World Journal of Advanced Engineering Technology and Sciences

eISSN: 2582-8266

Cross Ref DOI: 10.30574/wjaets

Journal homepage: https://wjaets.com/

(Research Article)

Check for updates

Improving vegetable tannins chemistry: A remarkable advancement in salt-free high tannin fixation

Mahdi Haroun [1,*], Inas Osman Khojalyi [2] and Manal Mohammed Ahmed [1]

[1] Department of Industries, College of Applied and Industrial Sciences, University of Bahri P.O. Box13104-Khartoum, Sudan.
[2] Department of Chemistry and Industrial Chemistry, Collage of Applied & Industrial Sciences, University of Bahri, P.O. Box13104-Khartoum, Sudan.

World Journal of Advanced Engineering Technology and Sciences, 2023, 09(02), 206–213

Publication history: Received on 12 June 2023; revised on 22 July 2023; accepted on 25 July 2023

Article DOI: https://doi.org/10.30574/wjaets.2023.9.2.0217

Abstract

Traditional tanning practices often result in harmful waste products that pose significant environmental risks, including water pollution, non-biodegradable solids, hazardous emissions, and unpleasant odors. However, this study introduces a simple and effective alternative method for industrial-scale vegetable tanning, with the goal of minimizing environmental pollution. This innovative method eliminates the use of common salt and substantially reduces water consumption. The environmental benefits of this new approach are remarkable. It has led to a significant 70% reduction in water usage, a 25% decrease in energy consumption, and complete elimination of chloride discharge. These changes have also contributed to a notable reduction of 60-70% in tanning and treatment expenses. Furthermore, the leathers produced using this method exhibit comparable physical, chemical, and sensory properties to those produced through conventional tanning practices. This eco-friendly approach not only addresses environmental concerns but also offers economic advantages, making it a sustainable choice for vegetable tanning processes.

Keywords: Vegetable tanning; Chromium; Salinity; Chlorides; Skins and hides

1. Introduction

Vegetable tanning, the oldest known tanning process, held its reign until the introduction of chrome tanning [1,2]. The exceptional properties displayed by chrome-tanned leathers led to over 80% of the global industry adopting this method. Chromium tanning became renowned for its versatility and dominance in the industry. However, escalating concerns regarding the environment, health, and safety have compelled tanners to seek and embrace alternative, eco-friendly tanning systems, or revert back to vegetable tanning [3-6]. Consequently, a worldwide quest is underway to discover cleaner, safer, and economically viable tanning systems [7-10]. Numerous alternatives have been extensively examined, including aluminum, iron, zirconium, titanium salts, as well as organic compounds such as aldehydes or their combinations [11,12]. However, most of these alternatives fail to meet the functional requirements of leather or fall short of satisfying eco-friendly criteria. In response, research is actively focused on investigating combination tanning systems primarily based on vegetable tannins as potential substitutes for chrome tanning [13]. Consequently, there is a renewed surge of commercial interest in vegetable tanned leathers. Vegetable tannins, which are polyphenolic compounds found in plant extracts, play a crucial role in this revival. Vegetable tannins, with molecular weights ranging from 500 to 3000 Dalton, are known as mixed polyphenolic species based on chromatographic studies. These polyphenols have the ability to form multiple hydrogen bonds, enabling them to cross-link with collagen [14]. The resulting leathers from vegetable tanning offer notable advantages, including compatibility with human skin, enhanced comfort, and excellent dimensional stability. Furthermore, the chosen tanning methodology allows for effective treatment and disposal of spent liquors. However, it's important to note that the issue of salinity remains unresolved in vegetable tanning, posing a significant concern.

* Corresponding author: Mahdi Haroun

In traditional tanning methods, the pH of skins and hides is typically reduced to around 2.5-3.0 through the "pickling" process, involving the use of mineral acids. To counteract the swelling effect caused by the acid, a significant amount of common salt (sodium chloride) is added, ensuring the leather's physical stability. In vegetable tanning, a depickling step is carried out before tanning, where mild alkalis are used to raise the pH to 4.5-4.8 in a saline bath. While the presence of common salt in pickling and depickling prevents excessive swelling and preserves the strength and quality of the leather, it also results in a significant discharge of chlorides and total dissolved solids (TDS) in the effluents. Moreover, the conventional process is time-consuming, with skins and hides immersed in concentrated vegetable tannin liquor for an extended period of around 14 days. Due to the diverse molecular composition of vegetable extracts, a prolonged tanning process is necessary to ensure proper diffusion of vegetable tannins. To achieve high-quality leathers, the tanning is typically conducted using a static method. Extensive research has been dedicated to addressing the issues of common salt and salinity in effluents [11,12,15-17]. Previous attempts have been made to mitigate these concerns through the utilization of non-swelling acids, such as naphthalene sulfonic acid condensates, during pH adjustments, recycling of pickle liquor, and modification of tanning materials. Previous attempts to address the salinity concerns in vegetable tanning methods, such as altering leather characteristics through various methods, have not been widely accepted by users and have not gained commercial adoption [18-20]. Likewise, end-of-pipe treatment approaches to meet discharge regulations have proven to be neither successful nor economically feasible for salinity issues [21,22]. However, the current work presented here successfully overcomes these limitations, providing a commercially viable solution without compromising leather quality.

2. Material and methods

2.1. Materials

A total of ten wet salted cattle skins sourced from Sudan, each weighing approximately four kilograms, were selected. Commercial grade garad pods tannin extract derived from (*Acacia nilotica ssp tomentosa*) was utilized. To ensure effective monitoring of changes, the skins were halved, with one portion tanned using the conventional vegetable tanning system, and the other using the salt-free vegetable tanning system. This approach aimed to minimize variations in results arising from differences between individual skins. Following the assessment of the processed leathers' physical and chemical properties at the laboratory scale. This large-scale production took place in a commercial tannery located in the Khartoum, Sudan, enabling the evaluation of the new method's feasibility and effectiveness in a real-world setting.

2.2. Traditional and innovative tanning techniques

The dehaired and defleshed skins were prepared for further experimentation. They underwent a neutralization process before being utilized in both conventional and modified tanning experiments. Detailed information about the tanning procedures for both methods can be found in Tables 1 and 2. Following the tanning process, the skins were subjected to oiling, samming, and drying, with careful attention to achieving proper setting. In order to gain a comprehensive understanding of the ecological advantages, a comparison was made between the vegetable tanning methodology and the conventional chrome tanning system.

2.3. Chemical Analysis of leather

2.3.1. Preparation of Sample

Leather was cut into small pieces to pass through a screen with circular perforations of 4 mm. The pieces were thoroughly mixed and brought to a state of homogeneity by keeping them in a closed container for at least overnight. Then Moisture content, Fat content, Insoluble ash, hide substances, Water soluble % was determined [23].

2.4. The Physical analysis of Leather

Criteria such as tensile strength, tear strength, and grain crack resistance serve as indicators of the robustness and longevity of leathers. The shrinkage temperature, on the other hand, measures the leather's capacity to withstand deformation and disintegration during the fabrication process. Factors like color fastness are essential to maintain the aesthetic appeal and uniformity of products when exposed to different environmental conditions, contributing to their overall eloquence. The tanned experimental and control leathers underwent a thorough evaluation to assess their softness, grain tightness, fullness, and overall appearance. This evaluation was conducted using a standard tactile assessment technique, which is a subjective practice commonly employed in leather evaluation. Experienced leather technologists assigned grade scores ranging from 0 to 10 for each of the aforementioned properties, providing a comprehensive evaluation of the leathers' quality.

2.4.1. Conditioning

The specimens for physical testing were kept in a standard atmosphere of temperature 20 ± 2 ^{o}C and relative humidity 65% ± 2% during the 48 h immediately preceding their use in a test [24].

2.4.2. Tensile strength and percent of elongation

The jaws of the tensile machine (Instron 1026, Instron, UK) were set 50 mm apart, and then the sample was clamped in the jaws, so that the edges of the jaws lay along the midline. The machine was run until the specimen was broken and the highest load reached was taken as the breaking load. The tensile strength load is in Newtons [25].

$$\text{Tensile strength} = \frac{\text{Maximum breaking load}}{\text{Cross sectional area}}$$

2.4.3. Percent of Elongation at Break

Percent of Elongation at Break was measured according to the society of leather technologist and chemists [25].

Calculation

$$\text{Elongation, \%} = \frac{\text{Final free length} - \text{Initial free length}}{\text{Initial free length}}$$

2.4.4. Hydrothermal stability analysis

Tanned leather samples with conventional and innovative tanning were examined for measurement of hydrothermal stability. Differential scanning calorimeter is used for measurement of shrinkage temperatures (Ts). Results disclosed that extracts of *Acacia nilotica ssp tomentosa* pods performed better in terms of hydrothermal stability [26,27].

2.5. Statics analysis

The analysis is done using paired two sample for means t-Test.

Table 1 Procedure for traditional vegetable tanning method

Process	Chemical materials	Quantity, %	Time/min	Notes
Pickling (Drum)	Water	100		
	Common salt	15	15	
	Sulphuric acid	2.5	3X10	
	Formic acid	1	3X10+60	pH -3.0
Depickling	Water	100	30	Overnight ageing; drain
	Common salt	7.5	90	
	Sodium formate	2	60	
	Pretanning syntan	3		pH -3.9; drain
Tanning (pit)	Water	150		
I	Garad extract 25 ^{o}Be		5 days	
II	Garad Extract 35 ^{o}Be		8 days	

Table 2 Procedure for the modified vegetable tanning process

Process	Chemical materials	Quantity, %	Time/min	Notes
Acid treatment (Drum)	Water	100		
	Organic acid	1.5	120	pH 4.8-4.9
	Pretanning syntan	3	60	
Tanning (Pit)	Water	150		
I	Garad extract 25 °Be		5 days	
II	Garad Extract 35 °Be		8 days	

3. Results and discussion

3.1. Impact of the novel process on leather properties

Regarding the sensory properties, the modified processed leathers exhibited a more pronounced sense of fullness and enhanced softness in comparison to conventional leathers (Figure 1). This can be attributed to the increased tannin absorption by the cattle skins due to improved fiber opening, as observed in the new process. When skins were treated with unionized organic acid, it binds to the collagen chains at a molecular level, disrupting the hydrogen bonds present in the collagen. This process leads to improved fiber splitting and further contributes to the overall enhanced organoleptic properties of the leather.

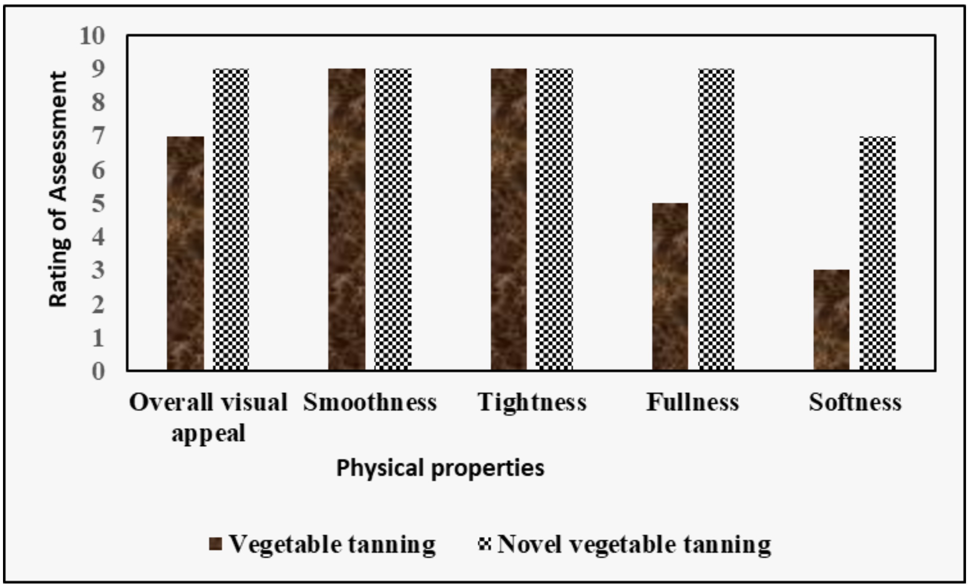

Figure 1 Evaluation of tanned leathers based on visual cues

The chemical analyses conducted on both conventional and salt-free tanned leathers reveal that all the parameters are comparable, indicating no significant difference in the tanning characteristics. This is further supported by the degree of tannage, as depicted in Table 3.

The reduced water solubility (8.5±0.3%) indicates that modified vegetable tanned leather ensures better water resistance compared with the Conventional (9.4±0.2%) (Table 3) (17). The shrinkage temperature of these leathers was also measured and documented in Table 4. There is not much of variation in the shrinkage temperature of conventional and novel tanned leathers.

Table 3 Chemical characterization of tanned leathers

Parameters	**Conventional**	**Novel**
Moisture content, %	11.6±0.4	11.5±0.2
Water Soluble solid, %	9.4±0.2	8.5±0.3
Metal Oxide, %	1.5±0.1	2.5±0.3
pH	4.3±0.2	4.9±0.2
Ash content, %	0.9±0.1	1.4±0.3
Water soluble organics, %	6.7±0.4	8.4±0.2
Hide Substances (T)%	39.4±0.7	36.9±0.2
Fat content, %	4.5±0.2	4.8±0.5
Degree of Tanning, %	81.5±0.6	82±0.2

Table 4 Shrinkage temperature of Tanned Leathers

Process	**Shrinkage temperature, ST, oC**
Chrome Tanning	98.6±3
Conventional tanning	83± 2
Novel tanning	80± 1

The tensile strength, percentage elongation, tear strength, and grain cracks of the tanned leather using conventional, novel methods are shown in Table 5. Vegetable tannins material is capable of diffusing into the molecular pore dimensions. An increase in the tensile strength can be interpreted in terms of the number of covalent cross-links formed during the tanning processes. However, a decrease in the tensile strength at a higher concentration of vegetable tannin material may be owing to the increased stiffness (shown by the decreasing elongation) results in a brittle fiber; consequently, it breaks more easily at a reduced load. Based on the outcomes of the statistical analysis tensile strength of skin tanned with conventional and novel methods showed significantly different results. Tensile strength values of tanned skin with novel method are higher than that tanned with conventional. On the other hand, tanned skin with novel method produced greater skin elongation 35 % compared to tanned with conventional and chrome which was 30 and 33% respectively. The bonds extent of the vegetable tanning skin collagen provides an explanation of the increased tensile strength of skin fiber [28].

Table 5 Physical testing characteristics of leathers

Types of tanning	**Tensile strength (N/mm^2)**	**Tear strength (N/m)**	**%, elongation at break**	**Grain cracks strength**	
				Load (kg)	**Distension (mm)**
Chrome	26±0.9	39.5±0.6	33±2	33	12±0.2
Conventional Tanning	23±0.9	34.6±0.6	30±2	25	8±0.2
Novel Tanning	25 ±0.9	45.5±0.6	35±2	30	10±0.2

3.2. Impact of the new process on the quality of tanning effluent.

Despite maintaining the same initial concentration of tan liquor for both tanning methods, the spent vegetable tan liquor indicates a higher absorption rate with the modified tanning process (Table 6). This can be attributed to the molecular association of the organic acid, which promotes better fiber bundle opening, facilitating the accelerated diffusion of vegetable tannins. Consequently, there is a noticeable difference in the values of biological oxygen demand (BOD) and chemical oxygen demand (COD) between the spent liquors, further validating the effectiveness of the modified tanning process in improving tanning effluent quality.

Table 6 Characteristics of the spent liquor effluent

Parameters (mg/l)	Process types		
	Chrome	**Conventional**	**Novel**
pH	3.8-4.0	4.2-4.3	4.5-4.6
Chemical oxygen demand	1100	18000	9000
Biological oxygen demand	3000	35000	10000
Chloride	30000	60000	-
		Including depickling	-
Total dissolved solids	95000	45000	15000
Total suspended solids	2750	8000	4000
Sulphates	17500	-	-
Chromium as Cr2O3	3800	-	-

The analysis of cumulative spent tan liquor, as presented in Table 6, demonstrates a significant decrease in total dissolved solids (TDS) and chlorides due to the elimination of traditional salt-based acidification and deacidification stages. With the removal of chloride ions from the waste streams, there is complete elimination of chlorides, while TDS reduction exceeds 67% due to the elimination of sodium chloride and the depickling process step. In conventional processing, pH fluctuations resulting from acidification and deacidification often contribute to the generation of substantial amounts of neutral salts. Due to concerns over toxicity and health issues associated with mineral tanning materials, there has been a resurgence of interest and increased global demand for plant-based and mineral-free leather and leather products. The availability of advanced post-tanning auxiliaries has facilitated the production of leathers with improved color characteristics, overcoming the conventional limitations of color deficiency while also reducing costs. Although the new tanning method results in a higher biological oxygen demand (BOD) compared to mineral tanning, as evident in Table 6, it is significantly lower than that of conventional vegetable tanning. When comparing the treatment costs, it is found that the expenses for treating BOD are much lower compared to the costs associated with salt and chromium treatment. Consequently, the present method proves to be both economically viable and safe when compared to conventional vegetable or chrome tanning methods.

For a sustainable process in a traditional industry like tanning, it should not only offer environmental improvements but also be economically viable. The findings reveal that the tanning system without pickling and depickling is more cost-effective compared to the traditional method. It is important to note that implementing this system does not require any additional infrastructure investment or changes in factory workflows. During an industrial-scale trial involving 1500 kgs of cattle skins, significant cost savings were achieved through the elimination of common salt and reduction in process time. Furthermore, adopting this salt-free vegetable tanning process brings additional benefits by reducing environmental pollution and associated risks, leading to further cost reduction. Overall, the salt-free vegetable tanning process is a cost-effective, environmentally friendly, and easily adoptable solution.

4. Conclusion

The aim of this novel study is to demonstrate the environmental benefits of a traditional tanning system based on vegetable tanning through a simple and viable method that eliminates the use of common salt. The trial conducted at commercial scales revealed that by implementing appropriate technical interventions in the vegetable tanning process, significant water savings could be achieved while producing leathers of comparable quality. The improved tanning system resulted in a remarkable reduction in water consumption (70%) and the complete elimination of salinity associated with vegetable tanning. These changes contributed to a reduction in tanning and treatment expenses by 60-70%, in addition to saving approximately 25% of power consumption. The proposed methodology not only yields environmental benefits but also brings about significant cost savings, thereby promoting the sustainability of the vegetable tanning process from both an environmental and economic standpoint.

Compliance with ethical standards

Acknowledgments

The authors are grateful to Bahri University and forest National cooperation, for support and national Centre for research for giving the possibility to use the resources and facilities of their laboratory.

Disclosure of conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Statement of ethical approval

The present research work does not contain any studies performed on animals/humans' subjects by any of the authors.

References

[1] Bayramoglu, E.E. (2013). Hidden treasure of the nature: PAs. The effects of grape seeds on free formaldehyde of leather. Ind. Crop. Prod. 41, 53-56.

[2] Sundar, V.J., Rao, J.R., Muralidharan, C. (2002). Cleaner chrome tanning - emerging options. J. Clean. Prod. 10, 69-74.

[3] Dixit, S., Yadav, A., Dwivedi, P.D., Das, M. (2015). Toxic hazards of leather industry and technologies to combat threat - a review. J. Clean. Prod. 87, 39-49.

[4] Kimbrough, D.E., Cohen, Y., Winer, A.M., Creelman, L., Mabuni, C. (1999). A critical assessment of chromium in the Environment. Crit. Rev. Environ. Sci. Technol. 29, 1-46.

[5] Leonard, A., Lauwerys, R.R. (1980). Carcinogenicity and mutagenicity of chromium. Mutat. Res. 76, 227-239.

[6] Sivakumar, V., Sundar, V.J., Rangasamy, T., Muralidharan, C., Swaminathan, G. (2005). Management of total dissolved solids in tanning process through improved techniques. J. Clean. Prod. 13, 699-703.

[7] Li, K., Chen, H., Wang, Y., Shan, Z., Yang, J., Brutto, P. (2009). A salt free pickling regime for hides and skins using oxazolidines. J. Clean. Prod. 17, 1603-1606.

[8] Morera, J.M., Bacardit, A., Olle, L., Bartoli, E., Borras, M.D. (2007). Minimization of the environmental impact of chrome tanning- A new process with high chrome exhaustion. Chemosphere 69, 1728e1733.

[9] Simon, C., Pizzi, A. (2003). Lightfast and high shrinkage temperature leather produced using vegetable tannins and novel melamine-urea-formaldehyde tanning formulations. J. Am. Leather Chem. Assoc. 98, 83-96.

[10] Sundar, V.J., Ramesh, R., Rao, P.S., Saravanan, P., Sridharnath, B., Muralidharan, C. (2001). Water management in leather industry. J. Sci. Ind. Res. 60, 443-450.

[11] Sundar, V.J., Gnanamani, A., Muralidharan, C., Chandrababu, N.K., Mandal, A.B. (2011a). Recovery and utilization of proteinous wastes of leather making - a Review. Rev. Environ. Sci. Biotechnol. 10, 151-163.

[12] Sundar, V.J., Rao, J.R., Muralidharan, C., Mandal, A.B. (2011b). Recovery and Utilization of chromium tanned proteinous wastes of leather making - a review. Crit. Rev. Environ. Sci. Technol. 41, 2048-2075.

[13] Sundar, V.J., Muralidharan, C., Mandal, A.B. (2013). Eco-benign stabilization of skin protein e role of Jatropha curcas oil as a co-tanning agent. Ind. Crops Prod. 47, 227-231.

[14] Covington, A.D. (1997). Modern tanning chemistry. Chem. Soc. Rev. 26, 111-126.

[15] Lofrano, G., Meric, S., Zengin, G.E., Orhon, D. (2013). Chemical and Biological treatment technologies for leather tannery chemicals and wastewaters - a review. Sci. Total Environ. 461e462, 265-281.

[16] Moretton, J., Baro, P., Daquino, M. (1992). Genotoxic potential of waste waters from a leather industry. Water Air Soil Poll. 63, 81-85.

[17] Munz, K.H., Sundar, V.J., Muralidharan, C., Parthasarathi, K. (1997). Chrome tannage without pickling. Das. Leder 48, 128-132.

[18] Mwinyihija, M., Meharg, A., Dawson, J., Strachan, N.J.C., Killham, K. (2006). An ecotoxicological approach to assessing the impact of tanning industry effluent on river health. Arch. Environ. Cont. Toxicol. 50, 316-324.

[19] Sundar, V.J., Muralidharan, C. (2009). Eco-benign skin preservation through salt substitutionda low salt approach. Desali. Water Treat. 11, 314-317.

[20] Vankar, P.S., Dwivedi, A., Saraswat, R. (2006). Sodium sulphate as a curing agent to reduce saline chloride ions in the tannery effluent at Kanpur: a preliminary study on techno-economic feasibility. Desalination 201, 14-22.

[21] Aleixandre, M.V.G., Clar, A.I., Pia, A.B., Roca, J.A.M., Uribe, B.C., Clar, M.I.I. (2005). Nanofilteration for surface removal and water reuse of the pickling and tanning processes in a tannery. Desalination 179, 307-313.

[22] Cassano, R., Molinari, R., Romano, M., Drioli, E. (2001). Treatment of aqueous effluents of the leather industry by membrane processes - a review. J. Membr. Sci. 181, 111-126.

[23] Borasky, R. and Nutting, G.C. (1949). Microscopic method for determining shrinkage temperature of collagen and leather. J. Am. Leather Chem. As., 44:830-841.

[24] Adewoye, R.O. and Bangaruswamy, S. (2000). Acacia nilotica (bagaruwa)-chromium combination tannage–a boon to the leather industry. J. Soc. Leath. Tech. Ch., 73:141-143.

[25] Society of Leather Technologists and Chemists, (SLTC). (1996). Official Methods of Analysis. 3rd ed. SLTC. Redbourn, UK, 250p.

[26] Kuria, A.N. (2015). Evaluation of Tanning Strength and Quality of Leathers Produced by Selected Vegetable Tanning Materials from Laikipia County, Kenya Department of Public Health Pharmacology and Toxicology. University of Nairobi

[27] Kuria, A., Ombui, J., Onyuka, A., Sasia, A., Kipyegon, C., Kaimenyi, P., Ngugi, A. (2016b). Quality evaluation of leathers produced by selected vegetable tanning materials from laikipia county, Kenya. IOSR J. Agric. Vet. Sci., 9: 13-17

[28] Heidemann, E. (1993). Practical and theoretical aspects of tanning. In: Fundamentals of Leather manufacture, Eduard Roether K.G, Darmstadt, Germany, , p269-294