather. *Indian Journal of Chemical Technology* 15, 511-514.

6. Hedberg YS, Liden C, Odnevall Wallinder I. 2015. Chromium released from leather-I: exposure conditions that govern the release of chromium (III) and chromium (VI). *Contact Dermatitis* 72(4), 206-215.

7. Al-Mizan, Juel MAI, Alam MS, Pichtel J, Ahmed T. 2020. Environmental and health risks of metal-contaminated soil in the former tannery area of Hazaribagh, Dhaka. *SN Applied Science.* https://doi.org/10.1007/s42452-020-03680-4

8. Ahmed S, Fatema-Tuj-Zohra, Khan MSH, Hashem MA. 2017. Chromium from tannery waste in poultry feed: A potential cradle to transport human food chain. *Cogent Environmental Science* 3, 1312767.

9. Kilicarislan C, Ozgunay H. 2012. Ultrasound extraction of valonea tannin and its effects on extraction yield. *JALCA* 107, 394-403.

10. Galvez JMG, Riedl B, Conner AH. 1997. Analytical studies on Tara tannins. *Holzforschung* 51, 235-243.

11. Mahdi H, Palmina K, Glavtch I. 2006. Characterization of *Acacia nilotica* as an indigenous tanning material of Sudan. *Journal of Tropical Forest Science* 18, 181-187.

12. Kuria A, Ombui J, Onyuka A, Sasia A, Kipyegon C, Kaimenyi P, Ngugi A. 2016. Quality evaluation of leathers produced by selected vegetable tanning materials from laikipia county, Kenya. *IOSR Journal of Agriculture and Veterinary Science* 9(4), 13-17.

13. Elgailani IEH, Ishak CY. 2014. Determination of tannins of three common acacia species of Sudan. *Advances in Chemistry* Article ID 192708.

14. Elgailani IEH, Ishak CY. 2016. Methods for extraction and characterization of tannins from some acacia species of Sudan. *Pakistan Journal of Analytical and Environmental Chemistry* 17(1), 43-49.

15. Chai WM, Huang Q, Lin MZ, Ou-Yang C, Huang WY, Wang YX, Xu KL, Feng HL. 2018. Condensed tannins from longan bark as inhibitor of tyrosinase: structure, activity, and mechanism. *Journal of Agriculture and Food Chemistry* 66, 908−917.

16. Shahid-ud-daula AFM, Basher MA. 2009. Phytochemical screening, plant growth inhibition, and antimicrobial activity studies of *Xylocarpus granatum*. *Malaysian Journal Pharmaceutical Sciences* 7(1), 9–21.

17. Baba S, Chan HT, Kainuma M, Kezuka M, Chan EWC, Tangah J. 2016. Botany, uses, chemistry and bioactivities of mangrove plants-III: *Xylocarpus granatum*. *ISME/GLOMIS Electronic Journal* 14(1), 1-4.

18. Pisitsak P, Hutakamol J, Jeenapak S, Wanmanee P, Nuammaiphum J, Thongcharoen R. 2016. Natural dyeing of cotton with *Xylocarpus granatum* bark extract: dyeing, fastness, and ultraviolet protection properties. *Fibers and Polymers* 17(4), 560-568.

19. Covington T. 2009. *Tanning Chemistry: The Science of Leather.* UK: The Royal Society of Chemistry.

20. Brown BE. 1997. *Integrated coastal management-South Asia.* Department of International Development, University of Newcastle, UK.

21. Zafar TB, Khan GM. 2018. A geographical overview of sundarban: the largest mangrove forest of Bangladesh. *International Journal of Geology, Agriculture and Environmental Sciences* 6, 9-10.

22. Das RK, Mizan A, Zohra FT, Ahmed S, Ahmed KS, Hossain H. 2022. Extraction of a novel tanning agent from indigenous plant bark and its application in leather processing. *Journal of Leather Science and Engineering* 4, 18.

23. International Union of Leather Technologist and Chemist Societies. IUP-16. 2001. Measurements of shrinkage temperature up to 100°C. *Society of Leather Technologist and Chemist.*

24. ISO-2419. 2012. Leather-physical and mechanical tests. Sample preparation and conditioning.

25. International Union of Leather Technologist and Chemist Societies. IUP-06. 2001. Measurement of tensile strength and percentage of elongation. *Society of Leather Technologist and Chemist.*

26. International Union of Leather Technologist and Chemist Societies. IUP-08. 2001. Measurement of tearing strength. *Society of Leather Technologist and Chemist.*

27. ISO-3378/IUP-12. 2002. Leather-physical and mechanical tests. Determination of resistance to grain cracking and grain crack index.

28. Zengin AC, Crudu M, Maier S, Deselnicu V, Albu L, Gulumser G, Bitlisli BO, Basaran B, Mutlu MM. 2012. Eco-leather: chromium-free leather production using titanium, oligomeric melamine formaldehyde resin, and resorcinol tanning agents and the properties of the resulting leathers. *Ekoloji* 21, 17-25.

29. Kasmudjiastuti E, Pidhatika1 B, Griyanitasari1 G, Pahlawan IF. 2018. November. The effect of alum addition on shrinkage temperature, chemical properties, and morphology in the manufacture of vegetable-tanned leather. IOP Conference Series: Materials Science and Engineering. 602(012044), Conference on Innovation in Technology and Engineering Science, Padang, Indonesia.

30. Yallappa S, Manjanna J, Sindhe MA, Satyanarayan ND, Pramod SN, Nagaraja K. 2013. Microwave assisted rapid synthesis and biological evaluation of stable copper nanoparticles using T. arjuna bark extract. *SpectrochimicaActa Part A: Molecular and Biomolecular Spectroscopy.* 110, 108-115.

31. Ricci A, Olejar KJ, Parpinello GP, Kilmartin PA, Versari A. 2015. Application of Fourier transform infrared (FTIR) spectroscopy in the characterization of tannins. *Applied Spectroscopy Reviews* 50, 407-442.

32. Foo LY. 1981. Proanthocyanidins: gross chemical structures by infrared spectra. *Phytochemistry* 20, 1397-1402.

33. Silva PMS, Fiaschitello TR, Queiroz RS, Freeman HS, Costa SA, Leo P, Montemor AF, Costa SM. 2020. Natural dye from croton urucuranabaill bark: extraction, physicochemical characterization, textile dyeing and color fastness properties. *Dyes and Pigments* 173, 1-14.

34. Musa AE, Gasmelseed GA. 2013. Development of eco-friendly combination tanning system for the manufacture of upper leathers. *International Journal of Advance Industrial Engineering* 1(1), 9-15.

35. United Nations Industrial Development Organization. 1996. Acceptable quality standards in the leather and footwear industry. Vienna, Austria. United Nations Industrial Development Organization (UNIDO).

36. Basaran B, Iscam M, Bitlisii B, Asian A. 2006. Heavy metal content of various finished leathers. *Journal of Society of Leather Technologists and Chemists* 90, 229-234.

37. Lawal AS, Odums CP. 2015. Tanning of different animal skin/hides and study of their properties for textile applications. *British Journal of Applied Science and Technology* 6, 588-594.