THE *Journal* OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

March 2024 Vol. CXIX, No.3 *JALCA* 119(3), 105–152, 2024

Contents

Distributed by
University of CINCINNATI
LIBRARY PUBLISHING SERVICES

An imprint of the University of Cincinnati Press

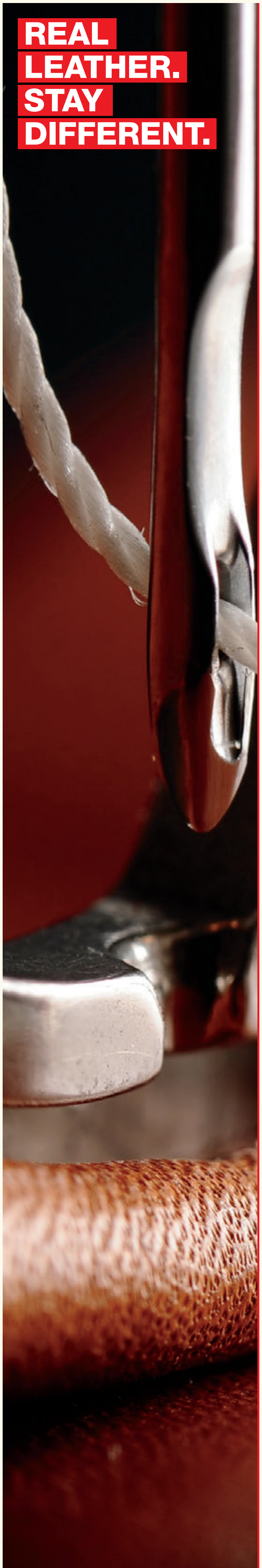
ISSN: 0002-9726

Communications for Journal Publication

Manuscripts, Technical Notes and Trade News Releases should contact:

Mr. Steven D. Lange, Journal Editor, c/o University of Cincinnati, 5997 Center Hill Ave., Bldg. C, Cincinnati, OH 45224, USA
E-mail: jalcaeditor@gmail.com Mobile phone: (814) 414-5689

Contributors should consult the Journal Publication Policy at:
http://www.leatherchemists.org/journal_publication_policy.asp



LEATHER BY NUMBERS:

FACTS AND FIGURES FROM THE US LEATHER INDUSTRY AND BEYOND

Note: All figures as of January 2021 or latest available.

ZERO cattle are killed to make US leather. US hides have been valued at JUST 1-2% of a cow's total value for the last two years, which is why they are considered a by-product and often end up as waste. The average price per head of US cattle is $2,000-2.200, while hides vary in price from $5 TO $35 PER PIECE, if sold at all. (1)

330M hides come from the meat and dairy industries around the world. Approximately **34M** were processed the US. (2) **AS MANY AS 2.4M US HIDES** ended up as landfill in 2019, this is **7%** of the national total.

Worldwide the waste figure is approximately **40%** or **132M** hides. With the average hide weighing 25Kg this means that **3M TONNES** are thrown away ever year.

Leather production turns more than **4.5M TONNES OF** potential waste, every year, into usable, durable goods. This saves **2.7M TONS OF GREENHOUSE GAS EMISSIONS** from landfill sites. (3)

Production, processing and distribution of hides and leather products directly employs an estimated **5,486** individuals, who collectively earn more than **$384M**. US exports of hides and leather was over **$1.5BILLION** in 2021. (4)

The US exports approximately **95%** of all cattle hide and wet blue leather products it produces, worth **$2.85BILLION**. (5)

Around **45%** of global leather production is used to make footwear, **22%** for clothing, bags and accessories, **18%** for car upholstery, and about **15%** for furniture. (6)

Water consumption for the production of leather from cattle hides has fallen by more than **35%** in the past 25 years, down from **60 CUBIC-METERS** per ton of hides to **38 CUBIC-METERS** per ton. US tanneries are required, by law, to connect to effluent treatment plants to prevent pollution. (7)

Leather will biodegrade in **LESS THAN 50 YEARS**. In contrast, it can take **500 YEARS** or more for synthetics, made from petrochemicals, to degrade. (8)

ReFed's conversion rate for food waste is for **EACH METRIC TON OF WASTE DISPOSAL** there is **9.8 7MT** of **CO2 EQUIVALENT** emitted. In this case, mostly as methane. (9)

This factsheet is produced by the Leather and Hide Council of America (L&HCA), established to promote the US leather industry which is responsible for a significant proportion of the international trade in hides. The L&HCA works to establish best practice in US leather production and to share this worldwide. Figures quoted refer to the USA unless otherwise stated.

SOURCE:

(1) https://downloads.usda.library.cornell.edu/usda-esmis/files/rx913p88g/w0893q25p/5d86qb66f/lstk0223.pdf
(2) https://downloads.usda.library.cornell.edu/usda-esmis/files/r207tp32d/pg15cj85z/hd76t466z/lsan0422.pdf
(3) 2020 LHCA Infographic
(4) John Dunham & Associates, Economic Impact of the Meat Industry (2016)
(5) https://thesustainabilityalliance.us/wp-content/uploads/2020/04/US-Hide-Skin-and-Leather-Factsheet-0420.pdf
(6) TBC
(7) 2020 LHCA factsheet
(8) https://en.wikipedia.org/wiki/Leather#:~:text=Leather%20biodegrades%20slowly%E2%80%94taking%2025,or%20more%20years%20to%20decompose
(9) https://insights-engine.refed.org/impact-calculator?inputs=%7B%22sector%22%3A%22manufacturing%22%2C%22type%22%3A%22fresh-meat-seafood%22%2C%22unit%22%3A%22tons%22%2C%22alternative%22%3Afalse%2C%22destinations%22%3A%5B%7B%22key%22%3A%22refuse-discards%22%2C%22current%22%3A1%7D%5D%7D

JOURNAL OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

Proceedings, Reports, Notices, and News
of the
AMERICAN LEATHER CHEMISTS ASSOCIATION

THE JOURNAL OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION (USPS #019-334) is published monthly by The American Leather Chemists Association, c/o University of Cincinnati, 5997 Center Hill Ave., Bldg. C, Cincinnati, Ohio 45224. Telephone (513) 290-2505. Single copy price: $10.00 members, $20.00 non-member plus shipping and handling. Subscriptions: $185 for hard copy plus postage and handling of $60 for domestic subscribers and $70 for foreign subscribers; $220 for ezine only; and $240 for hard copy and ezine plus postage and handling of $60 for domestic subscribers and $70 for foreign subscribers.

Periodical Postage paid at Cincinnati, Ohio and additional mailing offices. Postmaster send change of addresses to The American Leather Chemists Association, c/o University of Cincinnati, 5997 Center Hill Ave., Bldg. C, Cincinnati, Ohio 45224.

Website: www.leatherchemists.org E-mail: hallks@ucmail.uc.edu


ALL THE QUALITY
YOU NEED
MADE EASY
Ecotan 3400L
Erretre Tannery Innovations
PACA 3000
AMBRA self cleaning
RELIABILITY | CONTROL | HIGH TECHNOLOGY | SUSTAINABILITY
MILLING DRUMS
SPRAY BOOTHS
TUNNEL DRYERS
AUTOMATION
Erretre
Tannery Innovations
more
Via Ferraretta, 1 - 36071 Arzignano VI, Italy | +39 0444 478312 | info@erretre.com | erretre.com

Allium Cepa Peel Waste: A Sustainable Solution for Antibacterial Leather Dyeing with GS Powder Mordanting

by

Sathya Ramalingam,[a] Swethashree Rajendran,[a] Ambika Kumaresan,[b] Gladstone Christopher Jayakumar[c] and Alagumuthu Tamil Selvi[d*]

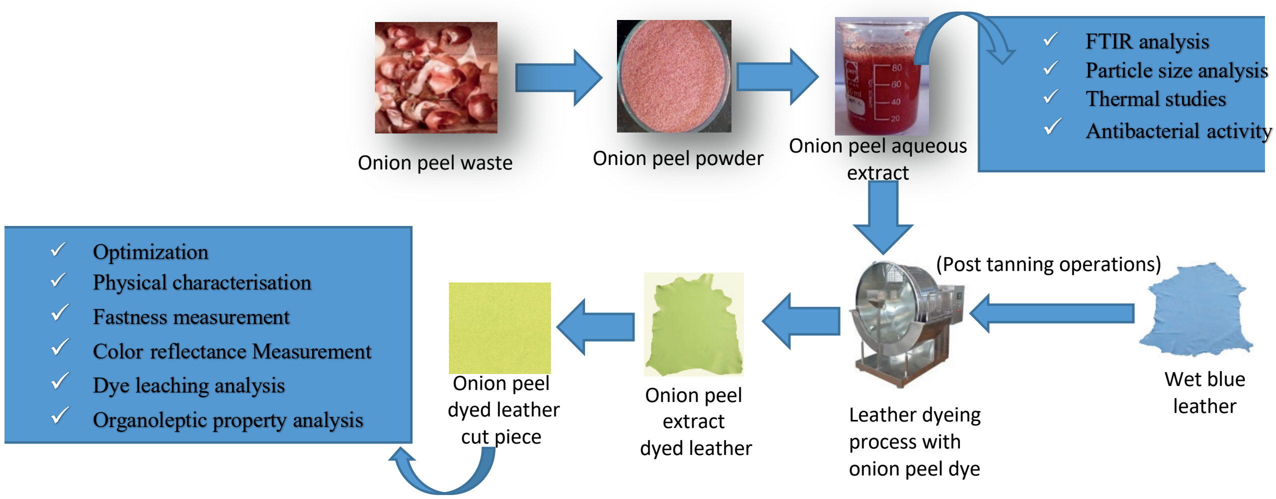
[a] *Leather Process Technology Department, Central Leather Research Institute,* Adyar, Chennai 600 020, India.

[b] *Shoe and Product Design Centre, Central Leather Research Institute,* Adyar, Chennai 600 020, India.

[c] *Centre for Academic and Research Excellence, Central Leather Research Institute*, Adyar, Chennai-600020, India.

[d] *Unit for Science Dissemination, Central Leather Research Institute*, Adyar, Chennai-600020, India.

Graphical Abstract



Abstract

Using natural dyes rather than synthetic dyes is an option that can be pursued to achieve sustainability in leather dyeing. The main disadvantage of natural dyeing is poor wet and dry rub fastness and the requirements of metal mordants for fixing. In this work, onion peel waste is the chosen raw material to produce natural dye for leather dyeing without metal mordant. Adding commercial syntans and vegetable tannins with the onion peel dye in the post tanning process produces good quality dyed leather without using any mordants. The optimal particle size of eco-friendly onion peel dye was extracted from onion peel (Allium cepa) using a modified aqueous extraction method. The extracted dye was examined by various instrumental techniques to characterize the functional groups by Fourier transform infrared spectroscopy (FT-IR), optical properties by UV-VIS spectrophotometry, size by Malvern Instruments, and thermal stability by Thermogravimetric Analysis (TGA). The results express the suitability for application in the leather dyeing process. The extracted dye was analysed for the antibacterial activity towards *Bacillus subtilis* and *Escherichia coli,* and the results revealed that the natural dye has an antibacterial effect Crust leather dyed only with extracted dye showed poor dye penetration. Thus, the optimized extracted onion peel dye, phenolic syntans and vegetable tannins were added to the leather substrate and processed in drum. It was the observed that the dye was uniformly penetrated inside the leather and fixed strongly on the surface. The good dyeing characteristics were confirmed using color measurements of the onion peel dyed leather. The result obtained from Universal physical testing of dyed leather deep-rooted that the strength properties of leather were not influenced by extracted onion peel dye. The quality of organoleptic properties of the same was found to be good. The simple combination of natural dye and the vegetable tannins improved the dyeing uniformity on the leather surface and fastness properties. Hence utilizing solid waste (onion peel) as a dyeing agent will create a sustainable environment during the dyeing process.

Introduction

Globally, natural dyes are environmentally safer than synthetic dyes in biomedical, textile, leather, and wool dyeing. There is a growing trend towards natural dyes usage due to the avoidance of environmental hazards caused by chemical dyes.[1] According to the

*Corresponding Author: tamilselvi@clri.res.in; Tel. +91 44 24437217
Manuscript received August 23, 2023, accepted for publication October 30, 2023.

current market scenario, it is assumed that the natural dyes show income of 5 billion dollars in the year 2024. However, natural dyes make up only about 2 percent of the leather and textile market because of various factors such as practical issues and withstand ability in production and application, limitations in reproducible shades, and inability to be available in standard form.[2] Even though the market potential is less, considering the advantages like biodegradability, cost effectiveness, eco-friendly in nature, and free from carcinogens, natural dyes are found to be good sources for dyeing applications.[3] By improving the commercial application of dye from natural sources in leather and textile industries, the cost-effectiveness, color efficiency, and stability should be optimized for its usage. Natural dyes can be extracted from available natural sources easily by means of solvent extraction techniques and can be utilized as a dyeing agent. Employing certain mordants, dye color can be changed to various shades. Even using pre-mordants in the natural dyeing process will enhance the UV resistance, antibacterial activity, and antioxidant activity in dyed fabrics. Many researchers have attempted to standardize the natural dyes extracted from various sources like roots, bark, leaves, flowers, and fruits for dyeing applications. For example, Okwuchi[4] used the Khaya senegalensis, Bixa Orellana, Allium cepa, Mangifera Indica, and Hibiscus sabdariffa as natural dyes. Sivakumar et al,[5] extracted natural dye from beetroot for leather and paper. Pervaiz et al,[6] applied Celosia cristata, Lantana camara, Rosa damascene, and Tagetes erecta dyes on goat leather. Several natural dyes are being used in leather applications with and without mordants. However, most of the leather dyed with natural dyes exhibit poor wet and dry rub fastness, uneven shades on the grain and flesh side, and high production costs. Mordants are necessary to enhance dyed leather's color fastness and prevent fading. Various mordants are used in mordanted dyeing processes, including tannin, oil mordants, and metallics like Aluminium, chromium, iron, copper, and tin. Most of the metal mordants are toxic for leather applications. As an alternative to metal mordants, several bio-mordants were introduced to produce dyed fabrics with limited toxicity.

Hence it is important to develop natural dyes from the waste and fix the dye to leather without mordant. In India, 23% of solid waste comprises vegetable waste, presenting an opportunity to utilize these materials innovatively. This study focuses on harnessing non-edible outer skin of Allium cepa, commonly discarded as waste, to create a novel dye product for leather dyeing applications. Collecting onion peel waste is a straightforward process. According to FAO (Food and Agricultural Organisation) statistics stated that India, as the second-largest onion-producing country, yields a staggering 19-20 MT (metric tonnes) of onions annually. Onion usage will generate approximately 73.5% to 81.6% of peel waste, constituting around 10-25% of the onion's total weight on a %w/w basis. This means that annually, a substantial amount of 2-5 MT (metric tons) of onion peel waste is generated. These peels, often overlooked, represent an inexpensive and abundant source for the production of natural dye.

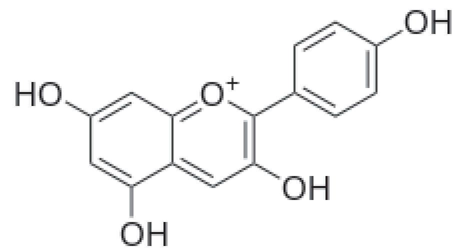


Figure 1. Pelargonidin structure.[7]

Although onion peel contains 89 % of carbohydrates, 0.88% of deficient protein, 0.39% of ash, and 0.15% of crude fiber, the dry non-edible onion skin is rich in a strong antioxidant called *Pelargonidin* having its chemical name as *3,5,7,4 Tetrahydroxyl anthocyanidol*, which is an anthocyanin, water-soluble glycosides (Figure 1). *Pelargonidin* is a dye in the onion peel that serves a major role in the leather dyeing process.[7]

The onion peel contains more pectin, primarily composed of galacturonic acid, giving it an acidic nature. In acidic conditions, Pelargonidin binds easily with leather substrates without the support of dyeing auxiliaries and mordants. Generated effluent contains only diluted unabsorbed onion liquor compound, which is biodegradable. In contrast, conventional dyeing processes require more energy to degrade dyeing chemicals such as auxiliaries, mordants, metals, and neutral salts. To avoid the discharge of unreacted dyes and auxiliaries in the wastewater, the synthetic dyes are modified with polymers or different functional groups to better interact with the leather. Quercetin, an anti-inflammatory compound from onion peel extract may lead to reduced swelling and pain for users.[8]

These natural dyes possess inherent antimicrobial properties that make them a valuable resource for various industries. A study by Smith et al.[9] demonstrated the efficacy of onion peel extract against a range of pathogenic bacteria, showcasing its potential for applications in food packaging and medical devices. Moreover, the study conducted by Brown and Lee[10] highlighted the specific mechanisms through which onion peel extracts inhibit bacterial growth. This valuable insight not only substantiates the antibacterial effect but also suggests how it can be harnessed for tailored coating solutions. The benefits of utilizing onion peel dye extract for coating applications are manifold. Firstly, it offers a natural and eco-friendly alternative to synthetic antibacterial agents, addressing growing concerns about environmental sustainability. Additionally, it holds promise for extending the shelf life of packaged food products, reducing the risk of contamination, and improving public health. Furthermore, its biocompatibility makes it suitable for medical equipment coatings, reducing the risk of nosocomial infections. The antibacterial properties of natural dye extracted from onion peel are increasingly recognized and have the potential to revolutionize coating applications, with ecological and health benefits.

In another end, applying onion peel waste as a natural dye in the leather dyeing process presents several challenges. Firstly, achieving consistent color outcomes is difficult due to natural variations in onion peel pigments, leading to batch-to-batch differences in the dyeing process. Secondly, onion peel dye may require mordants to set the color, and finding the right mordant and fixation process is crucial for stability and wash fastness. Thirdly, natural dyes, including onion peels, often have lower color fastness compared to synthetics, making them susceptible to fading or color changes when exposed to light, water, or other environmental factors. Addressing these challenges demands extensive research, experimentation, and innovation in dye preparation and leather dyeing. Hence, this work deals with a sustainable method of dyeing leather using onion peel extracted dye with vegetable tannin as a mordant. To reduce the cost of dye making, the onion peel dye was extracted from the onion peel waste by a simple aqueous based extraction process. In this study, we endeavored to utilize onion peel dye as a natural dye for leather coloring, completely avoiding the use of chemical mordants.

This work deals with a sustainable method of dyeing leather using onion peel extracted dye with vegetable tannin as a mordant, rather than metallic mordants, minimizing environmental problems associated with dyeing auxiliaries. To reduce the cost of dye making, the onion peel dye was extracted from the onion peel waste by a simple aqueous based extraction process. The extracted dye was characterized by particle size analysis (Malvern Instrument), FT-IR and TGA. After carefully evaluating dye properties, the natural dyes were used in the leather dyeing process to make good quality dyed leather. Variations in the process parameters like (dye percentage, duration, and pH) greatly influenced the dyeing process. Hence optimization of dyeing processing is done on the percentage dye exhaustion using different variables. Finally, the leather dyed with natural dye showed a uniform-colored surface on the cross section with improved fastness properties in the presence of vegetable tannins and phenolic syntans. Evidence from the current study indicates that the onion peel waste could become an attractive alternative for synthetic dye in the leather dyeing process.

Materials and Methods

Sample collection

The waste onion skins were procured from the regional bazaar, Koyambedu, Chennai. They were then cleaned, dried, and powdered.

Materials and Methods

Undyed chrome-tanned goat crust leather (1mm thickness) was selected for dyeing experiments. Other commercial natural dyes like Indigo and Madder were procured from KMA Exports. Retanning agents and fatliquors were procured from Buckman Laboratories (India) Private Limited for the post-tanning process. All other chemicals used for product characterization were of commercial grade.

Preparation and Extraction of Dye

First, 100 g of onion peel powder in 1L of distilled water is soaked overnight. The soaked solution was boiled to perform subsequent extraction by adding 500ml of water as a solvent in the 1-Liter round bottom flask. The aqueous extraction method was performed at 80°C for 30- 60 minutes. The obtained dye extract was cooled and passed through the Whatman No.1 filter paper. The crude extract is diluted in a 1:10 ratio and then subjected to characterization. Later, the aqueous extract was dried using a spray dryer apparatus. The extracted dye was kept at ambient temperature to use for further characterization and application.

Characterization of the Extracted Dye

The functionality of the extracted natural dye was analysed by the FTIR spectrum. The ABB MB3000 FTIR spectrometer records the spectrum. Spectral Analysis was performed by making the pellet sample using potassium bromide. The range runs in the region of 4000-400cm^{-1} with the 4 cm^{-1} resolution and is recorded at a 45°incident angle. Dynamic Light Scattering (DLS) was performed by He/Ne laser of wavelength 632.8 nm. The solution of extracted dye was subjected to filtration using PTFE 0.45 µm before DLS measurement. The Q50 TA instrument was used for thermogravimetry analysis (TGA) of the sample run at a heating rate of 5°C min^{-1}.

Anti-bacterial Activity

The anti-bacterial activity was performed using two bacterial strains, *Escherichia,* and *Bacillus* species based on the reported procedure.[11] Both strains collected from the microbiology laboratory were sub-cultured in a growth medium (Nutrient agar) and kept for incubation at 37°C overnight. Both strains were used for performing the anti-bacterial activity in onion peel liquor by agar well diffusion method and incubated at 37°C. The zone of inhibition was measured using a measuring scale.

Leather Dyeing Application

The extracted onion peel dye was used in leather dyeing as dyeing agent during the post tanning process. The raw material chosen for the dyeing experiment was chrome tanned wet blue goat leather. The dry weight of the crust was weighed, dyeing drum was filled with water and 2% ammonia solution was added and left over night to soften the leather for the further dyeing process. Then the leather was rinsed with water to remove excess amount of ammonia, and the onion peel dye was added to the leather substrate. The dry weight of leather was measured to be 300g and 12% of its weight was used as the dye. For dye fixing, 3% formic acid was used. The leather was dried in air condition. The dye penetration was checked by cutting a small piece of leather. As a control, the leathers were dyed with 12% of Indigo and Madder with 2% of chemical mordants like calcium carbonate. The properties of onion peel dye extract were studied by some of the leather characteristics such as wet and dry rub fastness, light fastness, tensile strength, tear strength, and elongation at break. In addition to physical characterization, organoleptic properties such as dye uniformity and penetration, grain smoothness, and softness were assessed by four experienced tanners. The detailed procedure for neutralization, retanning, dyeing, and fatliquoring for the production of garment types of leather is tabulated in Table I.

Photographic images of the leather surface and cross section

Celestron microcapture Pro USB digital microscope was used to take the grain and flesh images of the leather samples. The microscope provided a clear view of the leather surface and cross section.

Measurement of reflectance of colored leather

L*, a*, and b* values for the dyed leathers' grain shade and flesh shade were obtained according to CIE (Commission Internationale de l'Eclairage) system using Milton Roy Color Mate HDS instrument. More negative value and more positive value of L* denotes darker shade and lighter shade of the surface color respectively. More negative and positive values of a* show greener and redder color, respectively. More negative values and more positive values of b* means bluer color and yellow color respectively. Tone obtained by onion peel dyeing was analysed by measuring the color coordinates value of the grain side of the experimental leathers.

Fastness property of colored leather

According to IULTCS Standard EN 20 105: A02 and ISO 20433, the leather samples were analysed for color fastness to to-and-fro rubbing (wet/dry) cycles and crocking respectively. Fastness properties of the leather can be determined by the color transferred from dyed leather to cotton on damp or dry stage. ISO 105: A02 and ISO 105: A03 test protocols assess the samples' degree of washdown and cross-staining after 215 and 524 cycles, respectively. The grey scale ranges from 5 to 1 indicating no shade to severe shade change. Dyed leathers were tested for light fastness after conditioning, according to IS 6191e1971 (LF: 4) by using Xenon tester (Indian Standards, 1971). Samples were tested by using the standard method ISO 105-A02, and the crust leathers were exposed to xenon arc light under the prescribed conditions for 20 h along with the dyed blue wool standards. The amount of fading was then measured by comparison to the original color and a rating between 0 and 8 was awarded. Zero denotes extremely poor color fastness whilst a rating of eight is deemed not to have altered from the original and thus credited as being highly lightfast.

Dye leaching analysis

The 5 grams of small pieces of dyed leather were dipped into 50ml of water and kept under shaking for 5 days at 100 rpm. The amount

Table I

Post-tanning recipe for the production of garment type of leather.

Raw Materials: Chrome tanned leather (goat) – Shaved thickness -1 mm

Process	Chemical Name	% Offered[#]	Duration (drumming time)	Remarks
Neutralization	Water Sodium formate Sodium bicarbonate	100 1 1	(3 × 15 min) + 50 min	Cross-section pH 5.0±0.2 Drain/Wash/Drain
Retanning	Relugan RE Phenolic syntan Melamine syntan Biopolymer	3 5 5 2	20 min 60 min	
Fatliquoring	Synthetic fatliquor Semi synthetic fatliquor	3 3	(3 × 15 min) + 120	
Fixing	Formic acid	2	(3 × 5 min) + 60 min	Check exhaustion /Drain
Next Day: – Setting/ Hooking/ Stacking/Toggling/Trimming				
Wet Back	Wetting agent/ Ammonia	1.5*	60 min	Drain
Dyeing	Natural dye	12*	45 min	Check penetration
Fixing	Formic acid	3*	(2 × 5 min) + 60 min	Check exhaustion /Drain

Next day: - Hooking/ Stacking/Toggling/Trimming/Buffing.
[#]Offer of chemicals based on the shaved weight
*Offer of chemicals based on the crust weight

of dye leached from the leather into the water was estimated by collecting samples at different intervals. The 100 µL of the samples were collected at each interval, diluted with water, and the UV measurement was done to quantity the dye concentration.

Dye exhaustion studies

UV- Visible spectrophotometer was used to analyse the percentage of dye exhaustion by the leather matrix, and the absorbance value of the different dye solutions after dyeing was measured individually. Percent Exhaustion was calculated using the equation below. [12]

$$\%\ Exhaustion = \frac{Co - Cs}{Co}\ x\,100$$

where C_0 is the initial concentration of the dye used for dyeing and C_s final concentration of dye in the bath.

Organoleptic Properties

The organoleptic properties like dye penetration, uniformity, grain smoothness, softness, and overall appearance were visually examined and rated. The three experienced tanners rated the leather on a scale point of 0-10 to determine the organoleptic properties. The higher points indicate the better property of leather.

Result and Discussion

The natural dye was extracted from onion peel waste and used as a dyeing agent in the leather dyeing process. The extracted dye was characterized for its functionality and thermal stability to understand the possibility of using this extracted dye in the leather dyeing process. The dyed leathers were characterized for their dyeing properties as well as physical properties. The dye extracted from onion peel showed good dyeing behaviour towards leathers with enhanced antibacterial properties. The environmental problems associated with dyeing auxiliaries were avoided because no metallic mordants were used. To reduce the cost of dye making, the onion peel dye was extracted from the onion peel waste by a simple aqueous based extraction process. The extracted dye was characterized by Particle size analysis (Malvern Instrument), FT-IR, and TGA. After carefully evaluating dye properties, the natural dyes were used in the leather dyeing process to make good quality dyed leather. Variations in the process parameters like Dye Percentage, duration, and pH greatly influenced the dyeing process. Hence optimization of dyeing processing was done on the percentage dye exhaustion using different variables. Finally, the leather dyed with natural dye showed a uniform-colored surface on the cross section with improved fastness properties in the presence of vegetable tannins and phenolic syntans. Hence the onion peel waste will be a good alternative for synthetic dye in the leather dyeing process.

Fourier Transformation Infrared Spectroscopy (FTIR) Analysis

FTIR analysis of onion skin dye powder revealed the presence of different functional groups viz. hydroxyl group (Hydrogen bonded–OH- stretch), carbonyl group (C=O) and C=C stretch, quinone or conjugated ketone, methylene–CH- stretch, aldehyde group and organic sulphates, OH – bend (Figure 2). Onion skin dye powder contains C=O (carbonyl) and C=C (stretch) that function as chromophores. The hydroxyl (-OH) groups added depth to onion skin dye by acting as auxochromes. The FT-IR spectra of onion peel dye extract showed the presence of characteristic peaks at 3280 cm^{-1}, 2921 cm^{-1}, 1727 cm^{-1}, 1601 cm^{-1}, 1420 cm^{-1}, 1320 cm^{-1}, 1086 cm^{-1} and 893 cm^{-1} representing OH stretch, CH stretch, carbonyl and aldehyde group, quinone or conjugated ketone, organic sulphates, -OH bond, -C-C- stretch and ether, -CH=H- a stretch of total phenolics and flavonoids. The highest peak of the functional group was hydroxyl groups at 3280 cm^{-1}, methylene at 2921 cm^{-1}, carboxyl, and aldehyde group at 1727 cm^{-1}, and OH group of polyphenols at 1320 cm^{-1}. Thus, the peak at 3280 cm^{-1}, 1320 cm^{-1}, 1363 cm^{-1}, confirmed the presence of hydroxy groups (Auxochrome groups) of pelargonidin from onion peel dye which can be suitable for leather dyeing applications. Based on the reported literature [13] Bands at 3303 cm^{-1} and 3182 cm-1 were due to the –OH groups of pelargonidin. The band at 2932 cm^{-1}

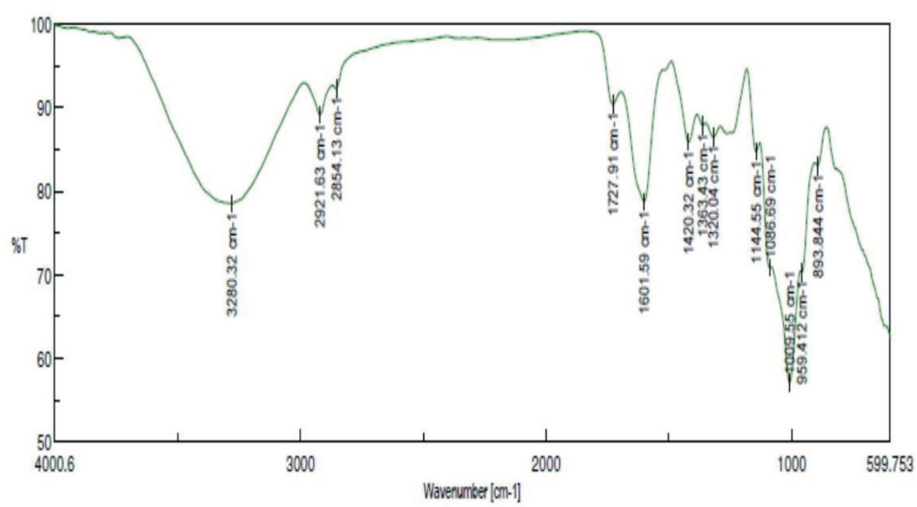


Figure 2. FTIR spectrum of onion peel dye powder.

indicated C-H stretching of the benzene ring. The bands at 1620 cm^{-1} and 1487 cm^{-1} were indicative of benzene –C=O and aromatic C=C, respectively. The band at 1349 cm^{-1} was due to a C-H bend. The bands present at 1160 cm^{-1}, 1079 cm^{-1} and 1023 cm^{-1} represented aromatic C-H in plane bend. Para di-substituted benzene was represented by the band at 838 cm^{-1}. The FTIR spectra comparison between the onion peel dye and pure pelargonidin undeniably establishes that the onion peel dye predominantly consists of pelargonidin.

Thermal stability of onion peel dye

The thermal behaviour of onion peel extract was studied by the TGA analysis at a range of 20°–200°C. The thermal decomposition analysis was conducted to detect mass change/loss of samples to temperature (Figure 3). The dye decomposing at the high-temperature profile shows a fall in the curve, indicating a sample mass loss. The TGA curve shows the two-stage dye degradation at 92.68°C and the other at 200°C. In the first stage (20°–92°C), a gradual decrease in the percentage mass of about 60% weight loss was observed. In this case, water molecules may evaporate and dye molecules may decompose. At the second stage (92°-200°C), the weight changes were minimized, and the little weight loss observed was likely related to the degradation of Pelargonidin and other phenolic compounds. At the end of the TGA analysis (at 200°C), the residual mass was about 2%. Such deep degradation indicates the complete degradation of the dye at a high temperature, but the result shows that the extracted onion peel dye was stable up to 90°C. Further, the stability of onion peel dye solution was also analysed by subjecting the solution to various temperature from 20° to 90°C in Peltier system chamber (keeping other parameters constant) and the corresponding excitation spectra were recorded and shown in Figure 3b. The maximum excitation peak demonstrates that onion peel dye does not discern any shift in maximum excitation which indicated the stabilisation of dye at the temperature range from 30°-90°C. Hence, the thermal stability of the onion peel dye solution makes it optimal for leather dyeing applications.

Particle size of the onion peel dye

The hydrodynamic diameter or particle size of onion peel dye was measured using DLS measurements. From Figure 4, the onion peel dye's particle size distribution (hydrodynamic diameter) showed an average diameter of 377± 5 nm. The average pore size diameter of goat leather ranges from 200 to 2000nm. Due to its smaller size, Pelargonidin can penetrate uniformly into leather pores, resulting in a uniform penetration of dyes. As per the literature reported by Tamil Selvi et al.,[14] Mohammed et al.,[15] and C. Kurinjimalar et al.,[16] the reported natural plant dye of Bixa Orellana, Mekmeko and Madder Root dye extract, respectively showed good dye penetration in the leather substrate due to its smaller particle size. Hence the optimal particle size obtained for onion peel dye facilitates the uniform distribution of dyes on the grain and flesh side of the leather. As part of the DLS measurement, the zeta potential of the dye molecules was

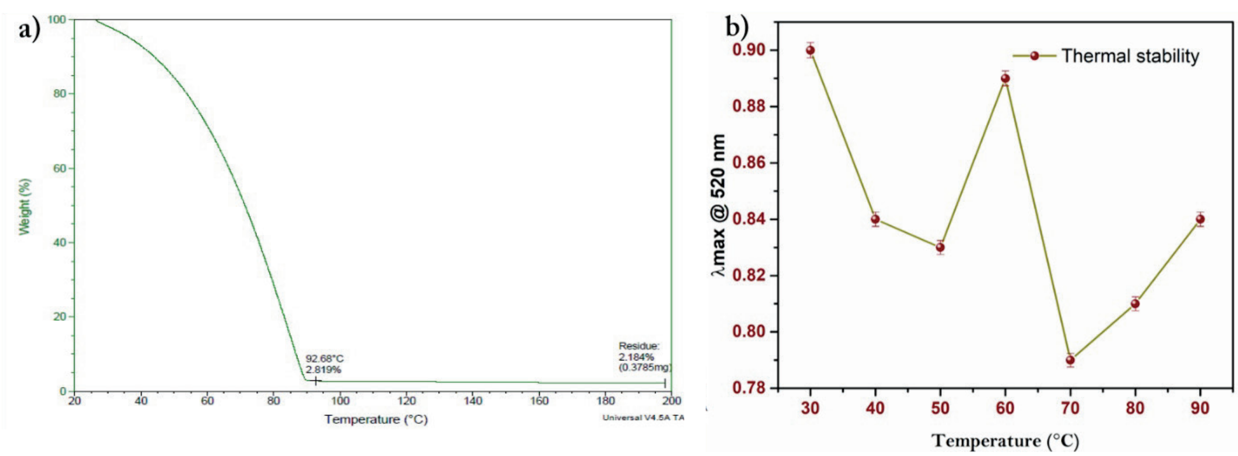


Figure 3. a) TGA of onion peel dye powder, **b)** change in the maximum absorbance of onion peel dye solution at different temperatures.

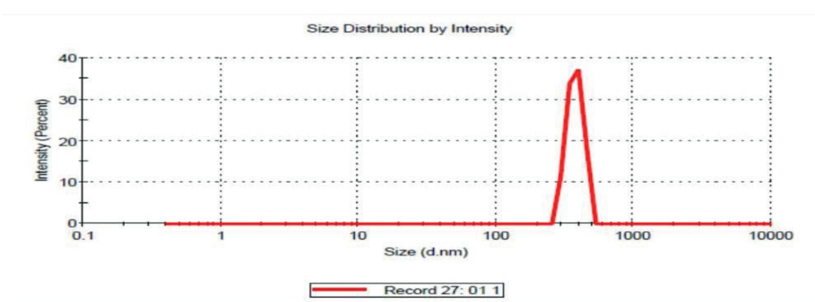


Figure 4. Particle Size Analysis of onion peel dye powder.

analyzed and found to be -32± 2 mV. The negative zeta potential of the dye molecules represents the presence of more flavonoids, and this will be favorable for dyeing chrome tanned leather.

Anti-bacterial activity

Different strains were used for performing the anti-bacterial activity in extracted dye by agar well diffusion method. A small amount of onion peel powder was taken in plates where cultures were treated in the nutrient agar medium and observed for the clear zone in the plate. Figure 5 shows antimicrobial property against the *E. coli* strain and B. *subtilis*. The zone of Inhibition in *E. coli* was measured to be 9 mm and 11 mm for B. *subtilis*. From Figure 5 it was found that onion peel dye showed antimicrobial properties against *E. coli* strain and B. *subtilis*. Major flavonoids like *Quercetin* present in the onion peel extract act as antimicrobial agents by disrupting cytoplasmic membranes and inhibiting nucleic acid biosynthesis. The antioxidant capacity promotes cell lysis. Similarly, the antimicrobial properties of control and experimental leathers were analyzed and shown in Figure 6. Furthermore, this test indicates that onion peel dye treated leathers showed better antimicrobial properties as compared to other natural dyes.

Natural dyeing with mordants

Mordants give affinity to dye and produce different colors and improve the dye fastness. Three types of mordants were used for the natural dyeing process: metals, tannins and oils. Amongst, tannins as natural dyes will produce yellow, brown, grey, and black colors. Not only that, but tannins were also used as retanning agents and it helps to improve dye affinity. Hence, this work used vegetable tannins and phenolic syntans to improve penetration of natural dyes. A scheme of the proposed interactions of onion peel dye with the leather substrate through hydrogen bonding with the help of vegetable tannins as

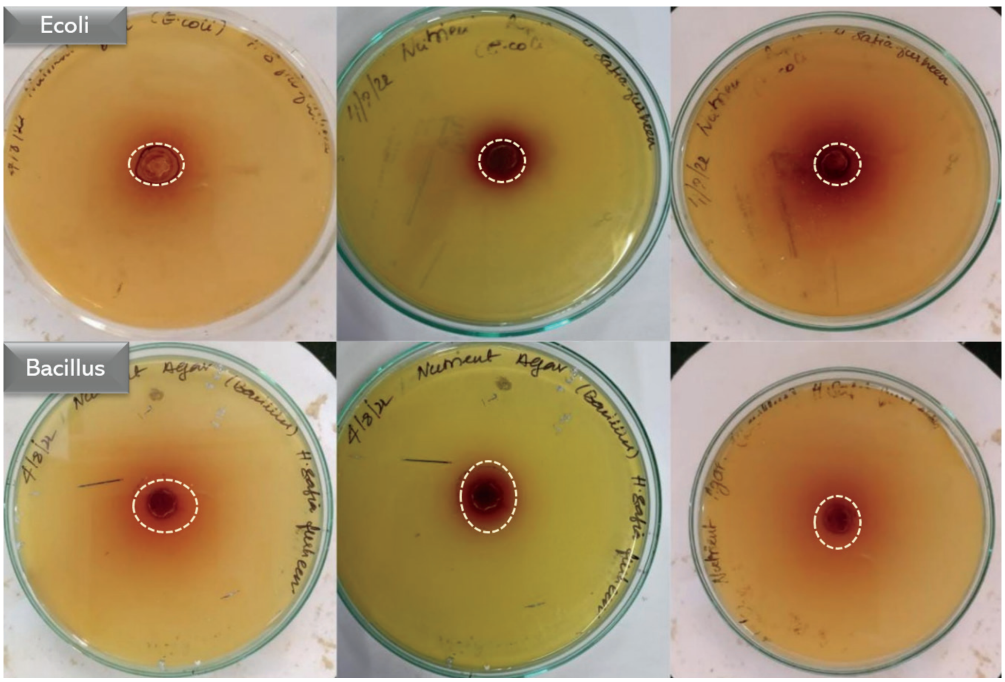


Figure 5. Zone of Inhibition in *Escherichia* species and *Bacillus* species

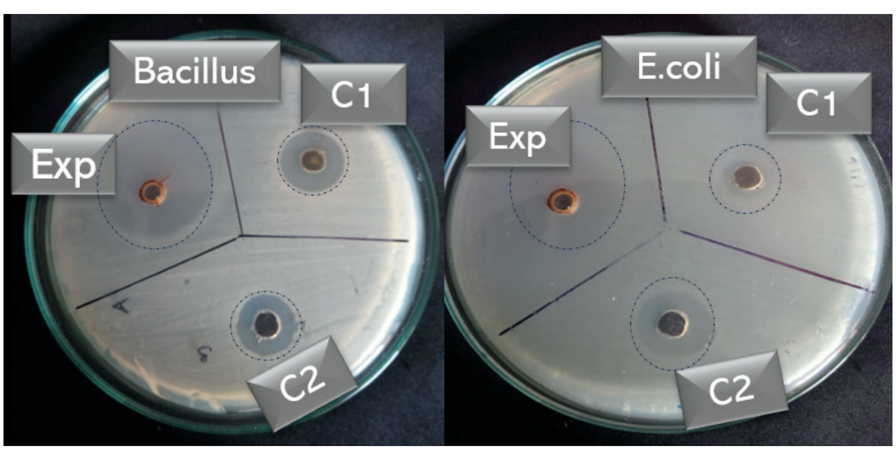
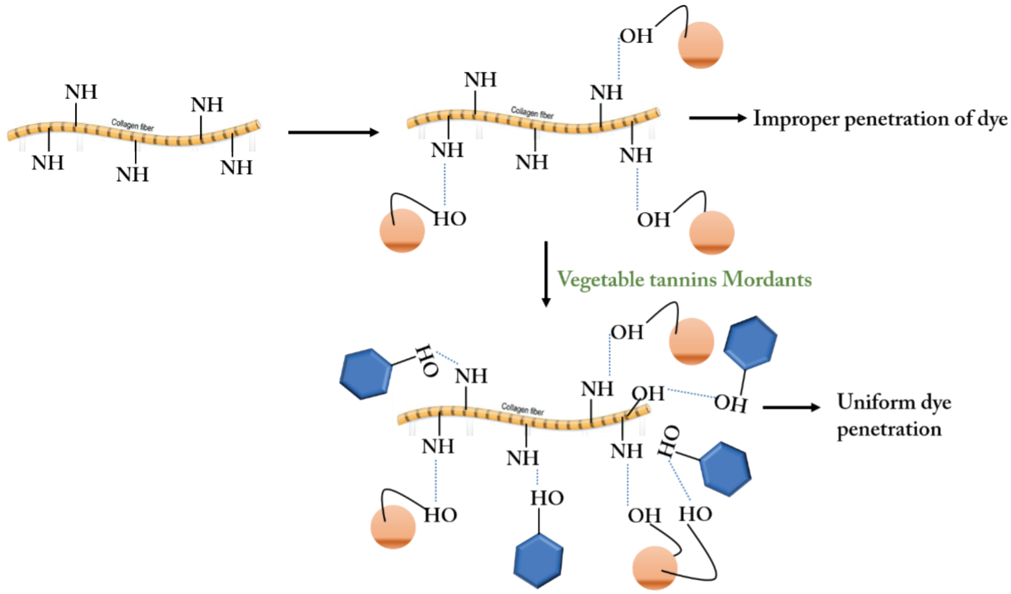


Figure 6. Zone of Inhibition in control (C1- Madder and C2- Indigo) and experimental (Exp- Onion Peel dye) leather against *Escherichia* species and *Bacillus* species



Scheme 1. Proposed scheme for the interaction of onion peel dye in the presence of vegetable tannin as a mordant.

mordant was given in Scheme 1. The presence of vegetable tannins enhances the dye penetration by multiple hydrogen bonding in the dye molecules and between the dye and leather matrix.

Dyed leathers were made by using the procedure given in Table I. The vegetable tannin (GS Powder) and phenolic syntan were used during the dyeing process, and their effect on dyeing is shown in Table II. Table II shows that the dye alone does not properly penetrate inside the leather matrix. But addition of GS powder after the addition of dye showed good penetration and improved dye exhaustion. Further addition of the phenolic syntan of 4% increases the dye exhaustion with a darker shade on the leather surface. Hence, without metal mordant, the dye was uniformly penetrated and fixed on the surface.

Optimisation of leather dyeing process using onion peel extract

To optimise the maximum percentage of dye offered for dyeing application, the dye concentration varied from 2- 24%. Amongst the percentage offered, 12-24% showed uniform penetration and surface dye fixation with a high hue on the leather surface. The percentage of dye exhaustion with respect to the different percentages of dyes (Figure 7a) were studied and showed that the 12% dye showed maximum dye uptake by the leather matrix. Lower dye percentages of 2-6 also showed high exhaustion but a very lighter shade on the leather surface. This may be due to the easy absorption of low percentage of dye into the leather matrix. Therefore, 12% was optimized for further experimental trials. Similarly, the pH of the crust leather was varied from 4- 6 by using an ammonia solution. The dye's high fixation and uniform penetration were observed at pH 6 compared to all pH. For proper dyeing, the duration of the dyeing process is also important. Hence the duration of the dyeing process varied from 10 minutes to 120 minutes, and the dye exhaustion results (Figure 7b) reveal that the duration of 60 minutes showed uniform penetration and surface fixation with high exhaustion. A shorter duration indicates the

Table II

Dyeing process mordanting with GS Powder and Phenolic syntan

Trials	Dye exhaustion	Observation	L	a*	b*	Colour swatch
Dye	62%	No dye penetration	46	-4	47	
Dye+GS Powder(2%)	88%	Dye penetration and surface fixed with acid	67	-5	65	
Dye+GS(2%) + Phenolic syntan (4%)	95%	Dye penetration and surface fixed with acid	63	-5	45	

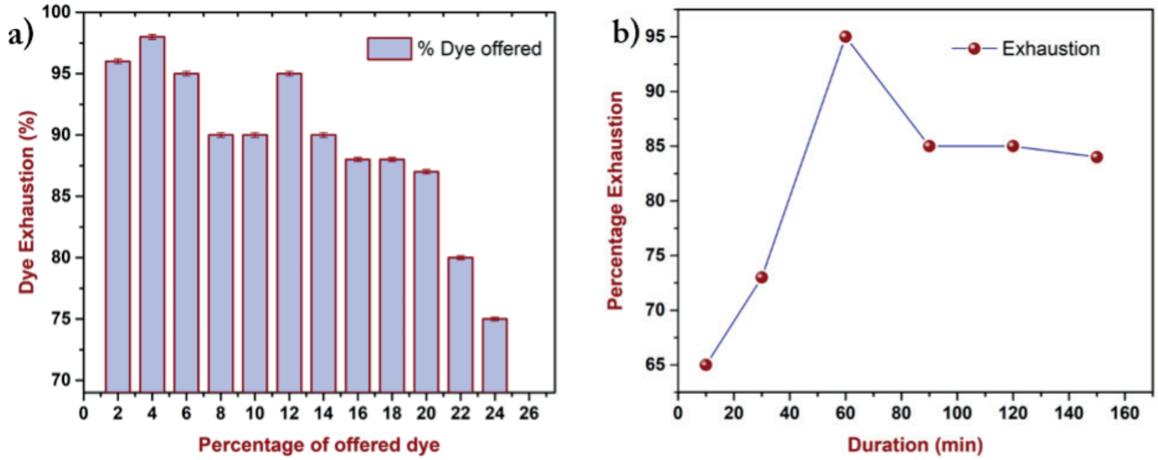


Figure 7. a) percentage exhaustion dye for a different percentage of dye and **b)** represents the percentage of dye exhaustion for different duration.

improper penetration of dye due to the less contact time between dye and leather. Similarly, the long duration of the dyeing process leads to some patches on the grain side of the leather. Hence the duration of 60 minutes dyeing process was optimised for good dyeing characteristics.

The grain and flesh sides of the leather sample are shown in Figure 8a and 8b, respectively. The photographic image of the dyed leather confirmed the surface fixation and uniform penetration of the dyes. Uniform color characteristics were obtained on both grain and flesh due to the appropriate particle size of onion peel dye, consistent with the obtained result from the particle size analyzer. Quercetin provides leather with a green hue. The higher the percentage of quercetin, the stronger the color of the leather. To confirm the uniform color on grain and flesh, the reflectance measurement of the dyed leather was analysed, and the graph is shown in Figure 8c. Similarly, the color strength (K/S) of the dyed leather was also analysed and shown in Figure 8d. The minimum reflectance encounters the maximum absorption of the dye, as compared to grain the flesh side does not show much difference in the color value or strength. Hence, using onion peel dye will give better and uniform dyeing on both leather surfaces.

Color coordinates measurement of dyed leathers

To further investigate the variation in surface color the color coordinates measurement was monitored and shown in the Table III. The onion peel dye showed higher in green tone color strength value due to the uniform surface fixation of the dye. Lightness

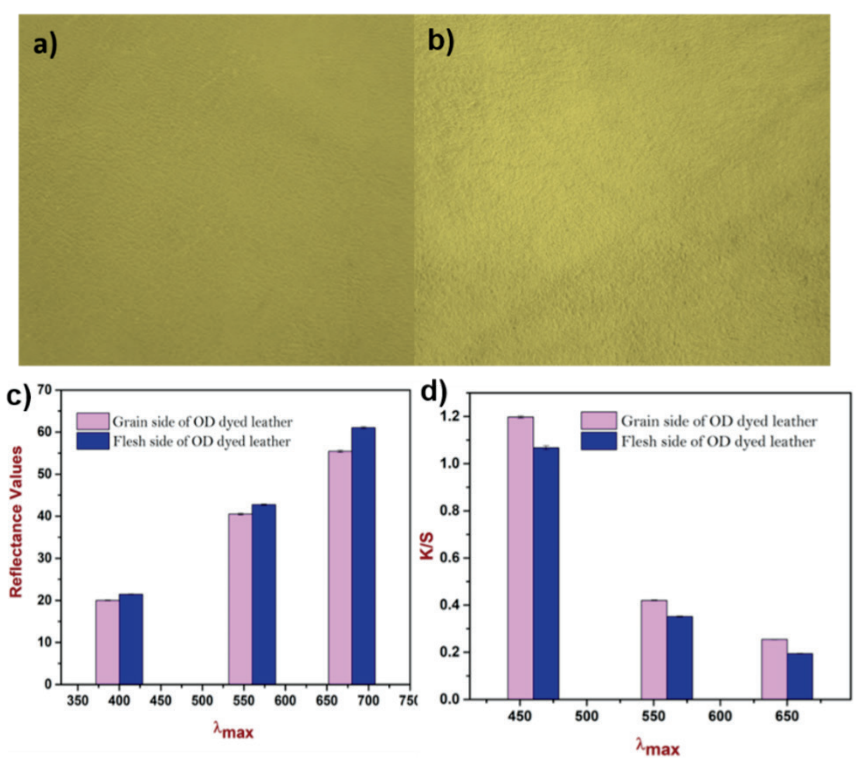


Figure 8. a) Grain side image of the leather dyed by onion peel, **b)** Flesh side image of the leather dyed by onion peel, **c)** represents the reflectance, and **d)** K/S value of the dyed leather.

Table III
Color coordinates of the dyed leather

Sample name	L	a*	b*	C	h
Onion peel dyed leather (Grain)	70.658	0.691	22.320	22.331	88.191
Onion peel dyed leather (Flesh)	69.109	-1.087	22.296	22.322	92.826

value indicates the darker shade of the color of the leather. L values obtained for both grain and flesh side of onion peel dyed leathers indicate the dark shade on both sides of the leather. Even surface and cross section tone has been obtained for leathers dyed with onion peel. Due to the smaller particle size the experimental dye showed uniform penetration which was confirmed by cross section of leather and surface color of leather. More OH groups in dye molecules of onion peel will interact with the leather substrate through hydrogen bonding.

Color Fastness measurement

The fastness properties were analysed for the dyed leather to determine the type of bond between dye molecules and leather substrates. Weaker the dye bonds with the leather, the dye can easily reverse from the leather substrate and show poor fastness against external environmental conditions. Table IV shows that the rubbing fastness of the experimental leathers was found to be better than control leathers. The presence of calcium carbonate in control leathers may lead to more dye bleaching as compared to experimental leathers. The applied onion peel dye may protect the leather from the photo-aging process due to its antioxidant activity and ability to protect against UV irradiation, like light resistance. Fastness against sweat in contact with different materials was also analysed and results divulge that the grey scale rating was above 4. This indicates that the better binding of onion peel dye improved the leather dye's fastness against physical disturbance, light and different substrates. The grey scale rating shows less color change in all leather material, and it is due to the strong binding of dye towards the leather.

The strength properties of the dyed leather

The addition of vegetable tannins as mordant during the dyeing process will change the strength property of leather, so the physical strength of leather was analyzed for dye with mordant and without mordant and presented in Table V. The physical strength properties like Tensile strength, Tear strength, and Percent Elongation at break for the leather treated with onion dye extract were comparable to the standard norms. The addition of vegetable tanning as a mordant for dyeing leather with onion peel extract resulted in improved strength properties and did not harm collagen fiber levels during the dyeing process. Hence the strength measurement confirms that the onion peel dye can be used as a dyeing agent without negatively impacting the bulk properties of the dyed leather.

Table IV
Color fastness properties of the onion peel dye treated leather

Color fastness to rubbing	**Experimental Leathers**	**Control Leathers**	
	Color change values of onion peel dyed leather	**Color change values of leather dyed by Indigo**	**Color change values of leather dyed by Madder**
Dry 150 rubs	4/5	4	4
Wet 50 rubs	4/5	3/4	3/4
Light Fastness	6	4	4
Cellulose acetate	4/5	4	4
Bleached cotton	4	3/4	3/4
Spun nylon	4	3/4	3/4
Spun polyester	4	4	4
Spun acrylic	4	4	4
Worsted spun wool	4	4	4

Table V

Strength properties of the Onion peel dyed leather.

Sample	Tensile strength (kg/cm_2) (Average value)	% Elongation at break (Average value)	Tear strength (kg/cm) (Average value)
Onion peel dye treated leather with mordant	24.0±3	66.59±5	93.49±1
Onion peel dye treated leather without mordant	23.1±2	59.21±3	88.75±2
ISO standard norms	Upper- Min.15	-	Upper Min.-40
	ISO 3376/ IUP 6 / SATRA TM 43	ISO 3376/ IUP 6 / SATRA TM 43	ISO 3377 Method 1/ IUP 40 /SATRA TM 30

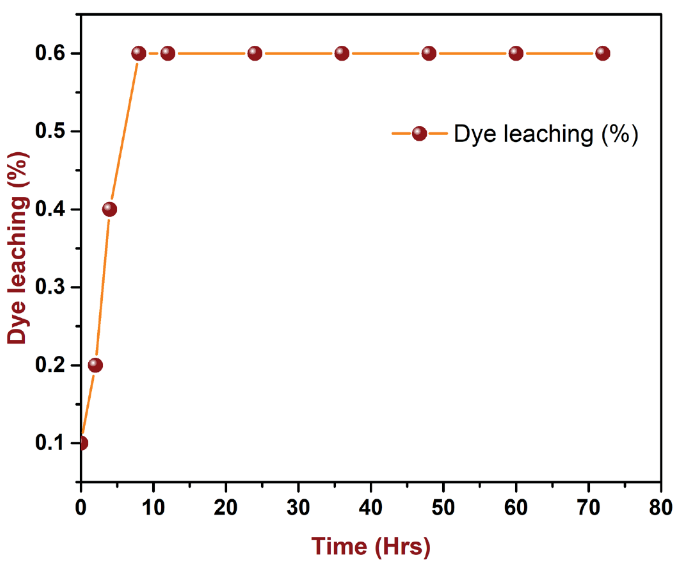


Figure 9. Dye leaching of onion peel dye treated leather.

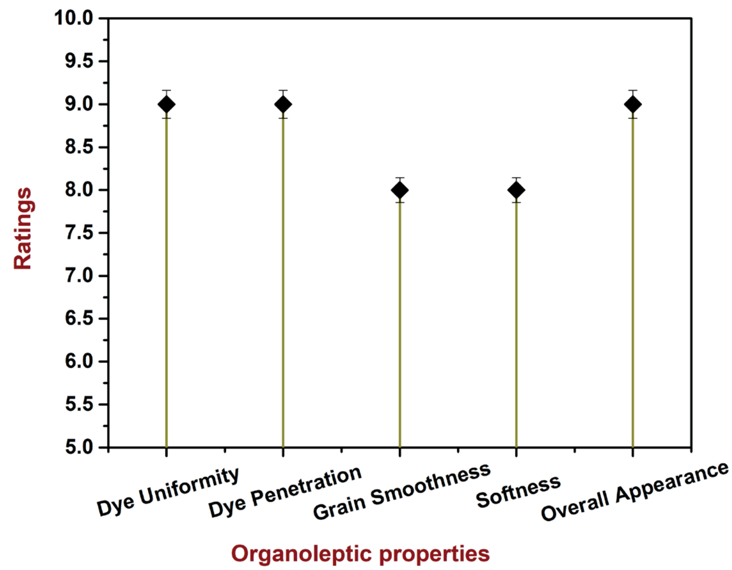


Figure 10. Organoleptic properties of onion peel dyed leather.

Dye Leaching Analysis

A small piece of leather was immersed in a known volume of the water for a week. It did not leach out any color and remains the same. This may be due to the strong binding of the onion peel dye compound to the leather material. Henceforth, *Pelargonidin* particle from onion peel dye has bonded strongly to the collagen fiber matrix of the leather.[17] The dye compound has fixed vigorously to the leather without any fixative agents and only the presence of commercial post-tanning agents. Herein, the lower amount of leached dye indicates good interaction and well penetration of the dye molecules inside the leather matrix (Figure 9).

Organoleptic properties measurement

Through standard hand and visual evaluation techniques, three experienced tanners evaluated the organoleptic properties of onion peel dye-treated leather on a scale of 1-10 based on dye uniformity, dye penetration, grain smoothness, and softness, and each property was rated on a scale of 1-10 and an average of three values are presented in Figure 10. Higher points indicate better properties. Figure 10 confirms that the onion peel dye-treated leathers showed good dyeing as well as physical properties. Dye uniformity and dye penetration rating clearly indicate that the auxiliary effect by commercial syntan and fatliquors greatly supports dye adhesion and penetration. The overall appearance of the leather also indicates that leather dyed with onion extract showed a good appearance in making various articles.

Conclusions

An organic dye was obtained from the onion peel waste by a simple water-based extraction method. The chemical characteristics of the onion peel dye were analysed for functionality, particle size, and thermal behaviour. The extracted dye showed a 377 nm average particle size with negative surface potential. FTIR Analysis confirmed that the autochrome groups (four hydroxy groups) of pelargonidin from onion peel dye were majorly present, and they were found suitable for leather dyeing applications. During the dyeing process, dye concentration, dye bath pH, and process duration were optimized based on dye exhaustion studies. There is an increase in dye exhaustion even though natural dye powder is offered up to 12%. The dye exhaustion results showed that the optimum pH and time to dye the leather were 6 and 30 minutes, respectively. Even though dye alone showed good penetration into the leather, the dye in combination with commercial syntan and fatliquors showed better dye richness on the leather surface and uniform distribution on cross-section. The leather dyed under the optimal process conditions above exhibited good rub and light fastness properties. Based on the major components of the dye molecules, it was concluded that the quercetin gives the leather a green hue. The dyeing studies concluded that newly extracted onion peel dyes are a potential eco-dyeing agent for leather processing and can be used successfully without chemical mordants.

Statements & Declarations

Author Contributions

Sathya Ramalingam and Swethashree Rajendran performed the experiments. Ambika Kumaresan performed the testing. G C Jaikumar and Alagumuthu Tamilselvi designed the experiments and corrected the manuscript.

Conflicts of Interest

All authors declare that there is no conflict of interest.

Competing Interest

The authors have no relevant financial or non-financial interests to disclose.

Acknowledgements and Funding

The authors would like to thank CSIR-CLRI under MLP 18 for financial support. The authors would like to thank Centre for Analysis, Testing, Evaluation& Reporting Services (CATERS), CLRI for the testing facility. CSIR-CLRI communication number: 1840.

References

1. Yusuf, M., Shahid, M., Khan, M. I., Khan, S. A., Khan, M. A., & Mohammad, F. Dyeing studies with henna and madder: A research on effect of tin (II) chloride mordant. *Journal of Saudi Chemical Society*, **19**(1), 64-72, 2015.
2. Saxena, S., & Raja, A. S. M. Natural dyes: sources, chemistry, application, and sustainability issues. Roadmap to sustainable textiles and clothing: eco-friendly raw materials, technologies, and processing methods, 37-80, 2014.
3. Bhuyan, R., & Saikia, C. N. Isolation of color components from native dye-bearing plants in northeastern India. *Bioresource technology*, **96**(3), 363-372, 2005.
4. Bechtold, T., Mussak, R., Mahmud-Ali, A., Ganglberger, E., & Geissler, S. Extraction of natural dyes for textile dyeing from colored plant wastes released from the food and beverage industry. *Journal of the Science of Food and Agriculture*, ***86***(2), 233-242, 2006.
5. Sivakumar, V., Vijayeeswarri, J., Swaminathan, G., Ultrasound assisted enhancement in natural dye extraction from beetroot for industrial applications and natural dyeing of leather. *Ultrasonics Sonochemistry* **16**, 782-789, 2009.
6. Pervaiz, S., Mughal, T. A., & Khan, F. Z. Leather dyeing with plants dyes: A review. *J. Biodiv. Environ. Sci,* **9**, 455-464, 2016.
7. Zubairu, A., & Mshelia, Y. M. Effects of selected mordants on the application of natural dye from onion skin (Allium cepa). *Science and Technology*, **5**(2), 26-32, 2015.
8. Ayfer Çalı, Gökçen Yuvalı Çelik and Hikmet Katırcıoglu Antimicrobial effect of natural dyes on some pathogenic bacteria, *African Journal of Biotechnology*, **8** (2), 291-293, 2009.
9. Smith A., Johnson B., & White C.Antibacterial Properties of Allium cepa Extract. *Journal of Natural Products*, 45(**3**), 237-250, 2020.
10. Brown E., & Lee S. Mechanisms of Antibacterial Action of Allium cepa Extract. *Journal of Applied Microbiology*, 32(**2**), 89-97, 2018.
11. Perez, C., Pauli, M., Bazerque, P.,An antibiotic assay by the agar well diffusion method. *Acta Biologiae Medicine Experimentalis* **5**, 113-115,1990.
12. Broadbent, A. D. Basic principles of textile coloration, Bradford, UK: *Society of Dyers and Colorists,* 132, 332-357, 2001.
13. Moumita, R., Rajat, P., Abhay, S, C., Pelargonidin-PLGA nanoparticles: Fabrication, characterization, and their effect on streptozotocin-induced diabetic rats. *Indian Journal of Experimental Biology*, **55**, 819-830, 2017.
14. Selvi, A. T., Aravindhan, R., Madhan, B., & Rao, J. R. Studies on the application of natural dye extract from Bixa orellana seeds for dyeing and finishing of leather. *Industrial crops and products*, **43**, 84-86, 2013.
15. Mohammed, S. A., Panda, R. C., Madhan, B., & Demessie, B. A. Rumex abyssinicus (mekmeko) extract as cleaner approach for dyeing in product manufacture: Optimization and modeling studies. *Asia-Pacific Journal of Chemical Engineering*, ***13***(2), 2165., 2018.
16. Kurinjimalar, C., Jayakumar, G. C., Selvi, A. T., Venba, R., Jawhar, M., & Kanth, S. V. Biocolorant for Leather Dyeing Applications: An Eco-benign Evaluation of Natural Coloring Agent. *JALCA* **116**(9), 322-331, 2021.
17. Ozan Deveoglu, A Review on Onion Skin, a Natural Dye Source. Journal of Textiles, Coloration and Polymer Science, *J. Text. Color. Polym. Sci.*, **19**, 2, 307-319.

Research on Innovative Design Methods of Intangible Cultural Heritage in Leather Products: A Case Study of Miao Cross-Stitch Patterns in Guizhou, China

by

Han Xu,[1] Han Chen,[2] Biyu Peng[1,3,4] and Luming Yang[1,3,4*]

[1] *College of Biomass Science and Engineering, Sichuan University,* Chengdu 610065, China

[2] *School of International Education, Zhejiang Sci-Tech University*, Hangzhou 310018, China

[3] *National Engineering Research Center of Clean Technology in Leather Industry, Sichuan University*, Chengdu 610065, China

[4] *Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Sichuan University*, Chengdu 610065, China

Abstract

Intangible cultural heritage is an important symbol of a nation's historical and cultural achievements, containing rich connotations and high artistic value. Leather products, as a significant component of modern fashion, have a wide range of market demand. To address the issues of traditional patterns in intangible cultural heritage not matching modern aesthetics and lacking application scenarios, this study takes leather products as carriers and proposes an innovative design paradigm for traditional clothing patterns. We chose the Miao cross-stitch patterns of Guizhou, China, as a case study. Analyzed their subject connotations, common structures and features. Using split grammar and shape grammar, the patterns are deconstructed and reassembled to obtain foundational innovative patterns. The Mean-shift clustering algorithm was applied to extract the classic colors of Miao cross-stitch patterns. Based on fractal theory and computer algorithms, a novel pattern model for Miao cross-stitch was proposed, incorporating representative patterns and colors to complete pattern designs. Finally, the feasibility of the proposed approach was validated through the practical design of leather fashion accessories on the Style 3D platform. This study aims to provide methodological references for the modernization and innovation of intangible cultural heritage, as well as the diverse integration of leather products design.

1 Introduction

Guizhou Miao cross-stitch is a traditional folk craft and one of China's intangible cultural heritages. Miao cross-stitch patterns hold unique ethnic spirit and rich cultural connotations. Cross-stitch involves picking out regular patterns with colored silk threads on a hessian backing. It is popular for its intricate and delicate features.[1] However, with the rapid development of society and changes in the general public's aesthetic preferences, the Miao cross-stitch craft is gradually facing challenges due to its low production efficiency and strong subjectivity.[2] Traditional Miao cross-stitch patterns struggle to meet the current aesthetic demands. It has become a major challenge to make Miao cross-stitch retain the essence of national culture while meeting modern aesthetic standards and adapting to the needs of social development.

Compared to other materials such as textiles and ceramics, leather can better meet consumers' demands due to its excellent elasticity, durability and malleability. It has gradually become an essential component in the modern fashion industry and is widely applied in clothing, footwear, household goods and other fields. Applying innovative Miao cross-stitch patterns to leather products is beneficial for enhancing the added value and cultural attributes of leather goods, further expanding their market share. Therefore, exploring innovative design methods for Miao cross-stitch patterns in leather products not only holds significant cultural value but also carries practical significance for the inheritance and innovation of traditions.

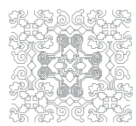
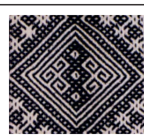
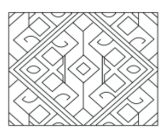
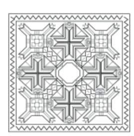
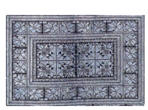
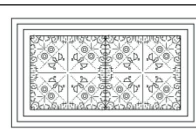
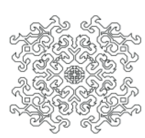
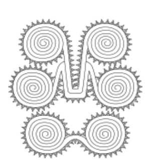
In 2003, United Nations Educational, Scientific and Cultural Organization promulgated the "Convention for the Safeguarding of the Intangible Cultural Heritage", which explicitly recognizes that intangible cultural heritage is an important factor in defining cultural characteristics, stimulating creativity and safeguarding cultural diversity. It plays an irreplaceable role in promoting mutual tolerance and harmony among different cultures.[3] Consequently, the importance of safeguarding intangible cultural heritage has been increasingly recognized internationally, leading to extensive academic attention and practical exploration.[4-8] Among them, the integration and development of intangible cultural heritage with industries such as fashion and design have emerged as new trends in practice and research.[9-13] The rapid development of science and technology has provided new possibilities for artistic expressions. Thanks to mathematical models, big data statistics and computer algorithms, valuable research outcomes have emerged in the related fields. Ding XJ started from the structure and characteristics of "She" ethnic clothing, summarizing the pattern features and spatial distribution characteristics. Combining the Bag of Visual Words model and K-means clustering algorithm, they proposed an automatic classification and redesign model for "She" ethnic

*Corresponding author email: ylmll1982@126.com

Manuscript received September 15, 2023, accepted November 9, 2023.

Table I

Classification and extraction of Miao cross-stitch patterns.

Category	Name	Actual Image	Line Drawing Extraction	Meaning
Plant motifs	Eight-petal flower			Local wild plants and flowers have auspicious meanings of warding off evil and bringing good luck.
	Pomegranate flower pattern			It signifies the pursuit of good things.
	Peony flower pattern			The local people believe that peony flower comes from the place where their ancestors once lived, expressing their nostalgia for their homeland.
Animal motifs	Fishbone pattern			The fishbone flower is one of the most representative basic motifs of the region.
	Butterfly pattern			The Miao people believe that butterflies evolved from maple wood and hatched the ancestors of humans.
	Frog pattern			Frogs, known for their strong survival and reproductive abilities, are considered symbols of gods by the Miao people.
Geometric motifs	Labyrinth pattern			They carry the meaning of wealth and good fortune.
	Rhombus pattern			Representing resilience, with the connotation of warding off evil and bringing good luck.
	cross-hatched pattern			They carry the meaning of joy and auspiciousness.
Other motifs	Silver hat flower pattern			Similar to the flowers on a silver hat, they mainly represent blessings and prayers for safety.
	Snowflake pattern			Based on the snowflake, this pattern has a neat and rigorous design, depicting the weather.
	Jar bottom flower pattern			It expresses a longing for a better life.

clothing.[14] Wang TX focused on textures and used ResNet to establish an image recognition model for willow weaving textures. They also proposed a deep learning-based willow weaving texture design method based on deep convolutional generative adversarial networks.[15] Ding N addressed the complex pattern elements in Miao wax-resist dyeing, a non-material cultural heritage in Guizhou, China. They proposed an ethnic pattern redesign method based on improved shape grammar and optimization algorithms.[16] Ju F started from colors and used ancient embroidery patterns on Chinese traditional garments as their study subject. Based on K-means++ clustering and the Canny operator, they introduced an intelligent color and contour recognition method capable of accurately identifying colors and contours of intangible cultural heritage embroidery images.[17] Nevertheless, researchers have mostly focused on one specific aspect of structure, texture, element, color, etc. when exploring the content of innovative design. Few researchers have approached the subject from multiple angles and proposed a more comprehensive pattern innovation design system.

For this purpose, this study was carried out as follows: Taking the Miao cross-stitch patterns as an example, representative physical and pictorial materials were collected as research objects and cultural connotations behind them were excavated. Design factors were extracted using split grammar and shape grammar, then evolved into unit patterns. The Mean-shift clustering algorithm was applied to segment the color images and extract the pattern colors, forming the cross-stitch classic color factors. Leveraging the fractal characteristics of brocade patterns, the Julia fractal theory was integrated with brocade pattern design to build a model. This model integrated unit patterns and classic colors to create new patterns that blended fashion and ethnic aspirations. Practical leather accessories design experiments were conducted on Style 3D platform, where innovative patterns were applied to develop contemporary and stylish leather apparel. This study aims to apply Guizhou Miao cross-stitch patterns to modern leather products and propose a set of traditional pattern innovation design paradigms. While respecting and preserving traditional intangible cultural heritage, it actively explores innovation and inheritance, intending to offer methodological references for the development and innovative application of intangible cultural heritage patterns in leather products.

2 Research basis

2.1 Patterns motifs

Miao cross-stitch patterns are characterized by their strong ethnic and regional styles, showcasing exquisite craftsmanship, delicate stitching techniques and rich patterns. They are dominated by abstract geometric shapes, with elements drawn from the daily life and local natural environment of the Miao people. This reflects their reverence for ancestors, love for beautiful things and pursuit of a happy life. Miao cross-stitch pattern elements can be mainly categorized into four types: plant motifs, animal motifs, geometric motifs and other motifs.

Handmade embroidered products are an expression of personal emotions. People imbue them with meaning to convey their desires and present them to the world.[19] The categories of Miao cross-stitch patterns, commonly used elements and meanings are shown in Table I. The Miao people use plants in nature as inspiration for their creations, and common plant motifs include the eight-petal flower, soybean flowers, plum blossoms, peonies and pomegranate flowers. The frequent appearance of animal motifs highlights the Miao people's fondness for animals. Common animal motifs include fishbone, butterfly, bird, frog and ram head patterns. Geometric patterns, comprising various lines and curves forming regular or irregular geometric decorative designs, often feature square, triangular, rhombus, spiral and zigzag shapes. Other motifs include snowflake, coin, silver hat flowers, sun and Miao king seal patterns. The geometrization and exaggeration of cross-stitch patterns enhance their decorative qualities. Despite lacking formal artistic education, local artisans can capture the essence of objects with simplified outlines, which is the charm of folk art.

2.2 Pattern structure

In the composition of Chinese folk art and craftsmanship, emphasis is placed on symmetry and balance. Common composition forms of Miao cross-stitch include clustered flowers, corner flowers and border flowers. Clustered flowers are one of the common forms of cross-stitch pattern composition, with symmetry and circular spatial layout features. Clustered flowers patterns often use fixed frames like "X-shape," "Crisscross-shape" or "Double cross-shape" to serve as the framework for the design (Figure 1). Based on the structural foundation, decorative motifs are added layer by layer

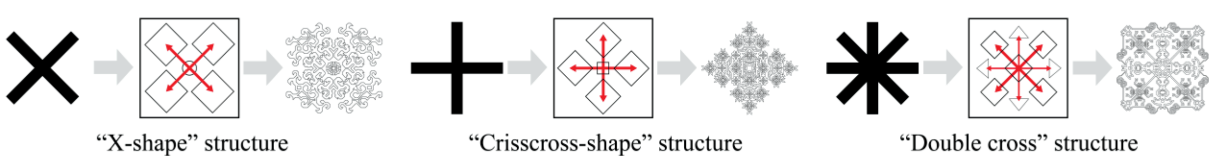


Figure 1. The three common structures of clustered flowers.

around the main body in the margins, with each layer having a different motif. Clustered flowers patterns occupy a relatively large area and are commonly found on the back or around the waist of Miao ethnic clothing. This expansion from the center to the outer layers transforms the pattern from points to surfaces, creating combinations.

Border flowers often appear on the edges of local Miao ethnic clothing, such as the edges of trousers, collars, sleeves and the edges of the waistbands. In cross-stitch, the border flower is mainly composed of bipartite continuity, which is repeated horizontally or vertically to form an infinite continuous pattern. Corner flowers are commonly used at the four corners of the pattern, emphasizing symmetry and balance. Corner flowers are often used in conjunction with clustered flowers to enrich the content of design. In Miao cross-stitch costumes, the clustered flower structure is usually located in the visual center and accounts for a large proportion, while border and corner flowers can complement clustered patterns in their variations. Therefore, this study focuses on exploring the structure of clustered patterns.

2.3 Pattern color

Cross-stitch patterns can be divided into two types based on color: "plain cross-stitch" and "colorful cross-stitch." In plain cross-stitch, the colors of the threads and the fabric are relatively simple, often using blue or black fabric with white threads. The juxtaposition of these plain colors creates a sense of tranquility and elegance.[20] Colorful cross-stitch requires higher craftsmanship from artisans. Artisans need to analyze the overall structure of the pattern first, then consider the use of colors in specific areas to showcase the spatial and layered aspects of the design. The Miao people seek vibrant aesthetics and incorporate their own feelings about colors, making the displayed colors in the patterns more unique. Miao cross-stitch is colorful and contrasting, with a strong local style.

3 Methods

3.1 Elemental derivation methods

3.1.1 Split grammar

Split grammars represent each non-terminal shape with a simple border shape.[21] Split Grammar breaks down graphic structures into individuals according to specific rules, showing their composition in detail and enabling the deconstruction of complex patterns.[22] The Miao cross-stitch pattern system is extensive, rich in hierarchy and diverse in designs. Split grammar is introduced into cross-stitch pattern design to subdivide and deconstruct the pattern, forming multi-level design elements and facilitating the redesign of pattern elements. This study adopts split grammar to decompose patterns and combines shape grammar to achieve the derivation of pattern elements. An example of split grammar to construct a cross-stitch pattern structure is shown in Figure 2. The initial shape was decomposed to obtain the center pattern X and the largest patterned structural unit of the outer circle F. The decomposition of the pattern unit F was continued and subdivided to obtain the minimal elements U, K. Besides, the decomposition rules were applied to the central pattern unit X, obtaining subdivided elements until they cannot be further decomposed. Multiple smallest elements and the final structure diagram were obtained, the elements obtained from the splitting process could be used in shape grammar for derivation.[23]

3.1.2 Shape grammar

Shape grammar was first introduced by George Stiny and James Gips.[24] It is a generative system that infers shapes through the application of substitution rules.[21] By executing corresponding operational rules, it preserves the original form while generating new forms. According to the definition of shape grammar, it can be represented as a function with four components:

$$SG = (S, L, R, I) \tag{1}$$

In the equation: S represents a finite set of shapes, $S = \{S_1, S_2, \cdots, S_t\}$ and S* represents the set of shapes derived from S through inference rules. L is a finite set of labels, $L = \{l_1, l_2, \cdots, l_n\}$ and $S \cap L = \emptyset$. R is a finite set of inference rules, $R = \{r_1, r_2, \cdots, r_p\}$. The form of an inference rule is $\lambda(S, L) \rightarrow \eta(S, L)$, where $\lambda(S, L)$ is the left-labeled shape for shape inference, $\eta(S, L)$ is the right-labeled shape for shape inference, $\lambda \subset (S \cup L)$, $\eta \subset (S \cup L)$, and η can be an empty set. I is the initial shape, $I = \{i_1, i_2, \cdots, i_u\}$ and $I \subset (S \cup L)$.[25] The inference rules in shape grammar mainly include move, replace, add, delete, scale, copy, mirror, etc. and the attributes of these rules can be categorized as generative (Figure 3) and derivative (Figure 4).

3.2 Mean-shift color clustering algorithm

Color image segmentation is the basis of quantitative image color analysis.[26] Traditional manual color extraction methods are subjective, which is difficult to meet the demand for accurate and quantitative analysis. Mean-shift is a density-based statistical iterative algorithm with fast convergence and a simple process. It can

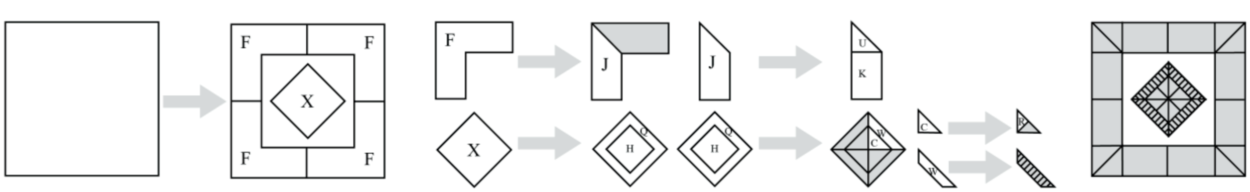


Figure 2. An example of split grammar to construct a cross-stitch pattern structure.

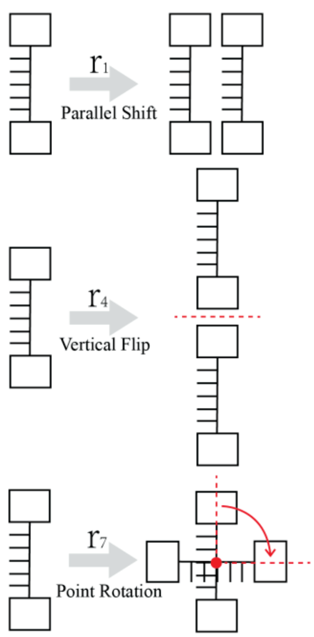


Figure 3. Generative rules.

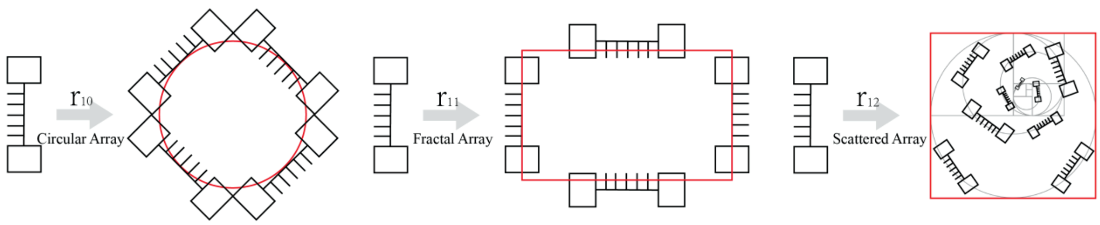


Figure 4. Derivative rules.

retain the main information of an image and is widely used in visual fields such as image computer processing. In this study, we employed the Mean-shift clustering algorithm for image segmentation and primary color extraction. Real-world images of cross-stitch patterns were captured using a digital camera. The Mean-shift clustering algorithm was applied to cluster and analyze the color pixels in the images, followed by extracting color cards for further use.

Assuming a bandwidth h as the drifting window, we calculate the sum of the offsets needed for the center point x_0 to move to the surrounding points x_i within the window. By taking the average of these offsets, we obtain the mean shift $M(x_0)$. Point x_0 is then drifted towards the direction of the average offset to obtain a new center point x_0'. We repeat the above steps until the algorithm converges. The mean shift $M(x_0)$ can be expressed as follows:

$$M(x_0) = \frac{1}{k} \sum_{x_i \in s_h} (x_0 - x_i) \qquad (2)$$

In the equation: s_h represents the high-dimensional spherical region centered at x_0 with a radius h. The number of points within the range of S is k and x_i is the set of points within s_h. By using equation (3), we can obtain the new center point:

$$x_0' = M(x_0) + x_0 \qquad (3)$$

Introducing the kernel function in mean shift, denoted as $m(x_0)$, allows us to transform low-dimensional inseparable data into high-dimensional separable data. The specific formula is as follows:

$$M(x_0) = \frac{\sum_{i=1}^{k} x_i g\left(\left\|\frac{x_0 - x_i}{h}\right\|^2\right)}{\sum_{i=1}^{k} g\left(\left\|\frac{x_0 - x_i}{h}\right\|^2\right)} - x_0 \qquad (4)$$

In the equation, the function g represents the negative derivative of the kernel function. In the aforementioned algorithm, the bandwidth h is a crucial parameter that affects the iterative results of the algorithm. Through experimentation and optimization, the optimal value of the bandwidth that yields the best segmentation effect is determined. Using the aforementioned segmentation algorithm with the optimized bandwidth h, the image is segmented, resulting in pattern segmentation with distinct colors.[27]

3.3 Fractal pattern design method

"Fractal" and "Fractal Theory" were discovered and proposed by Harvard University professor Mandelbrot. In general, we can regard a fractal as a mathematical set with characteristics of infinite subdivision and self-similarity, which means that it exhibits complex and intricate structures when zoomed in at any scale. Fractals have similar properties, information and functions both at local and global levels.[28] Julia fractals were introduced by French mathematician Caston Julia in 1919, they were extended from the theory of iteration of complex functions. Julia fractal connects various branches from its center, presenting an outward divergent effect and possesses rotational symmetry characteristics. Cross-stitch patterns have the characteristic of repetitive arrangement of unit patterns, the structure of cluster patterns, such as the "X-shaped," "Crisscross-shape," and "Double cross-shape" patterns, closely resembles the Julia fractal model. Therefore, incorporating the Julia fractal model in pattern design can efficiently and quickly create cross-stitch patterns that are rich in ethnic charm yet contemporary. Mathematical models are established in the complex domain, after computer processing, complex and futuristic Julia fractal patterns are generated.[29] The principle behind the creation of the Julia set graph involves considering an iterative process on the complex plane.[30]

$$z_{n+1} = z_n^2 + \mu \tag{5}$$

In this equation, $z = x + yi$, z is a complex function, where x and y are variables and i is the imaginary unit. Similarly, $\mu = p + qi$, where μ is a complex constant and both p and q are constants. By fixing the value of μ and performing iterative calculations, we can create a regular Julia fractal model. By adjusting the exponent, superimposition formula, algorithm, adding representative colors and rendering unit patterns, we can develop cross-stitch patterns that combine ethnic characteristics and a sense of fashion.

3.4 Design paradigm

This study delves into Miao cross-stitch patterns from three perspectives: color, structure and elements, proposes the design paradigm (Figure 5). Firstly, take photos and extract the physical object, then perform color segmentation on the image. Subsequently, we clustered the segmented pattern colors to identify the classic color factors of Miao cross-stitch. Multiple pattern colors were extracted, therefore secondary clustering of multiple sets of colors was required. Moving on to the element extraction process, we initiated by categorizing the themes and analyzing their cultural significance. Afterward, we extracted the pattern outlines and applied split grammar and shape grammar to evolve the patterns, resulting in innovative unit patterns that embody Miao ethnic characteristics. In the structure extraction, we commenced by isolating the pattern structure and assessing its compatibility with fractal models. Then, we established the initial model and made necessary parameter adjustments. The model incorporates classic color factors and innovative unit patterns, ultimately producing suitable fractal cross-stitch patterns. The patterns were rendered clearly and applied to modern leather fashion accessories, completing the design practice.

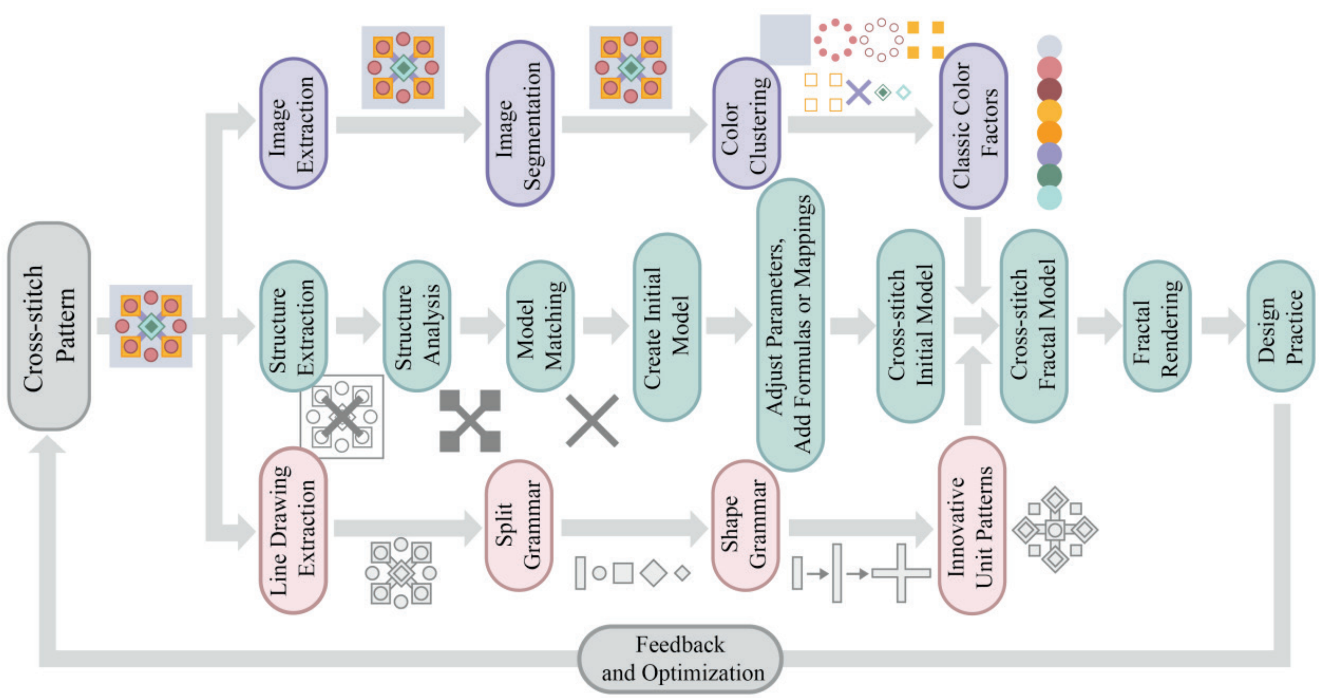


Figure 5. Design paradigm.

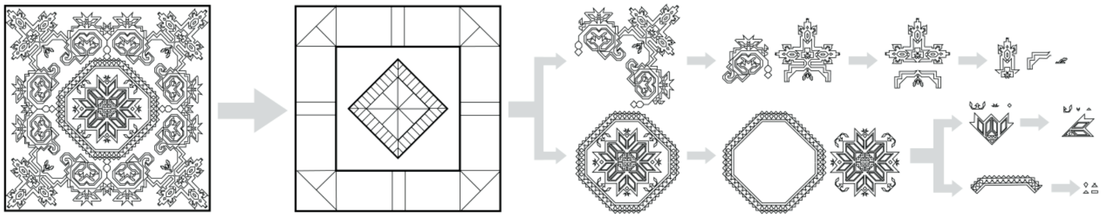


Figure 6. The structure of the eight-petal pomegranate flower pattern under the split grammar rule.

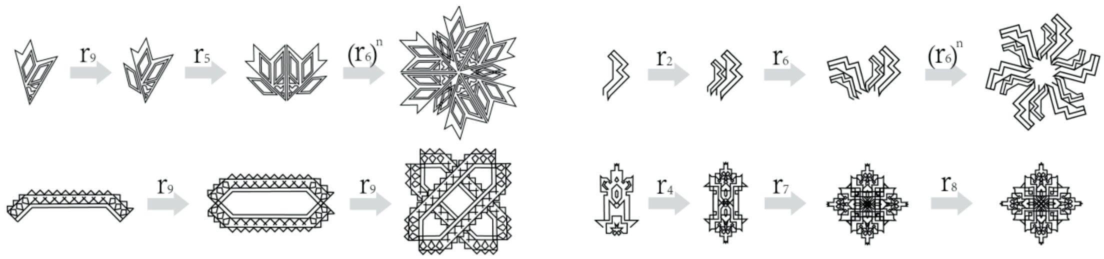


Figure 7. The innovative pattern units.

4 Application

4.1 Derivation of Miao cross-stitch element

Researchers extracted black and white outlines of cross-stitch patterns and applied the concept of split grammar for decomposition. We combined shape grammar to infer and derive decomposed pattern elements, resulting in new patterns with prototype characteristics. These new patterns can serve as novel basic pattern units. As an example, for structural analysis of cross-stitch patterns, the study focused on the eight-petal pomegranate flower pattern. This pattern was selected as the initial shape and used for structural analysis using splitting grammar (Figure 6).

By executing split grammar rules, the pattern was decomposed into a central eight-petal flower and an outer ring pomegranate flower. The outer circle pattern was repeatedly decomposed and then further analyzed until the pattern units could no longer be decomposed, obtaining multiple cross-stitch pattern elements. These split elements were subjected to inference and derivation using shape grammar, resulting in innovative unit patterns (Figure 7). Further utilizing shape grammar for combination and arrangement of the innovative unit patterns, produced more complete and innovative Miao cross-stitch patterns (Figure 8). The researchers completed several representative innovative pattern units, which could be applied and transformed as classic elements of Miao cross-stitch in subsequent fractal designs.

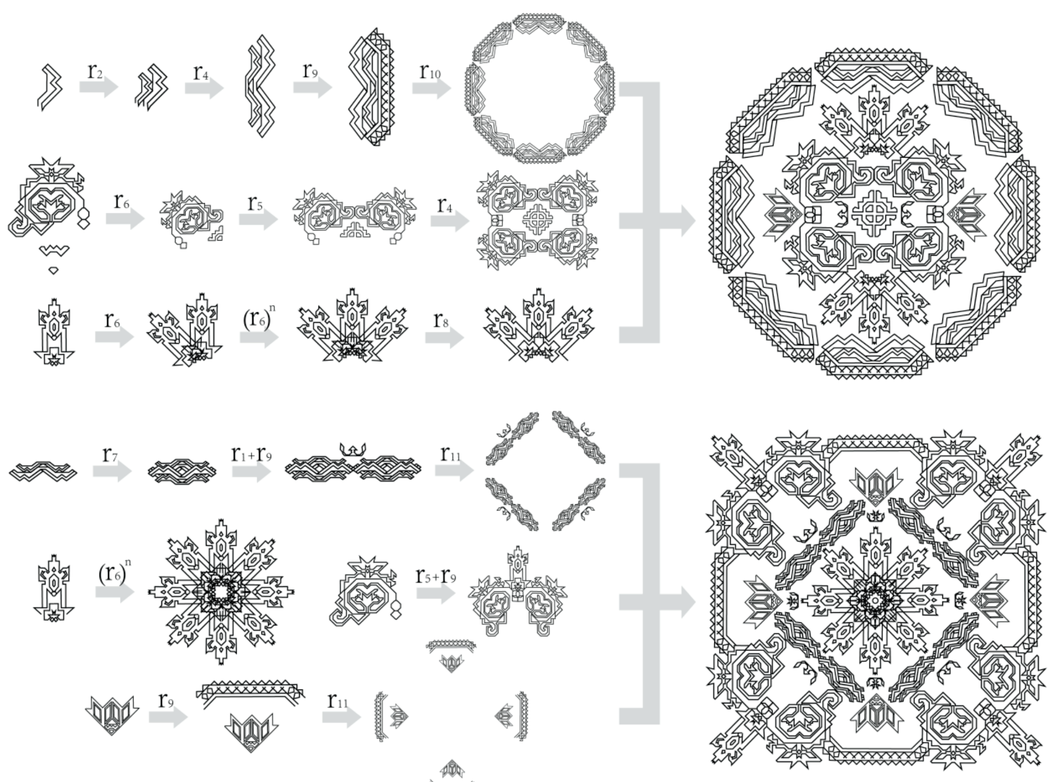


Figure 8. The combined effect of the innovative pattern units.

Figure 9. Nine sets of Miao cross-stitch patterns (the colored cross-stitch patterns are named Pattern 1 to Pattern 6 and the plain cross-stitch patterns are named Pattern 7 to Pattern 9).

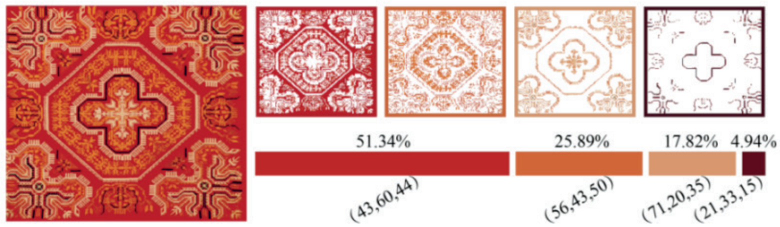


Figure 10. The color segmentation result of Pattern 1.

4.2 Color design of Miao cross-stitch

Color, as a medium of perception and a visual language, can intuitively reflect the character traits of different ethnic groups.[31] The combination of colors determines the visual effect presented in the local Miao cross-stitch. Researchers focused on two categories (plain cross-stitch and colored cross-stitch) to collect patterns. From the large collection of cross-stitch images, three sets of plain cross-stitch and six sets of colored cross-stitch were randomly selected (Figure 9). Taking colored cross-stitch pattern 1 as an example, the color segmentation of the image was carried out using the equations 2 to 4 (Figure 10).

Color segmentation and clustering extraction were applied to the nine sets of patterns using the same method. The extracted nine sets of colors were manually clustered again and the main colors and secondary colors were divided based on their proportion, serving as the classic color factors for Miao cross-stitch (Figure 11).

Four main colors and eight secondary colors were selected for the colored cross-stitch patterns, while two main colors and two secondary colors were selected for the plain cross-stitch patterns, as shown in Table II, with their corresponding RGB values indicated.

Figure 11. The Process of color extraction and selection.

Table II

Classic Pattern Colors and their RGB Values

Category	Main Color	(RGB Values)	Secondary Color	(RGB Values)
colored cross-stitch	black	(23, 21, 28)	light orange	(216, 184, 97)
			purple	(155, 72, 103)
	pink	(200, 164, 165)	blue	(27, 43, 87)
			orange	(199, 97, 51)
	red	(195, 36, 31)	dark red	(91, 22, 28)
			green	(47, 95, 70)
	white	(249, 246, 243)	khaki	(178, 138, 51)
			beige	(219, 205, 185)
plain cross-stitch	black	(23, 21, 28)	purplish grey	(135, 139, 154)
	grey	(201, 201, 202)	dark red	(91, 22, 28)

The selected colors will be further applied in fractal design as classic color factors for Miao cross-stitch patterns.

4.3 Miao cross-stitch pattern design

According to the layout of "X-shaped," "Crisscross-shape" and "Double cross-shape" structures in cross-stitch pattern, we modified the Symmetry Order index in the primary Julia fractal model in Ultra Fractal software version 6.04. We selected the symmetry order index of 4 for the primary model in the "X-shaped" structure design and adjusted the Rotation Angle to 45 degrees. By adding Inverse mapping, Newton formula and Aspect Ratio mapping, we obtained three different forms and effects of new models (Figure 12). On this basis, we can further superimpose new mappings or formulas to pursue more intricate and exquisite pattern effects. After completing the modification of the model to its color design, in the gradient adjustment window of the model to add the cross-stitch representative color factor, pattern elements obtained from the screening in the previous section, to obtain a complete fractal pattern.

When the symmetry order index was 4 and 8, the rotation angle was set to 0, we can also obtain the "Crisscross-shape" (Figure 13)

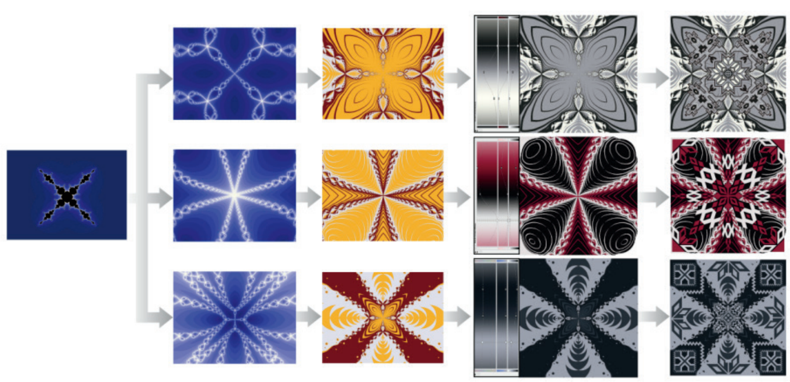


Figure 12. "X-shaped" structured fractal cross-stitch pattern

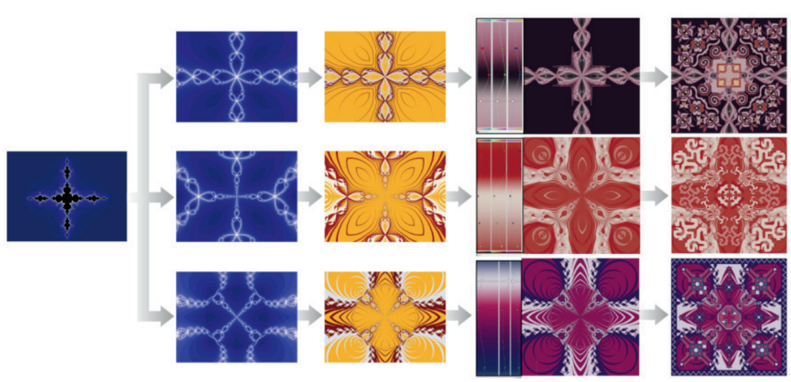


Figure 13. "Crisscross-shape" structured fractal cross-stitch pattern

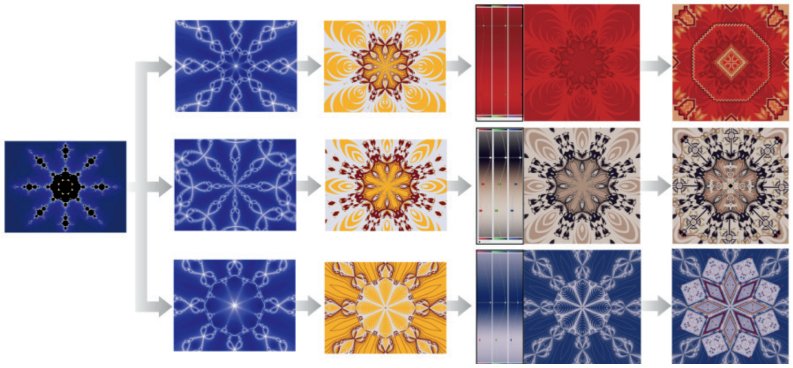


Figure 14. "Double cross-shape" structured fractal cross-stitch pattern

Figure 15. Nine sets of Miao ethnic fractal cross-stitch patterns

and "Double cross-shape" (Figure 14) structured fractal patterns through the above steps. Three structures generated nine sets of Miao ethnic fractal cross-stitch patterns (Figure 15). It can be observed that different index settings lead to vastly different fractal patterns and the variations in colors also result in distinct visual experiences.

4.4 The Application of cross-stitch Patterns in Leather Apparel

Clothing virtual display technology can simulate a more realistic wearing effect in advance. In recent years, 3D design software has been widely used in the fashion industry. 3D virtual clothing has many advantages, such as rapid adjustment of plates, reduction of resource waste, virtual try-on and show, which can help designers efficiently complete fashion designs. Currently, some mature clothing 3D software includes Optitex 3D from the United States, Lecra from France, Agms Industry 3D from Japan, V-Stitcher from Israel, Clo 3D from South Korea and Style 3D from China. To verify the feasibility of the fractal cross-stitch pattern design model, we chose Style 3D software for the design and 3D presentation of leather apparel and accessories.

Design practice was carried out on the Style 3D platform on a random set of 5 cross-stitch fractal patterns obtained (Figure 16). The front view of the leather apparel and leather accessory sets completed using the 5 sets of fractal cross-stitch patterns (Figure 17). Each set of patterns was applied to the design of a complete

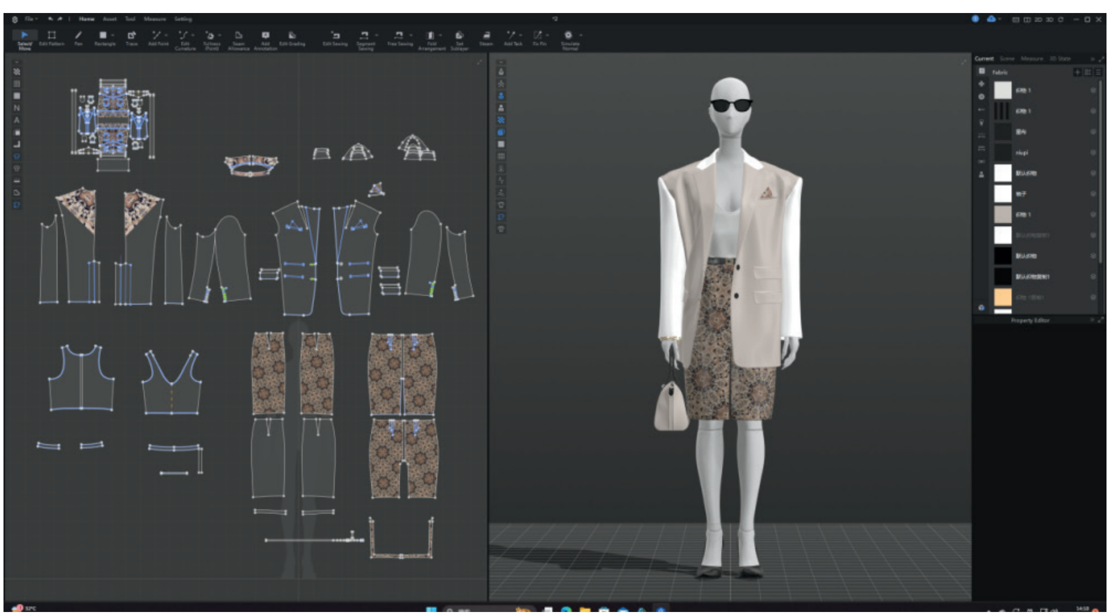


Figure 16. Style 3D modelling interface.

Figure 17. The front view of the leather apparel and accessory sets completed using the 5 sets of fractal cross-stitch patterns.

Figure 18. The overall design of the clothing's front and back, the display of the leather bag's detailed craftsmanship and the corresponding pattern

series of apparel and accessories. Apparel and accessory patterns were drawn using clothing CAD software and saved in ".dxf" file format before importing them into Style 3D software version V6.0.831 for clothing modeling. After importing the patterns into the 3D software, clothing and leather accessory pieces were placed and adjusted multiple times to ensure natural fall and stitching of the pieces in the simulation state. Any parts with unsatisfactory fit were promptly adjusted to maintain structural integrity. When presenting product effects in the field of leather product design and fashion design, realistic textures are usually required to be visualized.[32] Adding or adjusting the material and physical properties of the fabric can reproduce the realistic texture of leather materials. The designed fractal cross-stitch patterns were added to the samples to achieve the final presentation effect.

The overall front and back design of the leather garment, the details of the leather bag craftsmanship and the corresponding pattern effects are shown in combination (Figure 18). Researchers opted for modern and sleek straight-line silhouettes, presenting a minimalist and elegant style. For the color scheme, we chose to match the patterns with colors from the same color palette, creating a comfortable and classic visual experience. In craftsmanship, cross-stitch and printing techniques were selected to showcase rich three-dimensional effects and colorful decorative effects.

5 Conclusions

The protection and inheritance of intangible cultural heritage are crucial for maintaining cultural diversity and ensuring cultural sustainability. Miao cross-stitch, as an important intangible cultural heritage in China, showcases high cultural identity and artistic value. This study analyzed the thematic elements and representative motifs of Miao cross-stitch, as well as the color characteristics and pattern structure rules. By integrating split grammar, shape grammar and pattern evolution, precise pattern colors are extracted using clustering algorithms. Based on Julia fractal model and computer algorithms, a traditional pattern innovation design paradigm was proposed. Furthermore, the researchers have completed a series of five sets of leather apparel designs based on the generated innovative patterns. The results demonstrated that combining intangible cultural heritage cross-stitch craftsmanship with leather product design can not only preserve Guizhou's folk culture but also better meet consumers' personalized demands. The aim of this study was to support the dynamic inheritance of local excellent intangible cultural heritage, promote the transformation of economic benefits in leather product design, provide theoretical reference and methodological guidance for innovative design with intangible cultural heritage in leather products.

Acknowledgment

This work was financially supported by the Humanities and Social Science Project of Ministry of Education, China (21YJC850013).

References

1. Zhang, Y., He, Y.; Analysis on the modeling and technology of cross embroidery pattern in the women's upper outer garment of Miao nationality in Huaxi, Guizhou province. *Journal of Silk*. **55**, 82-87, 2018. doi: 10.3969/j.issn.1001-7003.2018.08.014.
2. Lee, J., Yi, J., Kim, S.; Cultural Heritage Design Element Labeling System with Gamification. *IEEE Access*. **8**, 127700-127708, 2020. doi: 10.1109/ACCESS.2020.3008270.
3. Aikawa, N.; An Historical Overview of the Preparation of the UNESCO International Convention for the Safeguarding of the Intangible Cultural Heritage. *Museum Int*. **56**, 137-149, 2004. doi: 10.1111/j.1350-0775.2004.00468.x.
4. Tang, X., Xie, N.; Research on the evaluation of tourism development potential of tea intangible cultural heritage based on grey clustering. Grey Syst. **9**, 295-304. doi: 10.1108/GS-12-2018-0065.
5. Lombardo, V., Pizzo, A.,Damiano, R.; Safeguarding and Accessing Drama as Intangible Cultural Heritage. *Acm J Comput Cult He*. **9**, 1-26. doi: 10.1145/2812814.
6. Zhang, X., Xiang, H., Liu, R.; Spatial pattern and influencing factors of intangible cultural heritage of music in Xiangxi, central China. *Herit Sci*. **10**, 1-12,2022. doi: 10.1186/s40494-022-00672-y.
7. Robischon, M.; Nonhuman Animal Behavioral Phenomena Are Central to the Emerging Concept of Intangible Natural Heritage. *Soc Anim*. **27**, 628-645, 2019. doi: 10.1163/15685306-12341560.
8. Dang, Q., Luo, Z., Ouyang, C., Wang, L., Xie, M.; Intangible Cultural Heritage in China: A Visual Analysis of Research Hotspots, Frontiers, and Trends Using CiteSpace. *Sustainability-Basel*. **13**, 2021. doi: 10.3390/su13179865.
9. Lan, Y.; Digital Sustainability of Intangible Cultural Heritage: The Example of the "Wu Leno" Weaving Technique in Suzhou, China. *Sustainability-Basel*. **15**, 9803, 2023. doi: 10.3390/su15129803.
10. Hannewijk, B., Vinella, F., Khan, V., Lykourentzou, I ., Papangelis, K., Masthoff, J.; Capturing the City's Heritage On-the-Go: Design Requirements for Mobile Crowdsourced Cultural Heritage. *Sustainability-Basel*. **12**, 2429, 2020. doi: 10.3390/su12062429.
11. Li, J., Kim, K.; Kano-QFD-based analysis of the influence of user experience on the design of handicraft intangible cultural heritage apps. *Herit Sci*. **11**, 59, 2023. doi: 10.1186/s40494-023-00903-w.
12. Xiao, Y., Chen, J.; Research on Innovative Design of "Intangible Cultural Heritage" Bamboo Products. Annual International Conference on Social Science and Contemporary Humanity Development. 2019. doi: 10.2991/sschd-18.2019.14.
13. Xiao, H.; Optimized soft frame design of traditional printing and dyeing process in Xiangxi based on pattern mining and edge-driven scene understanding. *Soft Comput*. **26**, 12997-13008, 2022. doi: 10.1007/s00500-021-06201-6.
14. Ding, X., Zou, C., Chen, J., Zou, F.; Extraction and classification of She nationality clothing via visual features. *Text Res J*. **86**, 225-231, 2016. doi: 10.1177/0040517515609260.
15. Wang, T., Ma, Z., Yang, L.; Creativity and Sustainable Design of Wickerwork Handicraft Patterns Based on Artificial Intelligence. *Sustainability-Basel*. **15**, 1574, 2023. doi: 10.3390/su15021574.
16. Ding, N., Lv, J., Hu, L.; Research on national pattern reuse design and optimization method based on improved shape grammar. *Int. J Comput. Int. Sys*. **13**, 300-309, 2020. doi: 10.2991/ijcis.d.200310.003.
17. Ju, F., Wang, Q., Tan, Z., Li, Q.; Intelligent Recognition of Color and Contour from Ancient Chinese Embroidery Images. *Fibers Text East Eur*. **30**, 79-92, 2022. doi: 10.2478/ftee-2022-0026.
18. Xu, Xing., Liao, C.; Decorative art of Xiaohuamiao tippet in Guizhou. *Journal of Silk*. **53**, 52-56, 2016. doi: 10.3969/j.issn.1001-7003.2016.03.010.
19. Genet, E., Wegene, J., Gebrehiwot, G., Thanikaivelan, P.; Ethiopian Ankelba: An Attempt to Modernize the Cultural Leather Artifact. *JALCA*. **115**, 435-443, 2020.
20. Zhao, X., Ning, J.; Color Rules and Characteristics of Miao Costume Embroidery Patterns in Southeast Guizhou Province. **41**, 21-28, 2021. doi: 10.16454/j.cnki.issn.1001-0564.2021.01.004.

21. Zmugg, R., Thaller, W., Krispel, U., Edelsbrunner, J., Havemann, S., Fellner, D.; Procedural architecture using deformation-aware split grammars. *Visual Comput*. **30**, 1009-1019, 2014. doi: 10.1007/s00371-013-0912-3.
22. Zhang, W., Chen, Y., Zhou, C.; Analysis of Tuanke pattern in Tang dynasty brocade and its innovative design. *Journal of Silk*. **58**, 126-132, 2021. doi: 10.3969/j.issn.1001-7003.2021.09.019.
23. Wonka,P.,Wimmer,M.,Sillion,F.,Ribarsky,W.;*InstantArchitecture.* Acm T Graphic. **22**, 669-677. doi: 10.1145/882262.882324.
24. Stiny, G.; Introduction to shape and shape grammars. *Environ Plan B-Urban*. 7, 343-351, 1980. doi: 10.1068/b070343.
25. Sayed, Z., Ugail, H., Reeve, C., Palmer, 1., Purdy, J.; Parameterized Shape Grammar for Generating n-fold Islamic Geometric Motifs. 2015 International Conference on Cyberworlds. 79-85, 2015. doi: 10.1109/CW.2015.54.
26. Wu, G., Zhao, X., Luo, S., Shi, H.; Histological image segmentation using fast mean shift clustering method. *Biomed Eng Online*. **14**, 24, 2015. doi: 10.1186/s12938-015-0020-x.
27. Hu, Q., Zhang, N., Pan, R.; Interactive color replacement method for printed fabrics based on Mean-shift. **42**, 97-102, 2021. *Journal of Textile Research*. doi: 10.13475/j.fzxb.20201103806.
28. Driscoll, J.; Fractal Patterns as Fitness Criteria in Genetic Algorithms Applied as a Design Tool in Architecture. *Nexus Netw* J. **23**, 21-37, 2021. doi: 10.1007/s00004-020-00490-4.
29. Pentland, A.; Fractal-based description of natural scenes. *IEEE T Pattern Anal*. **6**, 661-674, 1984. doi: 10.1109/TPAMI.1984.4767591.
30. Jia, F., Zhang, Y.; Application of generalized Julia set graphics in clothing pattern design. *Journal of Textile Research*. **36**, 104-109, 2015. doi: 10.13475/j.fzxb.20140804806.
31. Zhang, N., Yang, O., Wang, J., Chen, Y., Zhang, J.; Extraction and Application of Design Elements of Miao Embroidery under Eye Movement Analysis. *Packaging Engineering*. **41**, 248-254, 2020. doi: 0.19554/j.cnki.1001-3563.2020.10.039.
32. Wang, W., Wang, W., Zhang, G., Yang, L., Peng, B.; Simulation of Realistic Fur Texture Based on Piece Element Synthesis. *JALCA*. **117,** 520-533, 2022.

Influence of Different Products on Wet Finishing for Leather Properties and Waste Generation

by
Laisa Grassi, Luísa Gonçalves, Vânia Queiroz, Mariliz Gutterres and Caroline Agustini
Laboratory for Leather and Environmental Studies (LACOURO), Chemical Engineering Department, Federal University of Rio Grande do Sul (UFRGS), Av. Luiz Englert s/nº, Porto Alegre-RS, Brazil, 90040-040

Abstract

Leather is widely used for various applications. The processing involves a series of steps in which chemical processes and mechanical operations are carried out, with the addition of a series of products. Among the performance and quality parameters of the leather produced are the chemical and physical properties. The quality of the leather and the product obtained is influenced by its processing and the products used. Several studies are found in the literature on the effect of processing on leather properties. The present study brings the results of the influence of different products used in retanning, dyeing and fatliquoring (wet finishing) on the final properties of the leather. Physical tests of resistance to tearing, cracking and distension of the grain, the functional groups present in its structure, the thermal stability by DSC and TGA tests, dye uptake rate percentage and the remaining concentration of dye in the solution were used to evaluate the influence of different products on leather properties. It was observed that the parameter that influenced the applied force and the distension of the grain of the leather was the type of retanning agent used; the greater resistance to distension was obtained by Tara retanned leathers. As for the degree of dye uptake rate and remaining concentration of dye in the effluent, they were not affected by the studied parameters and all hides showed similar dye uptake. Regarding tear resistance, the type of grease was the parameter that had a significant effect on leather, higher resistance values were observed for leather greased with Coripol. The novelty of the work is in measuring how different dyeing, retanning and greasing products influence the properties of the final product, which is an advance towards greater cost-benefit in the choice of products to be used in the process.

Introduction

Leather is a material that can be used for various purposes such as making bags, belts, clothes, shoes, furniture, automotive upholstery, among others. The physical, chemical and strength properties are required of leather products depending on their field of use and determine the quality of the product.[8,9, 14]

The quality of the materials obtained depends on the quality of the leather that is produced. Leather production consists of converting the hide, a putrescible organic material, into a stable and flexible material that resists attacks by decaying bacteria. For this, a wide range of chemical processes and mechanical operations are carried out, with the addition of a series of acid products, bases, salts, tanning agents, surfactants, fatliquors, dyes, retanning agents, auxiliary agents and other products.[1,5,11]

The tanning operations can be grouped into beamhouse stages, tanning, drying and lowering, wet finishing stages and finishing. The beamhouse operations prepare the skin for tanning by removing hair, meat and fat. The tanning stage is responsible for stabilizing the skin and making it imputrescible, being called leather. The finishing operations involve the processes of retanning, dyeing and fatliquoring.[5,8, 17]

The quality of leather and its physical-mechanical and visual properties are defined by the quality of processing and the combination of reagents used in these steps. In the literature, there are studies to improve the quality of leather produced and the influence of processes on leather properties. Some study the effect of reagents applied at specific stages, such as the use of different tanning agents,[13,18] fatliquoring agents,[9,17] retanning agents[6, 20] on the final properties of leather. Nalyanya and contributors, for example, studied the influence of the presence and absence of tanning, dyeing and fatliquoring on leather properties.[12] However, little is said about how the different reagents used in combination in the steps will interfere with the final qualities of the leather. The aim of this study was to investigate the influence of the use of different products during wet finishing on the final properties of the leather. Tests were conducted with different retanning agents, dyes and fatliquors based on a 2^k factorial design.

Experimental

The wet-blue leathers used were obtained from tannery factories located close to Porto Alegre and properly stored until use. All test pieces originate from the same wet-blue hide. The leather samples used in each experiment were 1.1 - 1.4 mm thick and were cut into square pieces measuring 5x5 cm. Each trial was performed in duplicate, totaling 16 test pieces.

*Corresponding author email: agustini@enq.ufrgs.br
Manuscript received October 25, 2023, accepted for publication November 19, 2023.

Characterization

The leathers were characterized before and after the dyeing process concerning the functional groups present in their structure and in terms of thermal stability. DSC and TGA measurements on leather samples were carried out in the temperature range of 30° to 600°C, at a heating rate of 10°C/min in a nitrogen flow. Measurements were made with a TA Instruments thermogravimetric analyzer, model SDT Q600. FTIR analysis was performed on a Perkin Elmer FT-IR Frontier spectrometer equipped with a universal total attenuated reflector (UATR) in the spectral range of 4000-400 cm^{-1}.

Experimental design

The study of the process variables was carried out according to an experimental design of the 2k integer factorial type to determine the effect of the parameters evaluated in the finishing step on the final properties of the leather. The parameters of the variables in the finishing process were made in two levels (Table I). For tanning, two different tannins were chosen, Acacia tannin, which is classified as condensed because it does not undergo hydrolysis and contains low amounts of carbohydrates and gallic acid, and the other retanning agent is of the hydrolyzable type, releasing gallic acid when hydrolyzed. For the fatliquoring, a fatliquor based on deodorized sulphited fish oil and one based on sulphonated synthetic oils were chosen.

The independent variables analyzed are presented in Table I. Through the analysis of variances ANOVA, the statistical significance was analyzed, significant differences were accepted when p value < 0.05 (Microsoft Excel 2010).

The samples were named according to the initials of the products used in each experiment in the planning, as shown in Table II below.

The formulation used for the process followed the steps: soaking, washing, deacidification, tanning, washing, dyeing, fatliquoring and fixing according to the standard formulation for leather production, according to the quantities described in Table III. To carry out the experiments, a Wagner shaker was used. Dyeing time, fatliquoring time, and other fixed factors were established in previous experiments.

Table I

Variable parameters and levels considered in the experimental design

Variables	Level	
	(-1)	(+1)
Retanning agent (A)	Acacia (Condensed)	Tara (hydrolyzable)
Dye (B)	Dark Blue 2S (anionic)	Sellaset Red H (anionic)
Fatliquoring (C)	Lipodermliker (Based on sulphited fish oil deodorized, sulfated natural oils and phospholipids)	Coripol DX (Anionic emulsion based on sulphonated synthetic oils)

Table II

Sample names in the experimental design

Sample	Retanning agent		Dye		Fatliquoring	
ABL	(-1)	Acacia	(-1)	Blue	(-1)	Lipodermlicker
TBL	(1)	Tara	(-1)	Blue	(-1)	Lipodermlicker
ARL	(-1)	Acacia	(1)	Red	(-1)	Lipodermlicker
TRL	(1)	Tara	(1)	Red	(-1)	Lipodermlicker
ABC	(-1)	Acacia	(-1)	Blue	(1)	Coripol
TBC	(1)	Tara	(-1)	Blue	(1)	Coripol
ARC	(-1)	Acacia	(1)	Red	(1)	Coripol
TRC	(1)	Tara	(1)	Red	(1)	Coripol

Table III

Executed formulation for post-tanning wet-blue to procedure with different finishing products

Step	Description		Time (min)	Remarks
	%	Added		
Soaking	500	Water	1440	Overnight then drain float
Washing	100	Water		
	0,5	Soap	15	Drain float
Neutralization	200	Water		
	1,5	HCOONa	10	
	0,5	$NaHCO_3$	40	Verify pH
Retanning	4	Tanigan HO	30	
	8	Acacia of Tara extract	60	Drain float
Washing	200	Water	15	Drain float
Dyeing	250	Water		
	4	Dyestuff powder	30	Drain float
Fatliquoring	4	Coripol or Lipodermlicker	60	Check dye concentration Check dye penetration
Fixation	200	Water		
	2	Formic acid	20	Drain float

To evaluate the influence of retanning, dye and fatliquor on the final characteristics of the leather, several parameters were taken into account. Efficiency was expressed in terms of the following response variables: Hydrothermal stability through the analysis of the DSC/TGA; functional groups present in the structure of the substance using the Fourier-transform infrared spectroscopy; dye penetration degree in the leather samples evaluated by means of cutting, analysis and measurement in the OLYMPUS SZX16 stereomicroscope; the amount of dye remaining in the effluent analyzed using a UV-visible spectrophotometer (PG Instruments, Model T80 UV-Vis), the concentration was calculated using the absorptivity obtained from calibration curves according to the Lambert-Beer law.

Mechanical properties

Physical-mechanical tests were carried out to determine the tear strength of leather using a double edged tear (NBR ISO 3377-2) in an Oswaldo Filizola Testing Machine, Model AME - 5kN and determination of the grain cracking and distention- Lastometer (ABNT NBR 11669). Tear strength (tear resistance) is the measure of how much the material can withstand the effects of a tear, that is, it measures the resistance of the leather to the growth of the cut under tension (measured in N/mm). The lowest recommended tear strength for chrome-tanned shoe leathers is 40 N/mm as for leather for garment, the minimum accepted resistance to tearing is 15 N/mm.[12,19] The lastometer is a physical test that shows the mechanical property of distension of the grain of leather, by applying a force perpendicular to it, until the specimen ruptures, measuring its distension at this moment. The recommended minimum values for cracking and grain rupture for superior leathers are 6.5 mm and 7.0 mm, respectively.[7,16] The results obtained in the physical-mechanical tests were evaluated through analysis of variance, at a 5% probability level.

Results and Discussion

Characterizations

Figure 1 presents the spectra of all samples and the main absorption bands and their respective attributions are explained in sequence. All spectra show the characteristic absorption peaks of the elongation vibration of the O-H bonding, that correspond to the symmetric stretching groups in the collagen present in the leather around 2950-3750,[4] the peak in the 1620-1640 region characteristic of the Amide I complex and C=O stretch also relates to Collagen, it is mainly derived from the nitrogen-containing protein components characteristic of leather. The various peaks around 1540 cm^{-1} are the symmetrical of the N–H bond and vibration C–N bond, called the amide; it is also present in all spectra.[10] Between 975 - 1170 cm^{-1} are found the bands attributed to the vibration mode of C=O stretching present in keratin.[15]

The hydrolyzable tannins are differentiated from the condensed ones by the presence of a peak in the region of 1800-1680 cm^{-1} attributed to the carbonyl stretching present only in the hydrolyzable tannins,

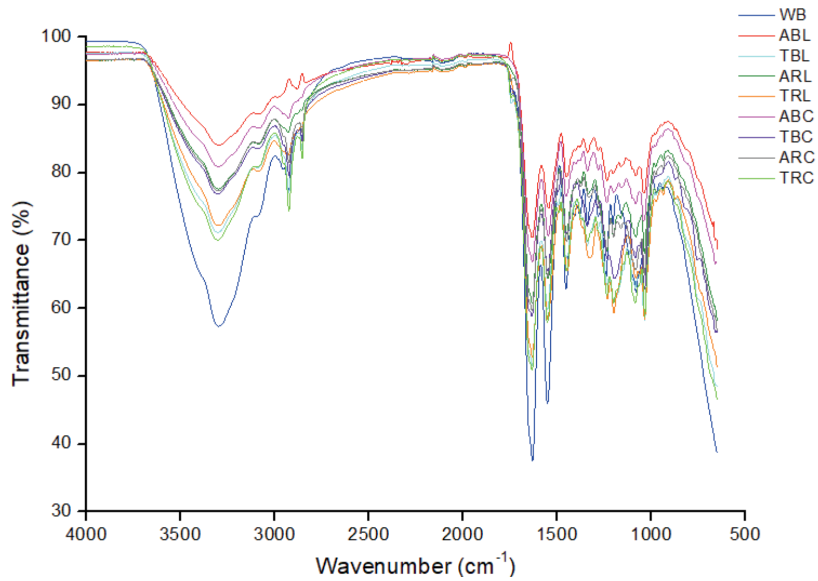


Figure 1. FTIR spectra for WB and ABL, TBL, ARL, TRL, ABC, TBC, ARC, and TRC after finishing

as the leather also presents a stretching in this region, one can only observe a greater intensity of the peaks for the samples that were retanning with Tara tannins (TRC, TBL, TRL and TBL).

The leathers finished with Acacia tannin also showed a similarity in the peaks of the wet-blue leather, because the wet blue leather has collagen while the leathers treated with Acacia tannin have polyphenolic groups. These two materials have hydroxyl (OH) and methyl (CH) groups.

The thermogravimetric analysis consists of continuously weighing a sample while it is dried in the presence of an inert gas. As the temperature increases, there is a loss of mass in the sample due to evaporation of water, decomposition or reaction of the sample. Figure 2 presents a TGA analysis of the wet blue sample and the leather samples after finishing with the different combinations established by the experimental design. As can be seen, all samples showed similar behavior, the mass losses of 25°-130°C are related to the water mass. The mass losses of 200°-500°C are related to denaturation and organic degradation of the samples. The wet blue leather showed a more pronounced initial mass loss than the other samples. Bajza, Z. and Vinkovic Vrcek (2001), showed that the use of fatliquoring improves the thermal resistance of leather. Which may explain the lower mass loss of the hides that went through the finishing process when compared to wet blue leather.

Leather properties

The mean values obtained in the tests to determine the grain cracking and distention are presented in Table IV. As can be seen, the flower distension values are above the minimum established by the standards for leather used in shoe uppers (6.5 mm). The finish practically did not interfere with the resistance to distension in the crack of the grain when compared to the wet blue leather. The values obtained for distention of the grain crack are similar to those found in literature.[3, 17]

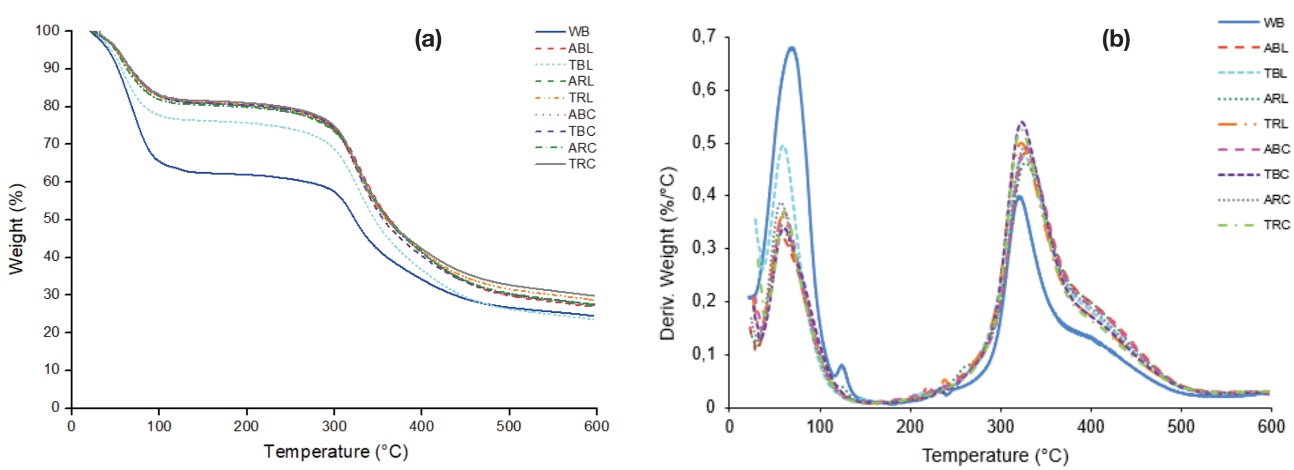


Figure 2. DTG (**A**) and TGA (**B**) for WB and ABL, TBL, ARL, TRL, ABC, TBC, ARC, and TRC after finishing

Table IV

Mean values of applied force (N) and distention at grain crack (mm) for samples of all leathers analyzed

Sample	Strength (N)	Distension (mm)
WB	10.54±1.3	9.74±0.7
ABL	17.1±3.4	10.1±0.4
TBL	20.7±7.6	10.8±0.6
ARL	14.1±2.7	9.6±0.3
TRL	20.2±3.6	9.9±0.6
ABC	10.0±0.6	9.0±0.4
TBC	16.2±0.8	9.7±0.1
ARC	13.6±2.2	8.9±0.1
TRC	19.7±1.3	10.8±0.3

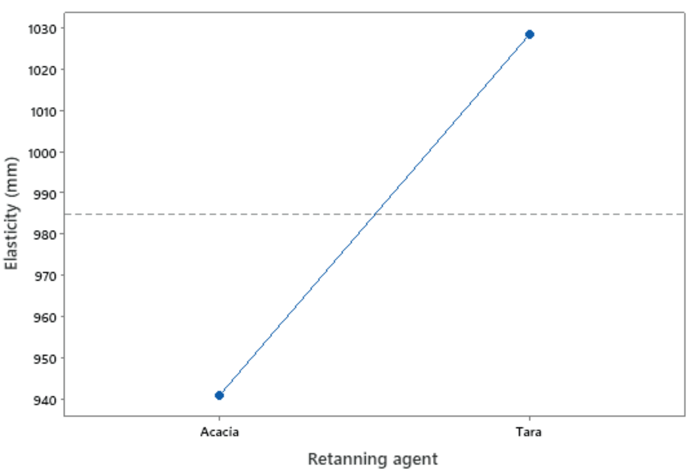


Figure 3. Main effects for Distension at the grain (mm)

The retanning, dye and fatliquor variables modified during leather finishing did not influence with 95% of significance, the strength values for the resistance to distension of the leather. The analysis of variance for the physical-mechanical tests shows that the values of distension (mm) were significantly changed only for the variable tanning agent used. It can be seen that the leathers tanned with the Tara retanning agent showed greater resistance to applied force and flower rupture.

Table V presents the mean percentage of dye penetration in the studied leather samples. According to the results of the ANOVA test, the change of products in retanning, dyeing and fatliquoring did not significantly influence the ability of the dye to cross the leather. In spite of all the leathers presenting a good superficial coloration, some samples did not obtain complete dyeing in all their thickness, even presenting values close to the complete dye uptake, which indicates that the dyeing time used was not enough for the complete coloration of some samples.

Table V

Results of the % of Dye uptake the leather

Sample	% Dye uptake
ABL	82.1±2.2
TBL	84.5±1.6
ARL	95.5±3.2
TRL	94.2±3.9
ABC	82.9±2.6
TBC	99.1±8.2
ARC	100.0±2.5
TRC	83.5±12.5

Table VI

Results of remaining concentration test

Sample	Remaining concentration (mg/L)
ABL	1463.8±426.9
TBL	1126.4±716.9
ARL	730.5±153.7
TRL	1351.8±22.9
ABC	1805.4±141.7
TBC	1055.5±262.6
ARC	1614.8±372.3
TRC	849.5±66.3

Table VII

Results of physical tests of resistance to progressive tearing

Sample	Strength (N)	Tear strength(N/mm)
WB	45.0±1.5	28.1±0.4
ABL	37.4±6.4	28.4±5.4
TBL	32.9±1.7	25.4±0.6
ARL	30.3±6.1	22.9±3.1
TRL	32.3±2.3	22.5±2.2
ABC	42.0±1.8	30.1±0.8
TBC	37.0±2.4	27.7±3.8
ARC	42.4±2.0	32.0±5.1
TRC	47.2±3.8	35.9±19

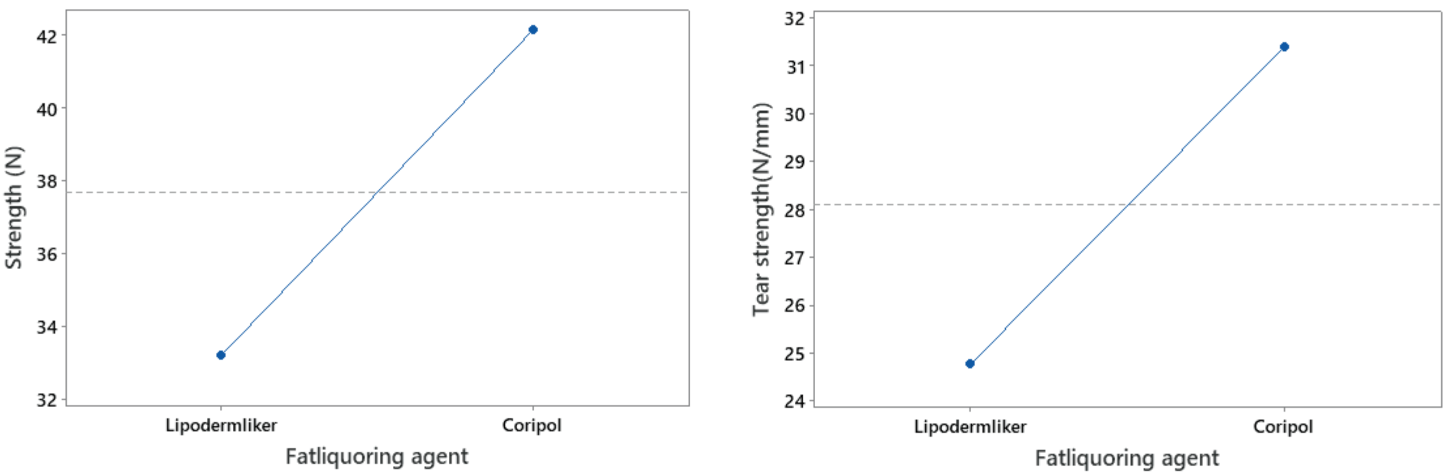


Figure 4. Main effects for Strength (N)

The mean amount of dye remaining in the bath after dyeing was measured by means of spectroscopy and the results are shown in Table VI. The different products used in the finishing did not influence the amount of dye that remained in the effluent after the finishing process according to the ANOVA analysis.

One of the most important mechanical properties for materials used for shoes, gloves, and apparel goods are tensile strength and tear strength. The determination of resistance to progressive tearing is carried out to assess the leather's ability to withstand the multidirectional stresses to which it is subjected when it is used. The mean results obtained during the tests are presented in Table VII. Among the evaluated parameters, the type of fat liquor significantly influenced the resistance to tearing, and the leathers treated with Coripol showed greater resistance to tearing. The values obtained for tear strength are above the minimum accepted for garments (> 15 N/mm), but below those required for shoes (> 40 N/mm).

Conclusions

The parameter that influenced the applied force and the distension of the grain of the leather was the type of retanning agent used, the greater resistance to distension was obtained by Tara retanned leathers. Regarding the degree of dye uptake and remaining concentration of dye in the effluent, they were not affected by the studied parameters, and all leathers showed similar dye uptake. Regarding tear strength, the type of fatliquor was the parameter that had a significant effect on the leather, higher values of resistance were observed for the leather that was treated with Coripol.

Acknowledgement

To Coordination of the Improvement of Higher Education Personnel - CAPES and FAPERGS Edital 10/2021 ARD/ARC for financial support.

References

1. Ali, F., Kamal, M. and Islam, M.S., Comparative study on physical properties of different types of leather in Bangladesh. *Int. j. eng. res. appl.*, **10** 2, 2020.
2. Bajza, Z. and Vinkovic Vrcek, I.; Fatliquoring agent and drying temperature effects on leather properties. *J. Mater. Sci*, **36**, 5265-5270, 2001.
3. Balasubramanian, P., Ramalingam, S., Javid, M.A., Rao, J.R. and Adyar, C.; Lignin based colorant: modified black liquor for leather surface coating application. *JALCA*, **11**, 311-317, 2018.
4. Dessimon, D., Chiká, L., dos Santos, L.M., Einloft, S., Morisso, F., Oliveira, C.T., Scheffels, L.F., Kunst, S.R., de Aquim, P.M. and Carone, C.L.P.; Microcompósitos de poliuretano contendo resíduo wet blue da indústria coureira, por polimerização in situ. *TMM*, **17**, 4, 2020.
5. Gutterres, M. and Mella, B.; Chromium in tannery wastewater. *Heavy Metals in Water: Presence, Removal and Safety*, 315-344, 2014.
6. Kanth, S., Ipe, A., Madhan, B., Venba, R. and Dhathathreyan, A.; Effect of different retanning systems on surface properties of leather. *JALCA*, **102**, 129-134, 2007.
7. Kuria, A., Ombui, J., Onyuka, A., Sasia, A., Kipyegon, C., Kaimenyi, P. and Ngugi, A.; Quality evaluation of leathers produced by selected vegetable tanning materials from Laikipia County, Kenya. IOSR Journal of Agriculture and Veterinary Science (IOSR-JAVS), 9-4, 13-17, 2016.

8. Maina, P., Moses A. O., and Esther W. N.; Trends in leather processing: A Review. *IJSRP* **9**, 12, 2019.
9. Manich, A., Barneys, J., Martinez, L., Lloria, J. and Marsal, A.; Effect of fatliquoring on grain and corium quality of leather assessed by ball bursting and tearing tests. *JALCA*, **111**(4), 127-140, 2016.
10. Mehta, M., Naffa, R., Maidment, C., Holmes, G. and Waterland, M.; Raman and ATR-FTIR spectroscopy towards classification of wet blue bovine leather using ratiometric and chemometric analysis. *J. Leather Sci. Eng.* **2**, 1-15, 2020.
11. Naffa, Rafea, C. Maidment, G. Holmes, and G. Norris. Strong skin, not always thick-30. (2019).
12. Nalyanya, K.M., Rop, R.K., Onyuka, A., Birech, Z. and Sasia, A.; Effect of crusting operations on the physical properties of leather. *Leather Footwear J.* **18**, 4, 2018.
13. Onem, E., Yorgancioglu, A., Karavana, H.A. and Yilmaz, O.; Comparison of different tanning agents on the stabilization of collagen via differential scanning calorimetry. *J. Therm. Anal. Calorim*, **129**, 615-622, 2017.
14. Pratama, M., Sahubawa, L., Pertiwiningrum, A., Rahmadian, Y. and Puspita, I.D.; The effect of mimosa and syntan mixture on the quality of tanned red snapper leather. *IOP Conf. Ser.: Earth Environ. Sci.* **139**, 1, 2018.
15. Reis, E.A., Budemberg, E.R. and Job, A.E.; Interação interfacial de elastômeros termoplásticos (pebd/bn) e resíduo de couro: uma análise estrutural. 12° Congresso Brasileiro de Polímeros (12°CBPol), 2013.
16. Roig, M., Segarra, V., Bertazzo, M., Martinez, M.A., Ferrer, J. and Raspi, C.; Chrome-free leather, tanned with oxazolidine. *J. Agric.* **63**, 4, 2012.
17. Sahu, B., Sathish, M. and Jayakumar, G.C.;. Chemically Modified Castor Oil for Softening of Leather–A Novel Approach. *JALCA*, **116**(4), 2021.
18. Tournier, R.; Tanning Chemicals' Influence in Leather Tensile and Tear Strength Review. *JALCA*, **115**, 409-412, 2020.
19. United Nations Industrial Development Organization, 1996. Acceptable Quality Standards in the Leather and Footwear Industry. UNIDO, United Nations Industrial Development Organization.
20. Wu, C., Zeng, Y., Liao, X., Zhang, W. and Shi, B.; Effect of retanning agents on dry heat resistance of leathers. *JALCA*, **108**(8), 294-299, 2013.

Application of Ultrasound in Eco-friendly Fatliquoring of Leather

by
Md. Abu Sayid Mia,[1,2] Mohammad Nurnabi[1] and Md. Zahangir Alam[1,3]*
[1]*Department of Applied Chemistry and Chemical Engineering, University of Dhaka,* Dhaka 1000, Bangladesh
[2]*Centre for Advanced Research in Sciences (CARS), University of Dhaka,* Dhaka 1000, Bangladesh
[3]*Atish Dipankar University of Science & Technology*, Dhaka 1230, Bangladesh

Abstract

This article describes the effect of ultrasound on fatliquoring of leather. Preparations of fatliquor-emulsions as well as fatliquoring of leathers were carried out in presence of ultrasound. Ultrasound aids in reducing the size of fatliquor emulsion and increasing fat content of leather. It was found that the particle size of fatliquor emulsion was reduced by more than 22% and fat contents of leather were increased up to 40% due to using ultrasound. Moreover, smooth penetration and uniform distribution of fat in the processed leathers were observed. Physical properties of both ultrasound-assisted fatliquored leather and conventionally fatliquored leather were also studied in detail. Tensile strength, stitch tearing strength, tongue tearing strength, grain crack load, ball bursting load, Bauman tear strength, color fastness and perspiration of ultrasound assisted fatliquored leather were better compared to that of without ultrasound.

Introduction

Fatliquoring is a very important step of leather processing in which fatliquoring agents penetrate into the empty spaces of leather. It imparts the softness, elasticity, and smoothness to the grain surface.[1] Fatliquors are mainly emulsifying mixtures prepared by the introduction of phosphate, sulphonate and sulphite groups into oils or fats or by the addition of surface-active agents to the mixture of fatliquoring agents.[2]

Ultrasound is a sound wave of 18 kHz–10 MHz and is generally applied for enhancing various processes and to reduce process time and pollution load. The use of ultrasound in the preparation of fatliquor emulsions to leather making is promising because it takes advantage of the typical effect of cavitation.[3] Ultrasound could be used to emulsify fatliquor efficiently and quickly.[4] In leather processing, a widespread change of chemical processes and reactions are also enhanced because of ultrasound.[5,6] This is due to the sonochemical effect called cavitation that is generated by the formation and collapse of microscopic bubbles.[7] Cavitation produces noteworthy mechanical and chemical effects for example intense agitation, dispersion, degassing, emulsification, micro-jetting in addition to making free radicals.[8] The application of ultrasound to leather processing has become more effective due to an increase in commercial availability, the advancement of ultrasound technology, the external applicability of ultrasound to leather making and the strict environmental laws that demand new efficient processing technology.[9,10]

Ultrasound is one of the best alternatives to make high quality dispersions of fatliquor.[11] Furthermore, it has also been shown to decrease the particle size of the fatliquor emulsion. Most commercial fatliquoring agents are provided as a mixture of raw oil and a certain type of surfactant. Fatliquoring agents may be anionic, cationic or non-ionic in nature. The most widely used fatliquoring agent in leather industry are anionic fatliquors that are made of the neutral oil, a sulfated or sulfited oil, and some free fatty acids.[12] The sulfated (-OSO_3Na) and sulfited oil (-SO_3Na) consist of water-soluble groups and act as surfactants to emulsify the neutral oil in order to replace the water molecules in leather resulting in better penetration. The higher the degree of sulfation or sulfitation the better the penetration of the emulsion. But, the lubricating effect of leather is decreased because of the reduction in neutral oil content.[13] Thus, the choice of the fatliquor type is dependent upon the end use of the products. In this study, the effect of ultrasound on fatliquoring process was investigated and compared with that of conventional fatliquoring.

Experimental

Materials

Remsynol ESI, an anionic fatliquor, was collected from Clariant, India and Figure 1 demonstrates the molecular structure of the sulphited fatliquor component.[14] Generally, 85% of the fatliquor emulsions work as active material and the percentage of the sulphited fatliquor component is 50-55%. Wet blue leather with a thickness of 1.2-1.5 mm was collected from Smith Leather International, Dhaka,

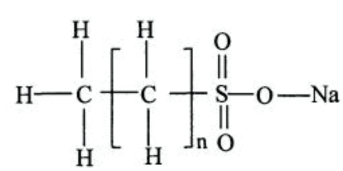


Figure 1. Structure of sulfited fatliquor component

*Corresponding author email: zahangir@du.ac.bd
Manuscript received September 8, 2022, accepted for publication December 5, 2023.

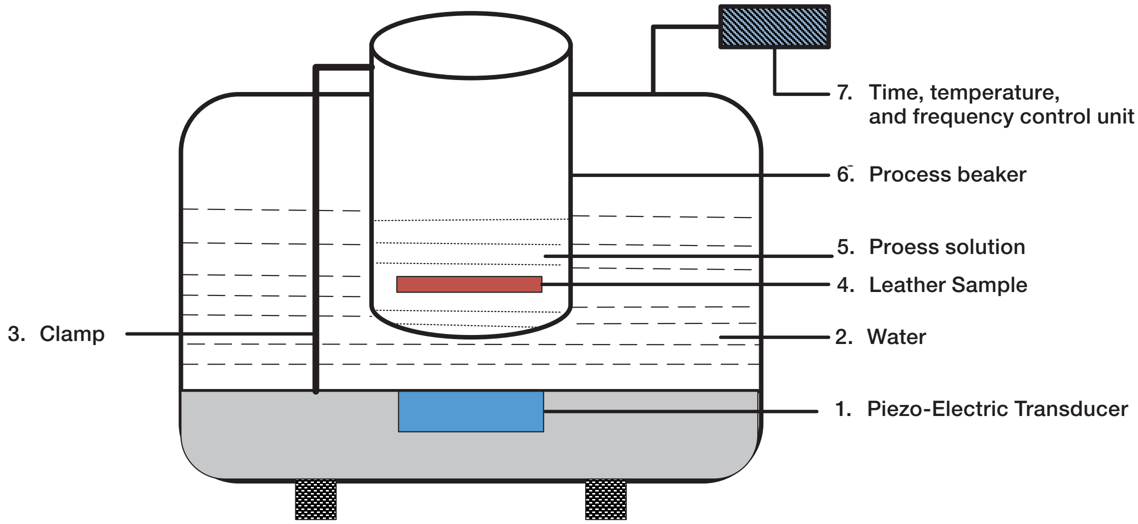


Figure 2. Schematic diagram of experimental setup

Bangladesh. Leather samples were cut (2 inch × 2 inch) adjacently from the same piece of leather to ensure almost similar properties of the samples. Weight of the samples was approximately 4.0 gm. All chemicals used in this study were of analytical grade and purchased from Merck India.

Experimental set-up

In this study, ultrasonic cleaner (HWASHIN TECHNOLOGY CO., KOREA), generating ultrasound at 350W and 40 kHz frequency was used for the experiments as shown in Figure 2. This type of equipment is generally used in the laboratory for ultrasonic experiments.[15] During fatliquoring, ultrasound was applied either continuously or for a short period at different stages, with or without the use of mechanical stirring. In the case of using mechanical stirring in conventional fatliquoring, leather samples were hung from the end of a bladed stirring propeller rotating at 50 rpm.

Fatliquoring of leather samples

All leather samples were first neutralized using alkaline solutions prior to fatliquoring. The gradient of pH across the leather cross section is important for the penetration and deposition of fatliquor. In practice, a pH value of 4.0 – 6.0 is desired. In this study, the neutralization pH was 4.5. Fatliquoring was carried out with 5% Remsynol ESI (5%) and distilled water (30%) either in the presence or absence of ultrasound at different temperatures. All the percentages of chemicals used are based on the weight of wet leather. The fatliquor emulsions were prepared using either ultrasonic irradiation or mechanical stirring for 30 minutes at the predetermined temperature of fatliquoring.

Measurement of particle size

The mean particle size of 1% (w/v) fatliquor emulsions were measured using a particle size analyzer (iSpect DIA-10, SHIMADZU, Japan) prepared by either sonicating or mechanical stirring at different times and temperatures.

Measurement of viscosity

Viscosity of 5% (w/v) and 10% (w/v) fatliquor emulsions were measured over a range of shear rates at 20°C, 30°C and 40°C using a cone-on-plate rheometer (RST-CPS Cone/Plate, AMETEK Brookfield, USA), where, emulsions were prepared at 25°C by either sonicating or mechanical stirring for 30 minutes.

Determination of fat content

Fat content of the fatliquored leather was determined by Society of Leather Technologists and Chemists (SLTC) standard method.[16] Then the samples were air-dried to a certain weight and crushed in a milling machine. Around 10g of ground leather was extracted using a Soxhlet extraction apparatus with dichloromethane (DCM) for at least 5 hours. The weight of DCM extractables was then obtained and expressed as the weight percentage of dried leather sample.

Results and Discussion

Effect of sonication time on the particle size

Particle size is a very significant factor that characterizes the nature and performance of emulsion. It also influences the stability and penetration of fatliquor. Generally, the smaller the particle size of a fatliquor emulsion, the easier penetration into leather.[17]

Figure 3 shows the changes in particle size as a function of sonication time at 40°C. As seen from the graph, after sonication for 10 minutes the particle size becomes 72 nm that is almost similar to the size prepared by conventional method. After sonication for 30 minutes the particle size obtained was 59 nm and further

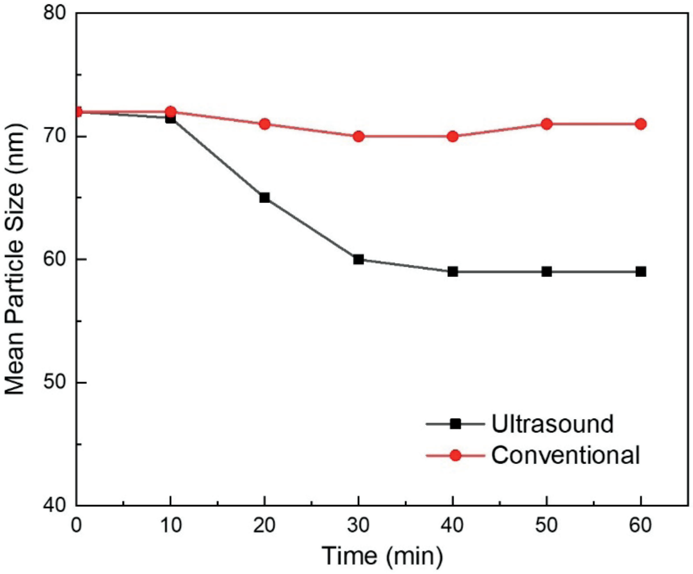


Figure 3. Mean particle size of fatliquor emulsion

sonication did not show any effect on the particle size of fatliquor. That means 30 minutes ultrasonic irradiation was optimum to maximize the reduction of particle size. It is assumed that this reduction in fatliquor particle size happened due to cavitation energy generated by ultrasound. The cavitation energy produced shock waves that raised local pressure and reduced the particle size.[18, 19]

Effect of ultrasound on the viscosity of fatliquor emulsions

The viscosity of fatliquor is another important parameter that influences the penetration of oil into leather. The lower the viscosity of a fatliquor, the better is its penetration. In this study, 5% and 10% Remsynol ESI fatliquor emulsion were made by both ultrasonic technique and conventional method. Figures 4 and 5 show the viscosity of fatliquor emulsion as a function of shear rate at different temperatures under ultrasound and conventional method. It was observed that viscosity of fatliquor produced by ultrasound was

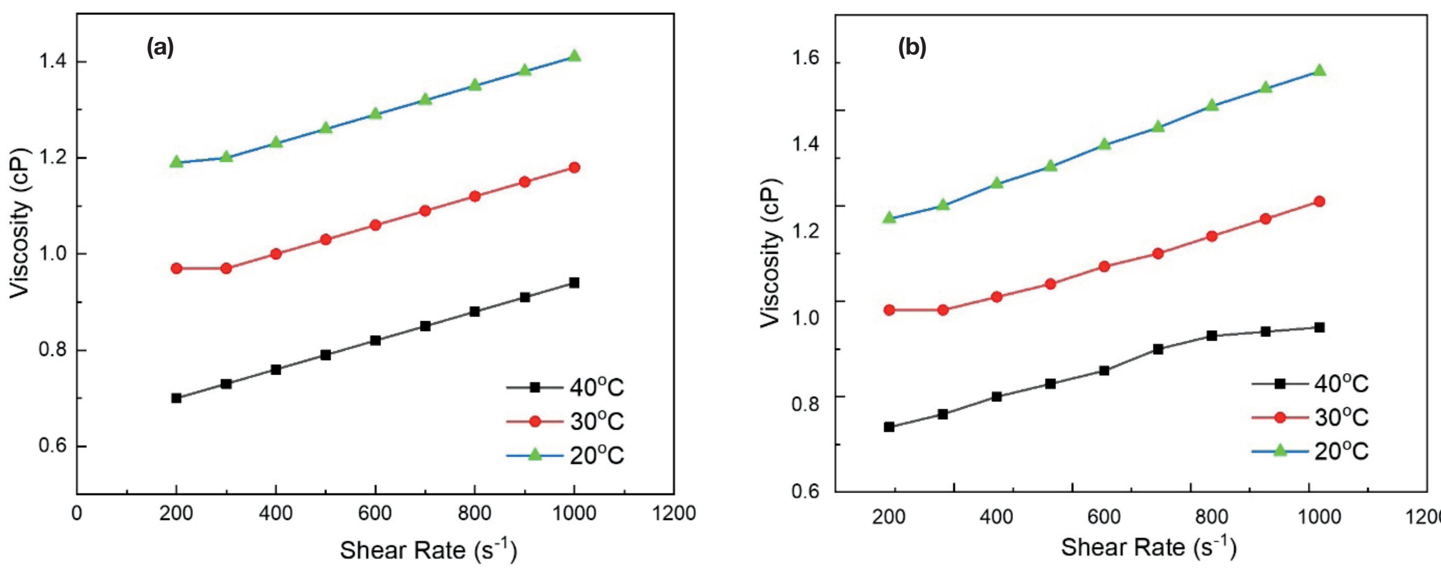


Figure 4. Viscosity as a function of shear rate of fatliquor emulsion at 5% (w/v) concentration using **(a)** ultrasound and **(b)** conventional technique.

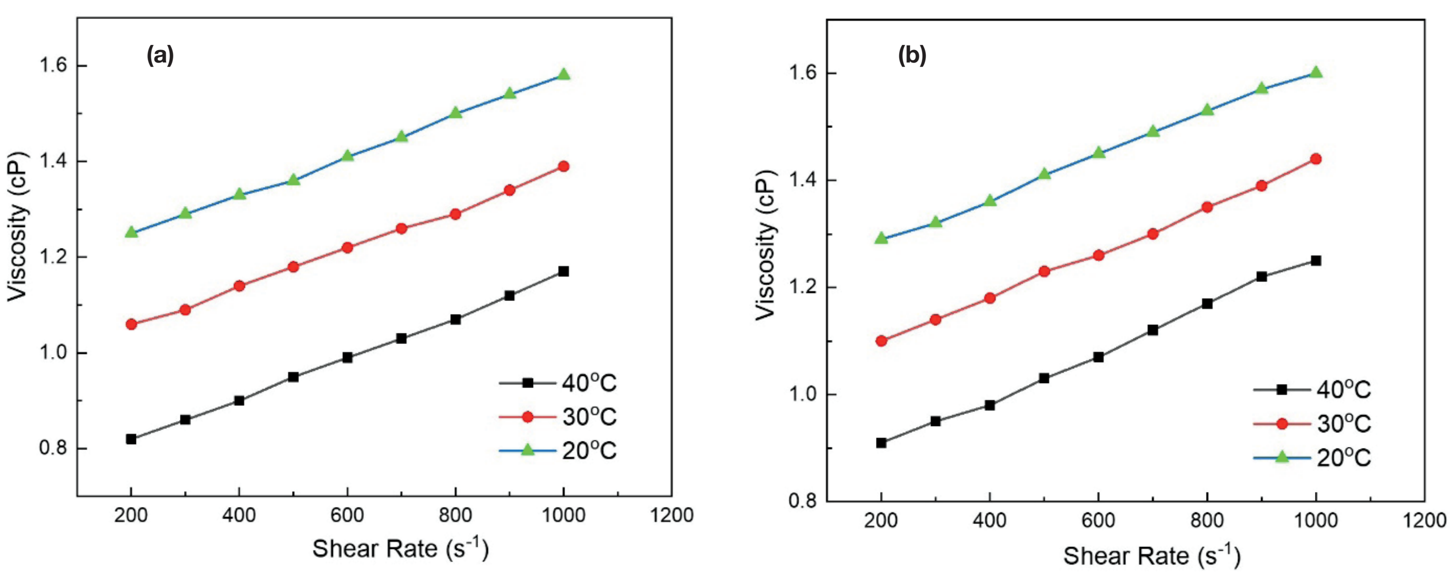


Figure 5. Viscosity as a function of shear rate of fatliquor emulsion at 10% (w/v) concentration using **(a)** ultrasound and **(b)** conventional technique.

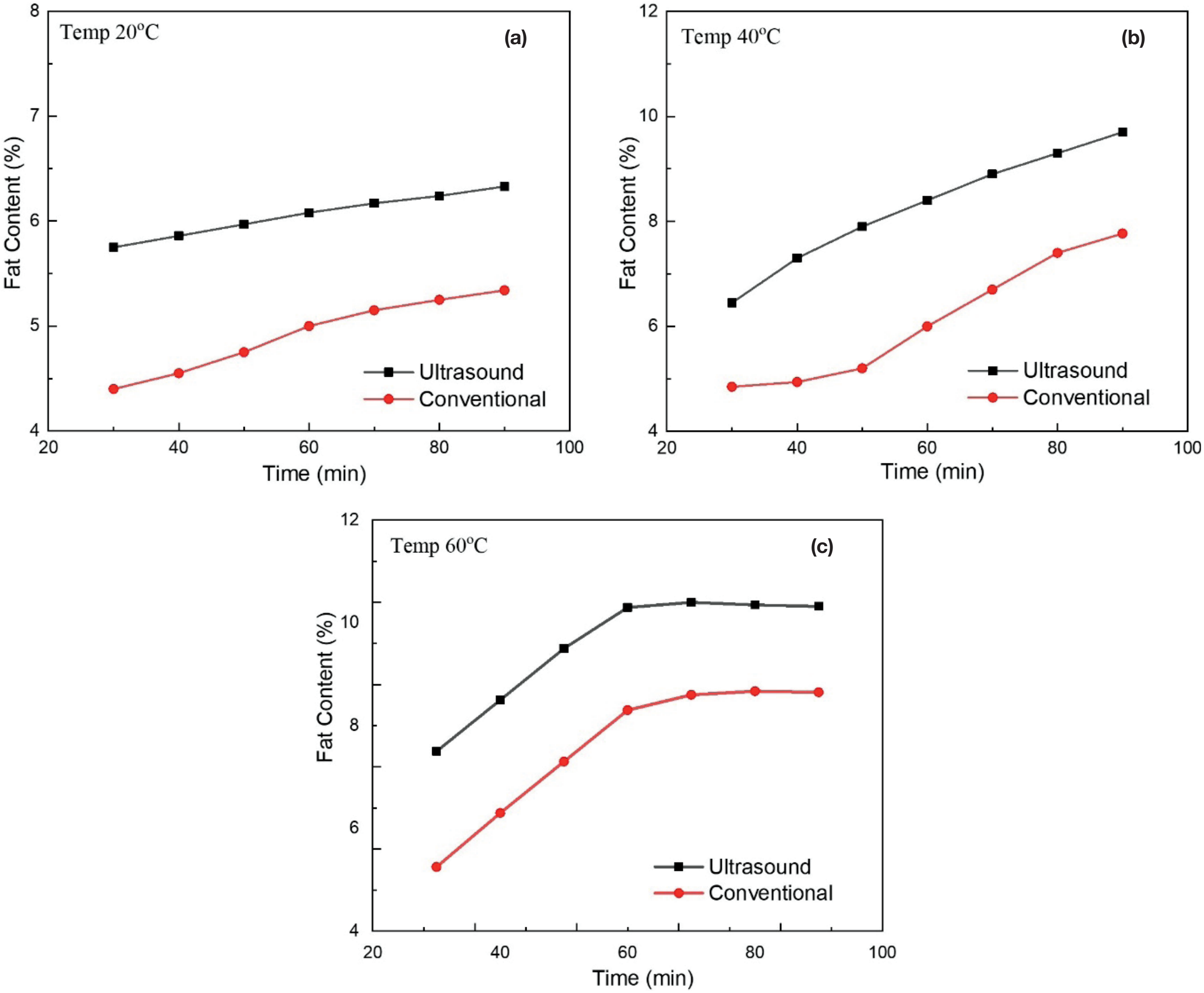


Figure 6. Fat content of leather fatliquored with 5% Remsynol ESI emulsion using ultrasound and conventional technique at **(a)** 20°C, **(b)** 40°C and **(c)** 60°C.

similar to that produced by conventional method. Both fatliquor emulsions were non-Newtonian in nature. It was also observed that viscosity of fatliquor decreased with an increase in temperature and viscosity of fatliquor increased with an increase in concentration. Thus, the effects of temperature, shear rate and concentration on viscosity of fatliquor emulsion are in good agreement with the behavior of emulsion.[20]

Effect of ultrasound on fat content of leather

Ultrasound plays a vital role in the fat content of leather. The effects of ultrasound on fat content of leather had been studied at different temperatures. Figure 6 (a, b, c) shows fat contents of leather fatliquored with 5% Remsynol ESI emulsion as a function of processing time using ultrasound and by conventional method at different temperatures. Fat content of leather at 20°C using ultrasound for 90 minutes was 6.3% whereas in conventional method it was only 5.1% (Figure 6a). Using ultrasound, the maximum fat content (10%) was obtained in 90 minutes at 40°C (Figure 6b) and 60 minutes at 60°C (Figure 6c). From the above data it can be concluded that using ultrasound same or even higher fat content can be obtained in shorter processing time or at lower temperature compared to conventional fatliquoring. Moreover, ultrasound aids in much better distribution throughout the whole cross section of the leather.

Physical properties of the fatliquored leathers

Physical characteristics namely tensile strength, stitch tearing strength, tongue tearing strength, Bauman tearing strength, grain crack load, and ball bursting strength of the leather fatliquored using ultrasound and conventional method were determined according to

Table I

Physico-chemical properties of leather fatliquored with 5% (w/v) Remsynol ESI emulsion using ultrasound and conventional method

Strength properties	Ultrasound-assisted fatliquored leather	Conventionally fatliquored leather	Standard Value
Tensile strength (Kg/cm^2)	332 ± 2	250 ± 7.64	Min. 200
Percentage elongation at break	64 ± 1.52	37 ± 4.04	Min. 30%
Stitch tearing strength (kg/cm)	98.5 ± 2.02	83.5 ± 3.68	80-100
Tongue tear strength (kg/cm)	60.5 ± 2.56	33.5 ± 3.01	Min. 30
Bauman tear strength (kg/cm)	71 ± 3	35 ± 3.21	Min. 30
Grain crack load (kg)	69.75 ± 2.60	46.5 ± 2.18	Min. 16
Grain crack distension (mm)	15 ± 1.53	9 ± 1	Min. 7
Ball bursting load (kg)	74 ± 2.52	52.5 ± 2.50	Min. 20

Table II

Fastness properties of the fatliquored leather

Experimental conditions	Fastness properties		
	Wet	Dry	Perspiration
Ultrasound-assisted fatliquored leather	4-5	4-5	4
Conventionally fatliquored leather	3	3-4	2

the standard procedures and tabulated in Table I. It was observed that all physical properties of fatliquored leather with ultrasound were found to be significantly higher than those of without ultrasound. It is assumed that this is due to the higher fat-fiber interaction in presence of ultrasound resulting in higher fat penetration into the leather.[21] Consequently, fastness of ultrasound treated fatliquored leather was increased significantly (Table II).

Conclusion

Potential application of ultrasound in fatliquoring of leather was studied in detail. Ultrasound helped to provide finer emulsion particle size distribution resulting in better penetration and uniform distribution of fat in fatliquoring of leather. Therefore, this study revealed the potential use of ultrasound to prepare fatliquor emulsion as a greener leather production option. The use of ultrasound reduced the discharge of unconsumed chemicals in the effluent, enhanced diffusion rate, reduced processing time, and improved the leather quality which will lead the leather industry towards a cleaner image. Thus, application of ultrasound in fatliquoring of leather will be a very environmentally benign technique for leather industries in Bangladesh.

Acknowledgements

The financial supports from the Ministry of Education (Reference No.: 37.20.0000.004.033.020.2016-86, GARE Project No.: PS20191086) and Ministry of Science and Technology (Reference No.: 39.00.0000.012.002.04.19-08, Physical Science-33), Government of the People's Republic of Bangladesh to carry out the research are highly acknowledged. The authors are also thankful to Mr. Md. Nur-E-Alam, Senior Scientific Officer, Leather Research Institute (LRI), Bangladesh Council of Scientific and Industrial Research (BCSIR) for his valuable suggestions during this research.

References

1. Sivakumar, V., Prakash, R.P., Rao, P.G., Ramabrahmam, B. V., and Swaminathan, G.; Power Ultrasound in Fatliquor Preparation Based on Vegetable Oil for Leather Application. *J. Clean. Prod.* **16** (4), 549–553, 2008.
2. Sivakumar, V., Chandrasekaran, F., Swaminathan, G., and Rao, P.G.; Towards Cleaner Degreasing Method in Industries: Ultrasound-Assisted Aqueous Degreasing Process in Leather Making. *J. Clean. Prod.* **17** 101–104, 2009.
3. Gourlay, P.; Emulsification and Dispersion by Using Ultrasonics. *Rev. Tech. Ind. Cuir.* **51** (11), 240–243, 1959.
4. Mia, M.A.S., Ashraf, R.E., Nurnabi, M., and Alam, M.Z.; Eco-Friendly Leather Dyeing Using Ultrasound Technique. *JALCA* **115** (6), 199–205, 2020.
5. Mason, T.J.; Practical Sonochemistry: A User's Guide to Applications in Chemistry and Chemical Engineering. *Ellis Horwood* 1991.
6. Lorimer, J.P. and Mason, T.J.; Sonochemistry Part. I- The Physical Aspects. *Chem. Soc. Rev.* **16** 239–274, 1987.
7. Ding, J.F., Xie, J.P., and Attenburrow, G.E.; Power Ultrasound in Leather Technology in Advances in Sonochemistry. *JAI Press Inc.* **5** 1999.
8. Suslick, K.S. and Casadonte, D.J.; Heterogeneous Sonocatalysis with Nickel Powder. *J. Am. Chem. Soc.* **109** (11), 3459–3461, 1987.
9. Contamine, F., Faid, F., Wilhelm, A.M., Berlan, J., and Delmas, H.; Chemical Reactions under Ultrasound: Discrimination of Chemical and Physical Effects. *Chem. Eng. Sci.* **49** (24), 5865–5873, 1994.
10. Ando, T. and Kimura, T.; Reactivity and Selectivity in Organic Sonochemical Reactions Involving Inorganic Solids. *Ultrasonics* **28** (5), 326–332, 1990.
11. Sivakumar, V. and Rao, P.G.; Application of Power Ultrasound in Leather Processing: An Eco-Friendly Approach. *J. Clean. Prod.* **9** (1), 25–33, 2001.
12. Han, Q.B.; Wool-Leather Chemical and Technology. *Ind. Press. Beijing* 224–232, 1990.
13. Timochin, N.A., Barinov, I.G., and Kraminora, K.G.; Chrome Emulsion Tanning Method. *Kozh. Obuv. Prom.* **3** (8), 15–16, 1961.
14. Sharphouse, J.H.; Leather Technician's Handbook. *Leather Prod. Assoc. Northampt.* 1971.
15. Sivakumar, V. and Rao, P.G.; Diffusion Rate Enhancement in Leather Dyeing with Power Ultrasound. *JALCA* **98** (6), 230–237, 2003.
16. SLTC (Society of Leather Technologists and Chemists). *IULTCS, Off. methods, UK* 1996.
17. Heidemann, E.; Newer Developments in the Chemistry and Structure of Collagenous Connective Tissues and Their Impact on Leather Manufacture. *J. Soc. Leather Traders Chem.* **66** 21–29, 1982.
18. Xie, J.P.; The Influence of Power Ultrasound on Leather Processing. *Univ. Leicester (United Kingdom)* 1998.
19. Khavari, M., Priyadarshi, A., Hurrell, A., Pericleous, K., Eskin, D., and Tzanakis, I.; Characterization of Shock Waves in Power Ultrasound. *J. Fluid Mech.* **915** (R3), 1–14, 2021.
20. Becher, P.; Emulsions: Theory and Practice. *Robert E. Krieger Publ. Company, Inc., USA.* 1977.
21. Devikavathi, G., Ramamoorthy, U., Sundar, V.J., and Muralidharan, C.; Influence of Fatliquor on Ageing Characteristics of Leather. *Rev. Piel. Incaltaminte* **10** (1), 31, 2010.


Chemtan waterproof
technology –
inspired by nature
CHEMTAN
Tel: (603) 772-3741
www.CHEMTAN.com

The American Leather Chemists Association

5997 Center Hill Ave. Cincinnati OH 45224 phone: 513.290.2502
Web: leatherchemist.org   email: hallks@ucmail.uc.edu

Past Issues of *Journal* Needed

The ALCA office is working to compile a complete collection of issue of *The Journal of the American Chemists Association.* If you or someone you know has copies of these missing issues you would like to donate to ALCA please contact the ALCA office.

Missing issues needed.

1924 - January

1937 - January and December

1939 - January, March and April

1940 - January

1946 - February

Lifelines

Sathya Ramalingam – Please see *JALCA*, Page No. 50, *Vol. 119*,2024.

Swethashree Rajendran received her M.Tech in Leather Technology from Anna University, Chennai. Currently, she works as a Research scholar at CFR, Anna University, Chennai. To her credit, she has published one Research paper in peer peer-reviewed journal.

Ambika Kumaresan received her B.Tech (Textiles) from VTU University, Bangalore, and her M.Des from NIFT. She works as a Scientist in the Shoe and Product Design Centre at CSIR-Central Leather Research Institute. Miss K. Ambika has extensive experience in the field of leather accessories, having worked in various international export and buying houses. In addition, she has started a start-up for Euro Leder Fashion Ltd, which specializes in leather accessories product development and is named Stitch and Turn.

Gladstone Christopher Jayakumar- Please see *JALCA*, Page No. 336, *Vol. 116*,2021.

Alagumuthu Tamilselvi - Please see *JALCA*, Page No. 336, *Vol. 116*,2021.

Han Xu received her Bachelor's Degree in Fashion and Apparel Design (2020) and Master's Degree in Art and Design (2023) from Jiangnan University, China. Now she works as a research assistant in the College of Biomass Science and Engineering, Sichuan University, China. Her main research focuses on leather apparel and smart apparel design.

Han Chen received his Master's degree in Art and Design from Zhejiang Sci-Tech University, China and Bunka Gakuen University, Japan (2018). He received his Ph.D. in Design from Jiangnan University, China (2023). He is now a full-time faculty member at Zhejiang Sci-Tech University. His main research focuses on digital fashion and sustainable design.

Biyu Peng received his Master's Degree (1994) and Ph.D. (1999) in Leather Chemistry and Engineering from Sichuan University, China. He pursued his postdoctoral research work as a visiting scientist at the Leather Research Institute of Texas Tech University, USA, from 2004 to 2006. Now he is a Professor in National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, China. Recently, his research work mainly focuses on waste resource utilization and biochemistry technologies in leather manufacturing.

Luming Yang received her Master's Degree (2004) in Leather Chemistry and Engineering from Sichuan University, China, and the Ph.D. (2007) in Chemistry and materials technology from Tomas Bata University in Zlin, Czech. Now she is a Professor in Department of Fashion Design, Sichuan University, China. Her broad research fields are functional and intelligent clothing design, footwear and health, foot biomechanics, with a particular focus on functional garment and sports biomechanics.

Laisa Grassi is an undergraduate student in the Federal University of Rio Grande do Sul, Brazil, majoring in Chemical Engineering. Her research interest is about leather processing formulation.

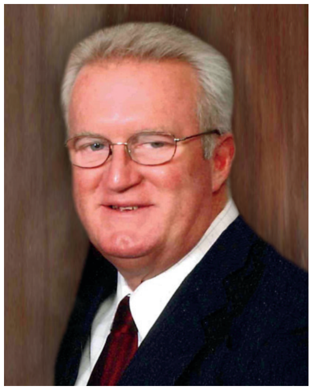
Luísa Gonçalves is an undergraduate student in the Federal University of Rio Grande do Sul, Brazil, majoring in Chemical Engineering. Her research interest is about energy use of finished leather waste.

Vânia Queiroz is a PhD student in the postgraduate program in chemical engineering at Federal University of Rio Grande do Sul, Brazil. Her research activity is in the field of kinetics and evaluation of the dyeing process. She is currently carrying out part of her PhD at the FILK Freiberg Institute, Germany.

Mariliz Gutterres received her PhD degree in 2001 from Technische Universitat Bergakademie Freiberg, T.U.B.F., Germany. She was a professor of the Chemical Engineering department of Federal University of Rio Grande do Sul, Brazil. Her research interests include the leather process and properties, as well as cleaner leather making. She received the IULTCS Merit Award for excellence in the leather industry in 2017. She has published more than 150 papers and edited 1 book in the field of leather process.

Caroline Agustini received her PhD degree in 2018 from Federal University of Rio Grande do Sul, postgraduate program in chemical engineering, Brazil. She is a professor of the Chemical Engineering Department of Federal University of Rio Grande do Sul, Brazil. Her main research interests include energy production from leather waste and clean technologies in the process. She received the IULTCS Young Leather Scientist Award - Sustainability/Environmental Grant in 2021. She has published more than 20 papers in the field of treatment and energy use of leather waste.

Obituary



Patrick H. Wilson, age 65, entered eternal rest on Saturday, December 02, 2023, in El Paso, Texas. He was a wonderful son, brother, husband, and father and will be greatly missed. He is survived by his loving wife; Kim Nance Wilson; his dearest children; Daniel Wilson & Katelyn Wilson; and his dear sisters; Paula (Steve) Padar, Penny (Roger) Babb, Barbara Ryan, Kay (Dion) Chilberg and several nephews and a niece. He is also survived by many extended friends and family to cherish and honor his memory.

Pat was an avid golfer and played as often as he could. He joined the ALCA in 2001. He worked for many years at Eagle Ottawa now Lear Inc. Pat also worked for Lackawanna Leather in Hickory, NC where he met the love of his life, Kim Nance. They married on July 3, 1993, in Grand Haven, MI, and enjoyed 30 years together moving from NC to Pennsylvania, Wisconsin, back to Michigan and ultimately being transferred to El Paso, TX in 2005 where he was Technical Manager for all of Mexico. Pat and Kim added Daniel Patrick in 2003, and Katelyn Renee in 2006 to the family. Pat was so proud of his children and wife. He was a gregarious person with an amazing quick wit and great sense of humor enjoyed by all.

Interment will be at the Spring Lake Cemetery.

INDEX TO ADVERTISERS

CALL FOR PAPERS

FOR THE 118th ANNUAL CONVENTION OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

Hershey Lodge, Hershey Pennsylvania
May 21–24, 2024

If you have recently completed or will shortly be completing research studies relevant to hide preservation, hide and leather defects, leather manufacturing technology, new product development, tannery equipment development, leather properties and specifications, tannery environmental management, or other related subjects, you are encouraged to present the results of this research at the next annual convention of the Association to be held at the Hershey Lodge, Hershey Pennsylvania, May 21–24, 2024

Abstracts are due by March 1, 2024
Full Presentations are due by May 1, 2024

They are to be submitted by e-mail to the
ALCA Vice-President and Chair of the Technical Program:

John Rodden
Union Specialties, Inc.
3 Malcom Hoyt Dr.
Newburyport, MA 01950
E-mail: johnrodden@unionspecialtiesinc.com

The **Abstract** should begin with the title in capital letters, followed by the authors' names. An asterisk should denote the name of the speaker, and contact information should be provided that includes an e-mail address. The abstract should be no longer than 300 English words, and in the Microsoft Word format.

Full Presentations at the convention will be limited to 25 minutes. In accordance with the Association Bylaws, all presentations are considered for publication by *The Journal of the American Leather Chemists Association*. They are not to be published elsewhere, other than in abstract form, without permission of the *Journal* Editor. For further paper preparation guidelines please refer to the *JALCA* Publication Policy on our website: leatherchemists.org

Full Presentations are to be submitted by e-mail to the *JALCA* editor:

Steven D. Lange, *Journal* Editor
The American Leather Chemists Association
E-mail: jalcaeditor@gmail.com
Mobile Phone (814) 414-5689

118th ALCA ANNUAL CONVENTION May 21 – 24, 2024 Hershey Lodge, Hershey PA

Featuring the 63nd John Arthur Wilson Memorial Lecture

By **Panos Mytaros**
Chief Executive Officer
ECCO

Tentative Schedule

Tuesday, May 21
Golf Tournament, Opening Reception and Dinner

Wednesday, May 22
John Arthur Wilson Memorial Lecture All Day
Technical Sessions, Fun Run, Reception and Dinner

Thursday, May 23
All Day Technical Sessions, Annual Business Meeting
Activities Awards Luncheon
Social Hour, Banquet Dinner

Visit us at www.leatherchemists.org for full details under Annual Convention as they become available