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Utilization of Natural Dye Extracted from Spent Tea Leaves (*Camellia sinensis*) for the Dyeing of Leather

Adhir Chandra Paul[1], Md. Waliullah[2], Md. Asadullah Al Galib[3]
[1,2,3]Department of Leather Engineering, Khulna University of Engineering & Technology, Khulna-9203, Bangladesh
E-mail: adhirkuet@gmail.com, md.waliullah2k14@gmail.com, dxgalib@gmail.com

Abstract

Tanners are generally interested with synthetic dyes for leather dyeing is not biodegradable due to their complex structure and xenobiotic characteristics. Besides, it has health problems including carcinogen effect. In this study, natural dye extracted from spent tea leaves with water and ethanol solvent. To extract the dyestuffs, different ratio of spent tea leaves (Camellia sinensis) (g) with water (mL) and ethanol solvent (mL) were taken and the best one was chosen to carry out the procedure. The extracted dyestuffs were characterized and the conventional recipe for post tanning, dyeing process for manufacture of upper leathers was followed. It was investigated that the leather dyed with water extracted dyestuffs showed better value in Spectrophotometer analysis and chemical performance as compared to leather dyed with ethanol extracted dyestuffs. The detailed studies and technical investigations of natural dyes spent tea leaves over synthetic dye is required having maximum dye yield for dyeing of leather.

Keywords: Dye, water, ethanol solvent, spent tea leaves (*Camellia sinensis*), characterization

1. Introduction

The principal obligation of leather treated is to change over protein to non-putrescible cowhide by treating the previous with some tanning material. Dyeing is in this manner the initial step of activities which makes the leather alluring and appropriate for use [1]. The dyes are extensively characterized in to two which are Natural dyes and Synthetic dyes. Characteristic colors are utilized in shading nourishment, calfskin, fleece, silk, cotton and so forth since ancient time. As of late, with the expansion in the interest for items hued with common colors, the quantity of studies in regards to characteristic color has begun to expand [2]. Normal colors have wide practicality and tremendous potential. They are non-dangerous and non-unfavorably susceptible. The extraction and cleaning of characteristic colors improves with logical data [3]. Progressively over common colors are in every case ecofriendly. It beats the ecological contamination brought about by the engineered colors. In this way it keeps up a sound relationship among nature and human. Leather is a staggeringly magnificent characteristic texture which has been utilized for a large number of years in making articles of clothing, gloves, shoes, wallets, bags, upholstery, outdoor supplies, book covers and substantially more [4]. Manufactured colors are commonly utilized for the coloring of calfskin in businesses. Engineered colors are destructive to individuals and to nature as the greater part of these colors are cancer-causing also, unfavorably susceptible [5]. Tea is a blend of differently prepared leaves of one of the assortments of an evergreen bush, *Camellia sinensis*, which is the most famous non-mixed drink on the planet. Flavonoids, flavonols and phenolic acids make up around 30% of dried *Camellia sinensis* by weight. The majority of the polyphenols present are flavonols ordinarily known as catechism, with epicatechin and its subsidiaries being the most prevalent structures. Tea contains theaflavins and thearubigins as the head shading parts and both of such segments are having hydroxyl bunches in their structures in a position great for development of buildings with reasonable metal [6]. Green tea plants have been named *Camellia sinensis*. There are numerous imperative kinds of mixes present in green tea leaves, for example, amino acids, catechin, lipids, minerals, nucleotides, caffeine, starches, carotenoid substance, chlorophyll, some natural acids, saponins, polyphenols, unsaponifiable and numerous mixes with low unpredictability volatility [7]. Among the financially accessible normal colors, green tea has exceptional properties because of its broad use as beverage or refreshment. The utilization of green tea remove as a colorant has been accounted for extraordinarily for cellulose texture coloring. In any case, there is still space for research take a shot at advancement of states of color extraction from tea leaves for most extreme shading yield volatility. According to Bangladesh Tea Board data in 2017, Bangladesh produced 79 million kg tea against a consumption of nearly 86 million kg [8].

Thus, the present study aims to extract color from *Camellia sinensis* with water and ethanol solvent for the dyeing of leather, which will be environmentally and economically beneficial for the glorious leather sector. This approach causes minimal environmental and health impact. Furthermore, this is a cost-effective way for the dyeing of leather.

2. Materials and Methods

2.1 Materials

A wet blue goat skin were collected from Superex Leather Ltd., Uttar Dihi, Phultala, Khulna, Bangladesh and spent tea leaves were collected from nearby tea stalls of Fulbarigate, Khulna without any dirt and dust in a bucket. After that, the collected tea leaves were dried in sunlight to reduce the absorbed moisture. Finally, dried tea leaves were stored in a cleaned bucket. All commercial were collected from BASF Bangladesh Limited.

2.2 Preparation of leather for leather dyeing

Collected wet blue goat skin was packaged properly as if any moisture from atmosphere would not penetrate into the skin and any bacterial attack would not happen as well. In case of dyeing process, it was done with water extracted and ethanol extracted dye as well.

2.3 Extraction of Dyestuffs with water and ethanol solvent from spent tea leaves

Water and ethanol solvent were used to isolate natural dyestuffs from spent tea leaves. Initially, there are some proportion were fixed for optimum dyestuffs collections and these were like, 10:90; 15:85; 20:80; 25:75; 30:70;35:65 and 40:60 for tea leave: water. Similarly, the proportions of 10:90; 15:85; 20:80; 25:75; 30:70; 35:65 and 40:60 for tea leave: ethanol solvent. The expressed measure of dry spent tea leaves was absorbed water for around 10 minutes. After that, reflusked at 80°C for 2 hours. Amid this period the dyestuffs were extricated. The removed arrangement was sifted through Whatman filter paper no.1. The extended range of sizes includes 10 mm to 500 mm diameter circles and 460 mm × 570 mm sheets.

2.4 Characterization of the extracted dyestuffs

To decide the molecule size of the separated dyestuffs, two distinct sizes work were utilized for example-work 60 (Unique Standard Test Sieves, As per ISS 460) and work 200 (Unique Standard Test Sieves, As per ISS 460). The p^H of the sample was dictated by shaking 1 g of spent tea leaves in 100 ml of refined water for 16 to 24 hours pursued by SLC 13 [9]. Moisture content of the dyestuffs, tests of the tea leaves was first weighed and put in a broiler at 105°C for 24 hours. It was kept in desiccators for around 30 minutes and after that weighed and recorded. The volatile organic compound and ash content were determined after burning the dry solids in a furnace at 600 to 650°C for 2 hours. The samples were again sent to a desiccator for about 30 minutes and weighed.

2.5 FTIR Analysis

Fourier Transform Infrared Analysis was conducted by FTIR Spectroscopy (IR Tracer 100, Shimadzu) in Chemistry Lab. KUET. Some functional groups are liable for giving color these are called chromophore and another functional groups are contribute to color fixation, they are known as auxochrome.

2.6 Spectrophotometric analysis

A spectrophotometer (USVIS1922, Hunter Association Lab., Inc.) is an instrument that estimates the measure of light consumed by a sample. The spectrophotometer procedure is to measures light power as a component of wavelength. Spectrophotometer was utilized to recognize natural mixes by deciding the assimilation maxima which for most mixes and gatherings of mixes have particular fingerprints that is the thing that are called retention bends and pinnacles [10].

2.7 Physical and Chemical performance properties of the dyed leather

The developed dyed leather was conducted some physical and chemical tests for knowing the existing value of the dyestuffs. There are two scale used here for measuring the changes in color and stain [11]. Firstly, illuminate the surfaces with north sky light or equivalent source with illumination of 50 lumens/sq. ft. or more. The light should be incident upon the surfaces at approximately 45° and the direction of viewing approximately perpendicular to the plane of the surfaces [12].

3. Results and discussion

3.1 Recipe for Post tanning, dyeing process for manufacture of upper leather

Raw material: Wet blue of a goat skin

Shaved weight: 500 g

Table 1. Recipe for wetback

Reagents/Chemicals	%	Amount(g)	Remarks
Water	150	750	
Wetting agent	0.25	1.25	

Acetic acid *	0.50	2.5	Run 25 min, p^H 3.0-3.2
		Drain the float	

* Add through hollow axle, dilute (water: acid= 1:10)

Table 2. Recipe for rechroming

Reagents/Chemicals	%	Amount(g)	Remarks
Water	100	500	
Relugan GT50	0.5	2.5	Run 15 min
Chromosal B	3.0	15	
Sodium Formate	0.3	1.5	Run 40 min
Relugan RF	0.5	2.5	Run 30 min
Sodium Bicarbonate*	0.6	3.0	Run 120 min, pH 3.8-4.0
	Pile up and leave overnight		

* Sodium Bicarbonate dilute 1:20 and solely to avoid patchy

Table 3. Recipe for Basification

Reagents/Chemicals	%	Amount(g)	Remarks
Magnesium Oxide	0.6	3.0	Run 6 hr, Check pH 3.8-4.0
Busan 30L	0.1	0.5	Run 20 min, Drain/Pile up

Table 4. Recipe for Neutralization

Reagents/Chemicals	%	Amount (g)	Remarks
Water at 45ºC	100- 150	500-750	
Sellasol NG	1.5	7.5	Run 30 min, Check p^H
Sodium Formate	0.25	1.25	Run 320 min, Check p^H
	Check pH 5.0-5.2, Drain and wash		

Table 5. Retanning/ Dyeing/ Fat liquoring for water extracted dye

Reagents/Chemicals	%	Amount (g)	Remarks
Water at 50 ^{0}C	60	300	
Intan TP340	4.0	20	20 min
Relugan D	3.0	15	
SB 124	2.0	10	50 min
Dye*	0.75	3.75	40 min (Check penetration)
SB 124	1.25	6.25	
Lipsol LQ	2.0	10	60 min
Formic acid	2.0	10	10 min + 20 min
		Drain and wash	
Water at 60 ^{0}C	100	500	
Dye*	0.5	2.5	20 min
Formic acid	1.0	5	Overnight
Cationic Fat	1.0	5	15 min

Drain and Pile up

* Represents water and ethanol extracted dye respectively.

3.2 Extraction of Dyestuffs with water and ethanol solvent from spent tea leaves

Percentage of extracted dyestuffs based on water was maximum (1.3%) but yield was decrease on in higher ratio of spent tea leaves and water. Contrary, in the ration of 30:70, 35:65 and 40:60 of spent tea leaves and ethanol solvent yielding dyestuffs was not detected.

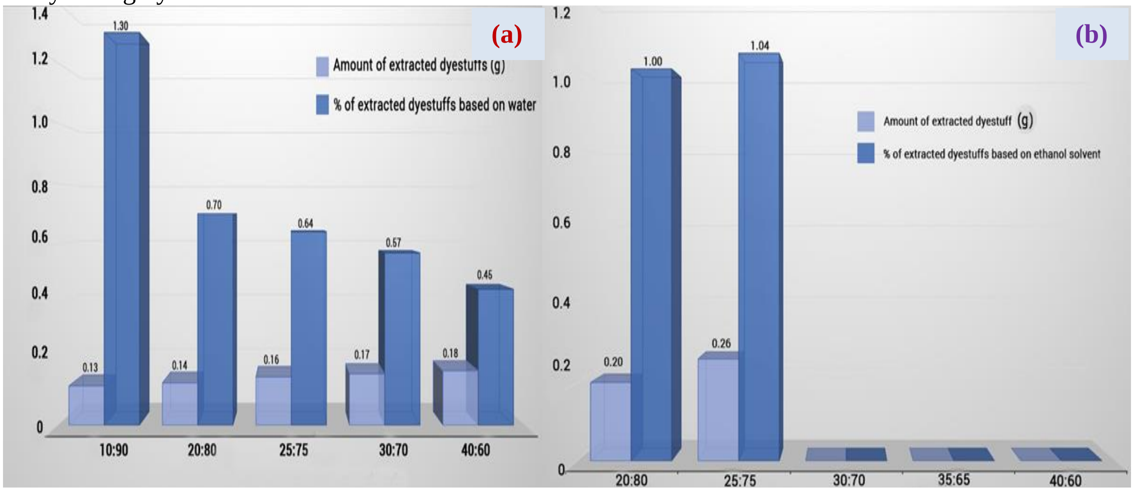

Fig. 1. Yield of dyestuffs in Ratio of - (a) Tea and water (g:ml) vs. (b) Tea and ethanol solvent(g:ml).

3.3 Characterization of the extracted dyestuffs

Table 6. Characteristics of the extracted dyestuffs with ethanol solvents and water

Parameters	Extracted dyestuff with ethanol solvent	Extracted dyestuff with water
Particle size (mm)	$\leq$ 0.25 and $\leq$ 0.074	$\leq$ 0.25 and $\leq$ 0.074
Moisture content	0.89%	1.33%
VOC content	3.64%	3.43%
Ash content	96.36%	96.57%
p^H	6.3	6.5

3.4 Spectrophotometric Analysis

Assessing the value of L, it has been revealed that maximum value of L* (52.67) and 52.34 for ethanol and water treated dyestuffs respectively. Observing a* values, minimum value of a* 3.90 (red) was found for ethanol and 6.81 for water treated dyestuffs leather sample. Analyzing b* values, maximum value of b* (9.33) for water treated dyestuffs leather sample whereas minimum value of b* (8.30). Again, dL*, da*, db* are measured for ethanol sample (Standard) based on water sample (Base). The value of dL*, da*, db* found for ethanol sample are 0.33, -2.91 & 1.03. Finally, ethanol treated dyestuffs leather sample fails compared to water treated dyestuffs leather sample for the stated ID. For spectral plot-1, water treated dyestuffs cowhide test is taken as a base and ethanol treated dyestuffs calfskin test is taken as a standard dependent on water treated dyestuffs leather sample. So, the reflectance performance of the leather dyed with water extracted dyestuffs is better than the leather dyed with ethanol extracted dyestuff.

3.5 FTIR Analysis

It was analyzed the functional groups at the wavenumbers 3344.57 cm^{-1}, 2922.16 cm^{-1}, 1604.77 cm^{-1} and 1031.92 cm^{-1} are N-H, C-H, C=C and C-F respectively for the water extracted dyestuffs. It was also analyzed the functional groups at the wavenumbers, 2918.30 cm^{-1}, 1608.63 cm^{-1} and 1199.72 cm^{-1} and 1033.85 are C-H, C=C, C-O and C-F respectively for the water extracted dyestuffs.

3.6 Physical and Chemical performance properties of the dyed leather

3.6.1 Test for bleeding

No stains or dark edge are formed on the upper for both leathers, dyed with water and ethanol solvent treated dyestuffs. So, both leathers do not contain unreacted dyes.

3.6.2 Test for water-fastness

There is no difference in thickness of water and ethanol solvent treated dyestuffs which indicates that the leather, dyed with both dyestuffs is water fastness.

3.6.3 Resistance to water-stain

No stain is developed. So, both dyed leathers (water extracted dyestuffs and ethanol solvent extracted dyestuffs) are good water-stain resistant.

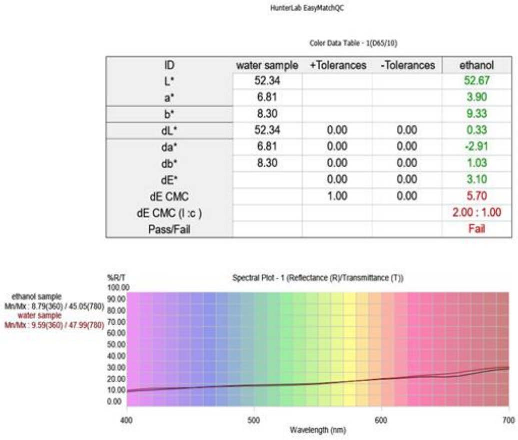

Fig. 2. Graphical representation of spectrophotometric analysis

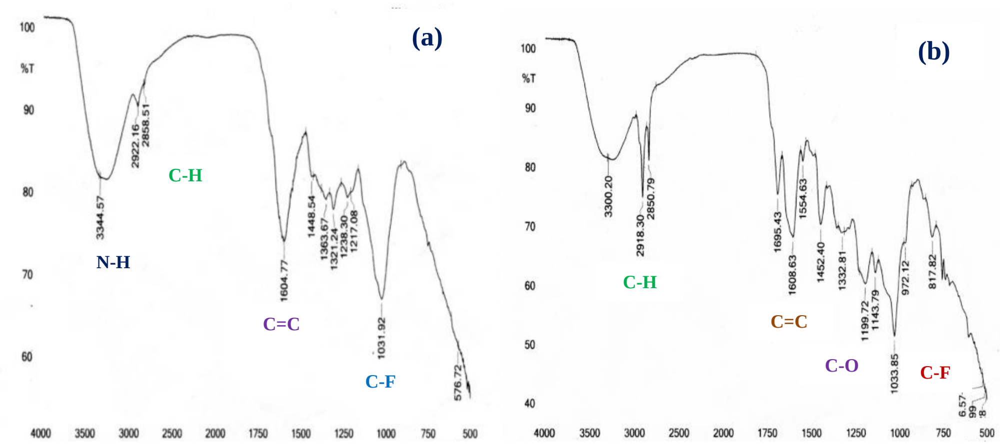

Fig. 3. FTIR analysis for the dyestuffs: (a) extracted with water (b) Extracted with ethanol solvent.

3.6.4 Wet and dry Rub fastness

Result of dry and wet rub fastness of the dyed leather with extracted dyestuffs from spent tea leaves was good according to the gray scale rating (4/5 to 5).

Table 7. Dry rub fastness test for change in color

Sample	Cycles				
	1024	2048	4096	8192	16384
Leather [a]	5	5	5	5	4/5
Leather [b]	5	5	5	4/5	4/5

[a]Water extracted; [b]Ethanol extracted leather

Table 8. Wet rub fastness test for staining

Sample	Cycles				
	1024	2048	4096	8192	16384
Leather [a]	5	5	5	4/5	4/5
Leather [b]	5	5	5	5	4/5

[a]Water extracted; [b]Ethanol extracted leather

3.6.5 Resistance to solvents

The result of resistance to solvent(Benzene, ketone ester and so on) of resultant dyed leather was also good in respect of gray scale rating(4/5 to 5).

Table 9. Dry rub fastness test for change in color

Sample	Cycles				
	1024	2048	4096	8192	16384
Leather [a]	5	5	5	5	4/5
Leather [b]	5	5	5	5	5

[a]Water extracted; [b]Ethanol extracted leather

Table 10. Wet rub fastness test for staining

Sample	Cycles				
	1024	2048	4096	8192	16384
Leather [a]	5	5	5	5	5
Leather [b]	5	5	5	5	4/5

[a]Water extracted; [b]Ethanol extracted leather

The result of resistance to plasticizer and light fastness were also good in respect of obtaining rating from gray scale value (4/5 to 5).

Table 11. Gray scale assessment for staining (plasticizer)

Sample	Cycles				
	1024	2048	4096	8192	16384
Leather [a]	5	5	5	5	5
Leather [b]	5	5	5	5	4/5

[a]Water extracted: [b]Ethanol extracted leather

Table 12. Gray scale assessment for staining (light fastness)

Sample	Cycles				
	1024	2048	4096	8192	16384
Leather [a]	5	5	5	5	4/5
Leather [b]	5	5	5	5	4/5

[a]Water extracted: [b]Ethanol extracted leather

4. Conclusion

It has been discovered that the required logical examinations and efficient reports on coloring of leather with common colors are as yet lacking. In this exploration, coloring tests were done utilizing normal colors from spent tea leaves (*Camellia sinensis*) on leather test. The color was extricated utilizing water and ethanol dissolvable. A correlation was performed between the two-colored cowhide tests. It was explored that the leather colored with water treated dyestuffs demonstrated better an incentive in Spectrophotometer test and was resolved better unique compound execution contrasted with leather colored with water treated dyestuffs. Moreover, utilization of spent tea leaves (*Camellia sinensis*) as a colored a material lessen the import cost of engineered color and limits wellbeing and ecological perilous impacts. In addition, this methodology deals with the transfer of spent tea leaves (*Camellia sinensis*) as significant item.

5. Acknowledgement

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