

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

by

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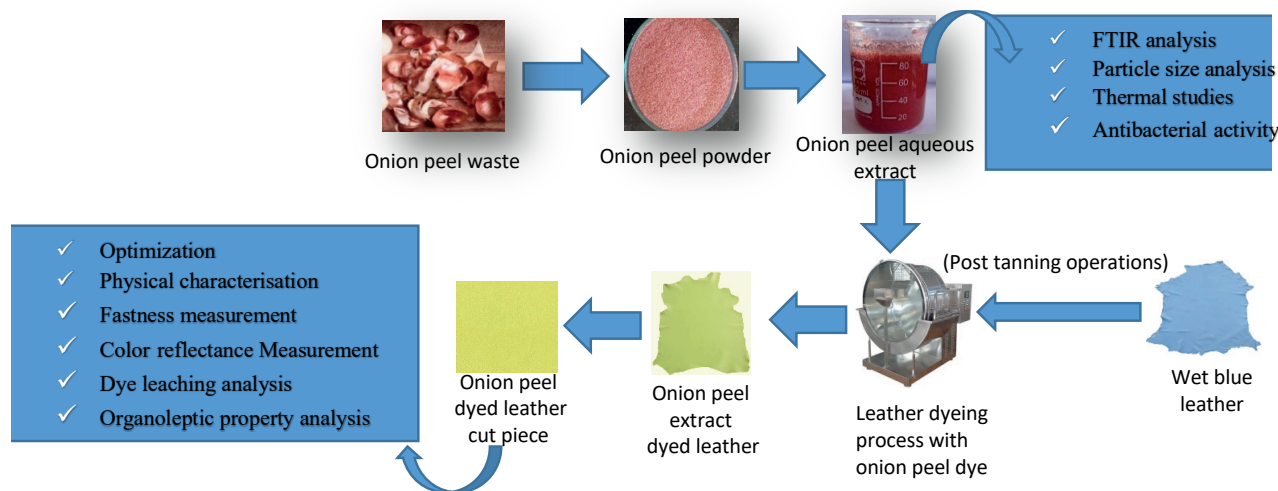
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Graphical Abstract



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 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

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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, Okwuchi⁴ 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.

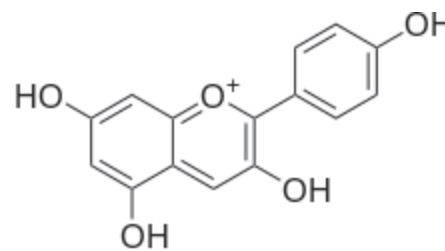


Figure 1. Pelargonidin structure.⁷

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 Lee¹⁰ 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'Éclairage) 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	100	(3 × 15 min) + 50 min	Cross-section pH 5.0±0.2 Drain/Wash/Drain
	Sodium formate	1		
	Sodium bicarbonate	1		
Retanning	Relugan RE	3	20 min	
	Phenolic syntan	5	60 min	
	Melamine syntan	5		
	Biopolymer	2		
Fatliquoring	Synthetic fatliquor	3	(3 × 15 min) + 120	
	Semi synthetic fatliquor	3		
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/Buffering.

*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 quantify 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

$$\% \text{ Exhaustion} = \frac{C_0 - C_s}{C_0} \times 100$$

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 literature¹³ Bands at 3303 cm^{-1} and 3182 cm^{-1} were due to the -OH groups of pelargonidin. The band at 2932 cm^{-1}

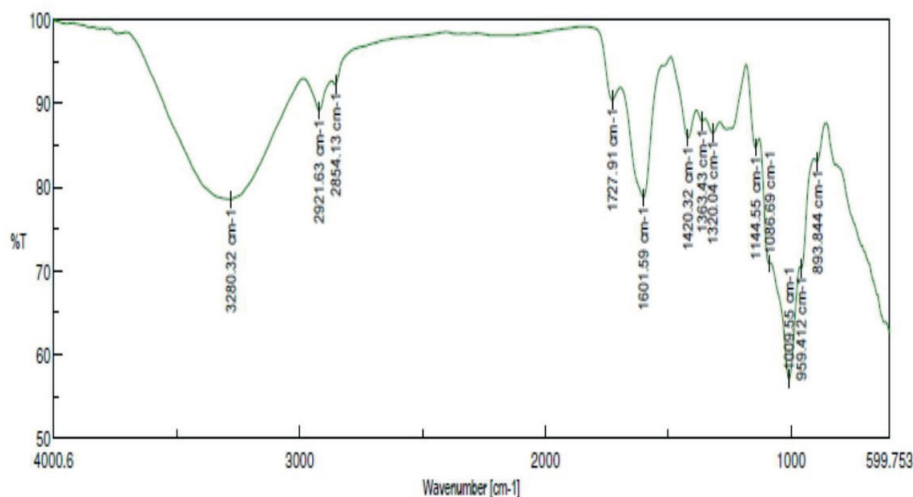


Figure 2. FTIR spectrum of onion peel dye powder.

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 $377 \pm 5\text{ nm}$. 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

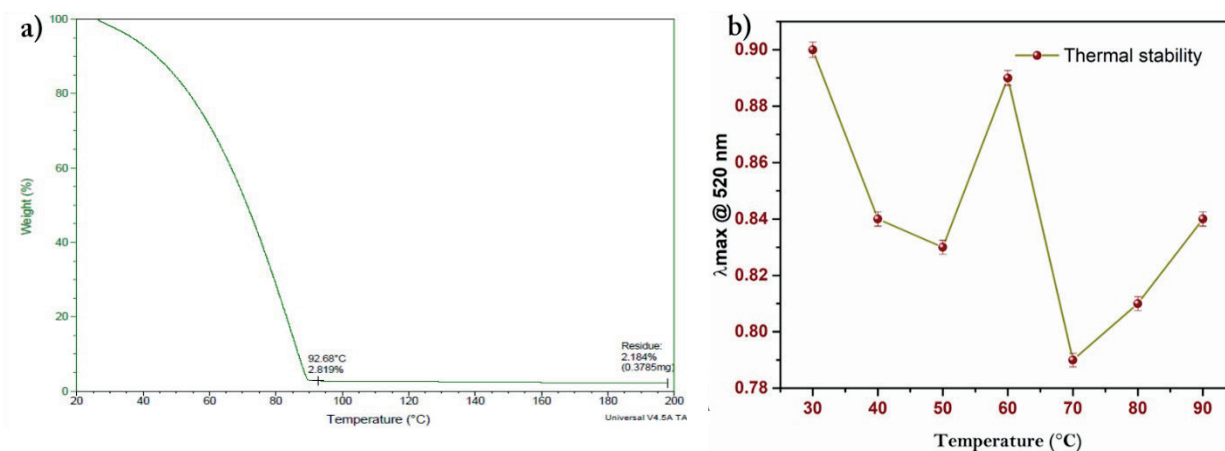


Figure 3. a) TGA of onion peel dye powder, b) change in the maximum absorbance of onion peel dye solution at different temperatures.

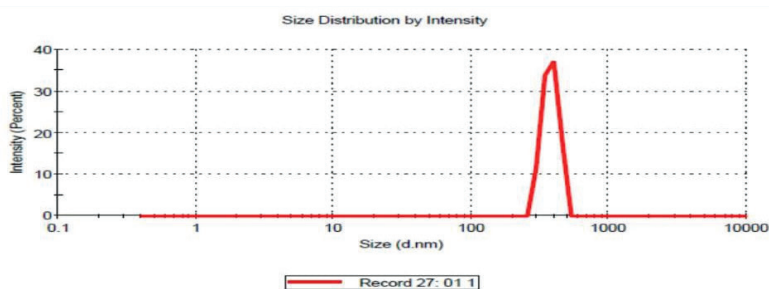


Figure 4. Particle Size Analysis of onion peel dye powder.

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

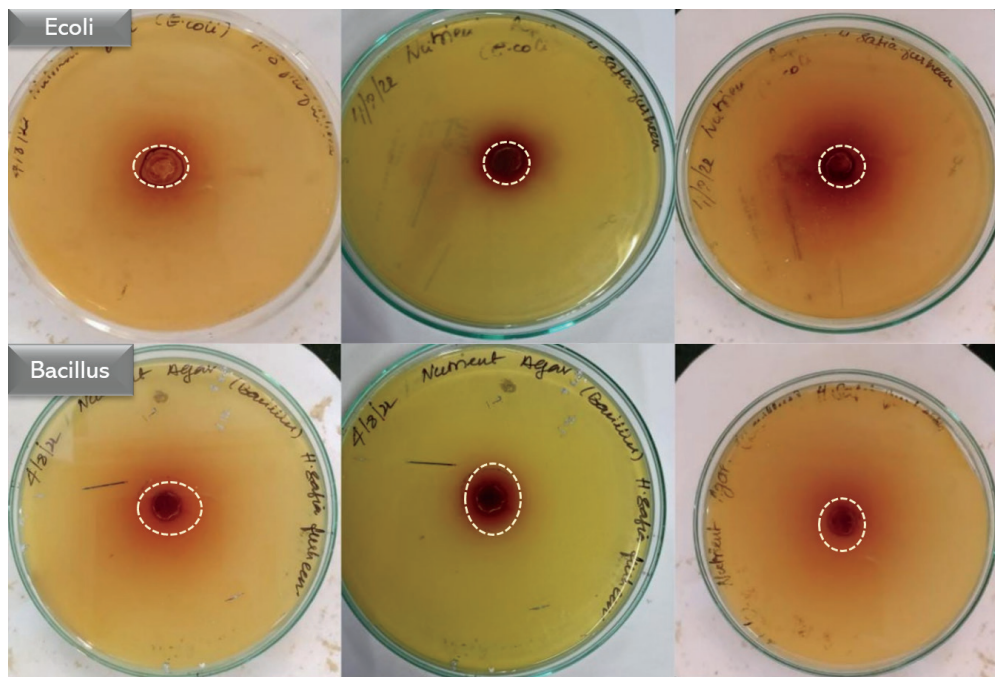


Figure 5. Zone of Inhibition in *Escherichia* species and *Bacillus* species

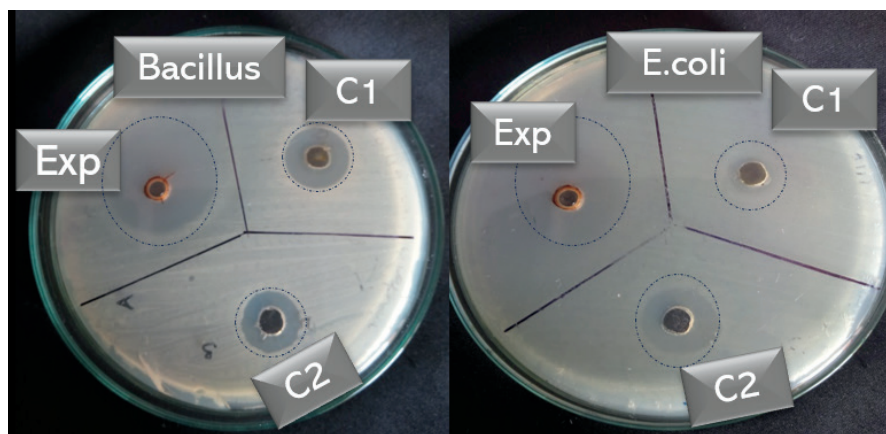
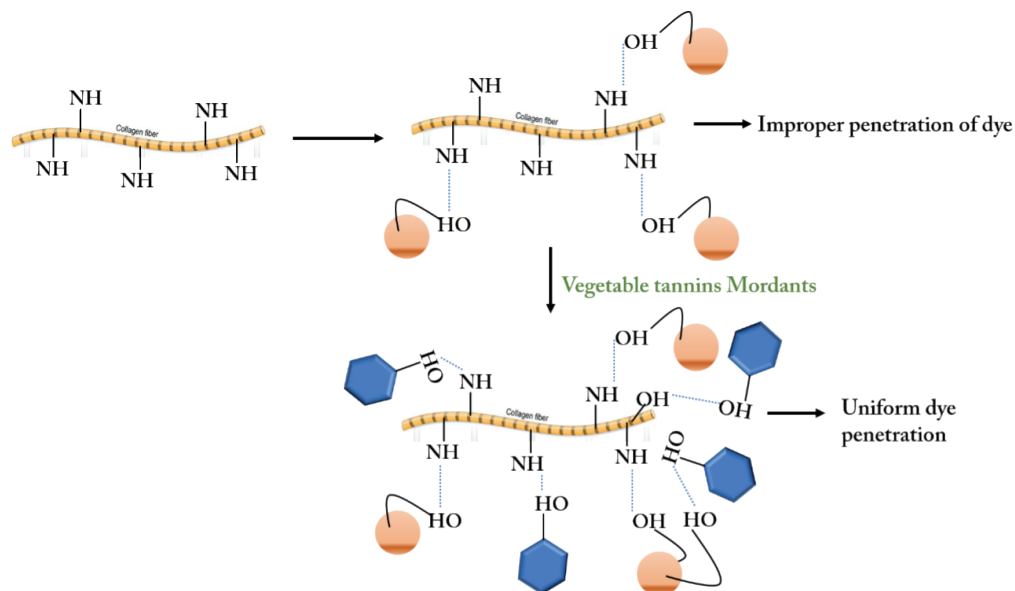


Figure 6. Zone of Inhibition in control (C1- Madder and C2- Indigo) and experimental (Exp- Onion Peel dye) leather against *Escherichia* species and *Bacillus* species



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*	Color 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	

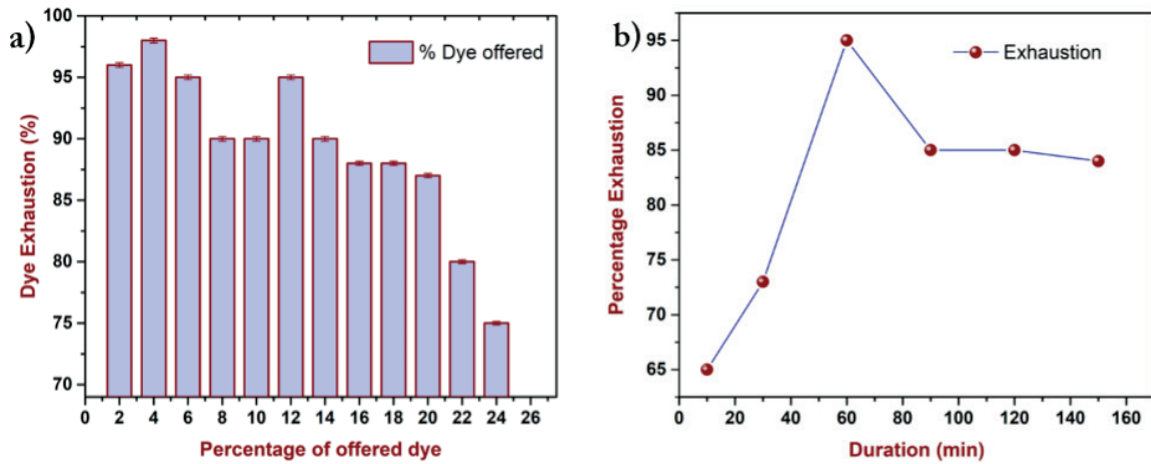


Figure 7. a) percentage exhaustion dye for a different percentage of dye and b) represents the percentage of dye exhaustion for different duration.

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

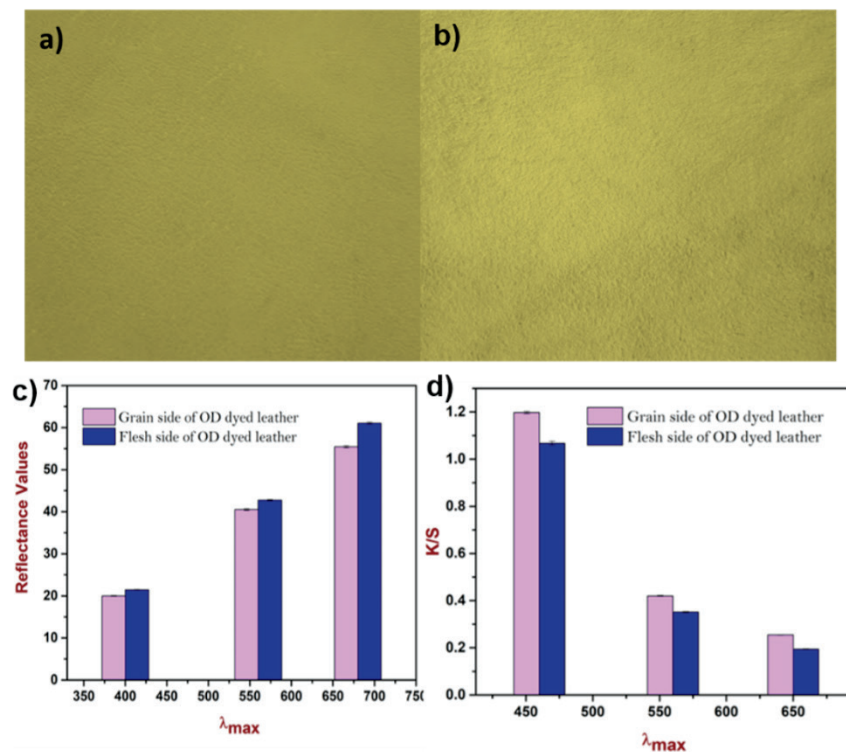


Figure 8. a) Grain side image of the leather dyed by onion peel, b) Flesh side image of the leather dyed by onion peel, c) represents the reflectance, and d) K/S value of the dyed leather.

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

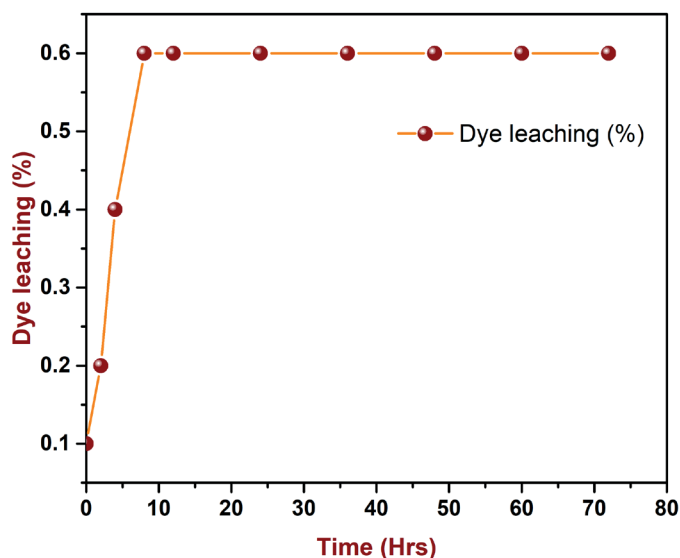


Figure 9. Dye leaching of onion peel dye treated leather.

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

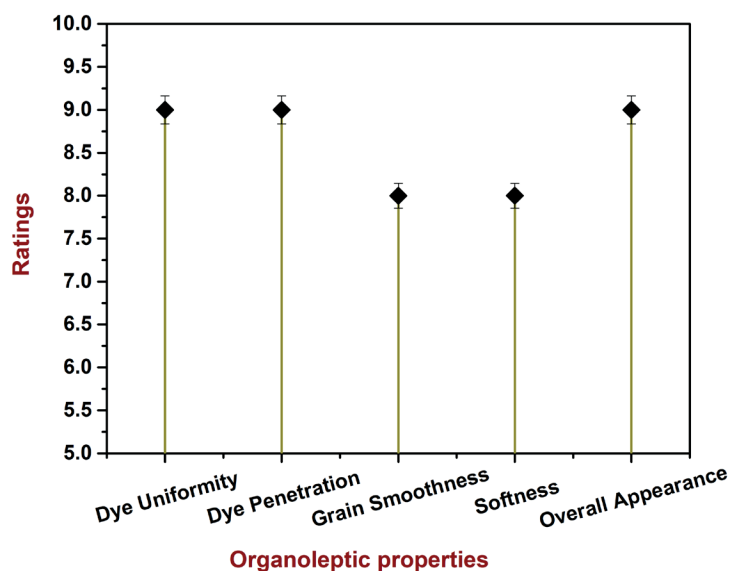


Figure 10. Organoleptic properties of onion peel dyed leather.

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.

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