Natural Approach to Improving Light Fastness of a Leather Dyed with a Microbial Colorant

by

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Abstract

Microbial colorants are becoming popular because they have the potential to overcome disadvantages of synthetic and natural dyes. However, for commercialization, their after dyeing characteristics especially light fastness needs to be improved preferably using natural agents to make the complete dyeing process eco-benign. Therefore, in this study, eco-friendly tannins and antioxidants were employed to improve the light fastness of wet blue goat nappa skin dyed with the colorant of *Penicillium minioluteum*. Their effect on color strength, fastness properties, and mechanical strength were also assessed. As a result, the only sample treated with tannic acid before dyeing showed moderate light fastness with improved perspiration, tear, and tensile strength. Further improvement in light fastness was recorded when tannic acid treated and dyed sample was padded with vitamin E - gum acacia emulsion (10% vitamin E, 10% glycerol, 4.5% gum acacia powder). Here, improvement in perspiration and rub fastness was also noticed.

Introduction

Colorants from microbes are gaining popularity due to their advantages over natural and synthetic dyestuffs and wide applicability in food, medicinal, beauty, textile, and leather.[1, 2, 3] In textiles, these colorants have been reported to dye with good uptake and good to moderate wash, rub, perspiration, and light fastness.[4, 5] However, this might not be the case for all the dyestuffs obtained from microbes. According to Joshi *et al.*[6] most of these colorants are fugitive and prone to degradation. Shirata *et al.*[7] in their study have reported poor light fastness of *Janthinobacteriun lividum* colorant on silk, cotton, wool, nylon, vinylon, and acetate. Like several other natural dyes,[8] microbial colorants also have light fastness issues that need to be catered using different agents preferably natural rather harmful synthetic mordants.[9] After treatment with tannins[10] or antioxidants like tocopherols and vitamin C can be used to retard fading.[11] Apart from these, peel of pomegranate and orange having antioxidant properties are potential agents helpful in scavenging free radicals.[12, 13] For leather application, vitamin E and glycerol have also been reported to increase UV and heat resistance.[14]

In this study, wet blue goat nappa skin that showed good rub fastness with poor light fastness with the red colorant of *Penicillium minioluteum* was treated with different natural eco-benign agents such as tannins and antioxidants to improve its photofading.

Materials and Methods

Material

Dyed Wet Blue Goat Nappa Skin

50 mL red color filtrate of *P. minioluteum* obtained after 28 days from sabouraud broth cultured at 15°C ± 2°C under static incubation was used to dye 2X2 cm^2 samples of neutralized wet blue goat nappa skin of 0.8 mm thickness sourced from GB Leathers, Karol Bagh, New Delhi, India. Dyeing was carried out in a static water shaker bath (NSW, India) with 50 mL colored filtrate at 80°C for 60 min at pH 2.0 (altered using 85% formic acid (Molychem, India) after 30 min of dyeing). After dyeing application of 2% fatliquoring agent Coripol®DX-3080 (TFL Quinn, India) at 60°C was carried out in the same bath for 30 min.

Methods

Treating Leather with Tannins

Extract of tannins was obtained using modified procedures as mentioned in Table I. Neutralized samples of wet blue goat nappa skin before dyeing and dyed samples were treated with the prepared extract at 60°C for 60 min in static water shaker bath.

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Treating Dyed Leather with Antioxidants

Extract of antioxidants was obtained using modified procedures as mentioned in Table II. Prepared extract of the pomegranate and the orange rind was then used to treat dyed samples at 60°C for 60 min in static water shaker bath. While, a solution of vitamin C (1 g/L) (Thomas Baker, India) was prepared in distilled water and applied on dyed wet blue goat nappa skin at 70°C for 30 min in the same bath.[11]

Testing Treated Samples for Light Fastness and Other Properties

Samples treated with tannins and antioxidants were tested for light fastness (ISO 105 BO2), rub fastness (SATRA TM 167: 2001), perspiration fastness (SATRA TM 335: 1994), tensile strength (SATRA TM 43: 2000), and induced tear strength (SATRA TM 162: 1992). Additionally, color depth (K/S) using a computer color matching system (Macbeth, Color Eye 3100, USA) was also computed and compared.

Treating with Vitamin E - Gum Acacia Emulsion

Best sample showing improved fastness was further treated with a modified recipe of Liu *et al.*[14] in which gum acacia (Fischer Scientific, India) was used as an emulsifier in different concentrations viz. 1.5%, 3%, and 4.5% to make three separate emulsion with 10% of vitamin E (CDH, India) and 10% glycerol (Molychem, India). For emulsion, all ingredients were stirred for 6 h using a laboratory stirrer (Remi Motors, India) kept at 200 rpm. The prepared emulsions were stored in a refrigerator for

Table I

Procedure for preparation of natural and commercial tannin extract.

Tannin	Amount (%)	Preparation of tannin extract	Reference
Catechu	2	Solid pieces of catechu were ground using pastel and mortar. The extract was prepared by boiling 2 g catechu powder in 100 mL distilled water for 1 h. After 1 h, prepared extract was strained using Whatman® qualitative filter paper, Grade 1.	15, 16
Tea leaves	2	The extract was prepared by boiling 2 g tea leaves in 100 mL distilled water for 30 min. The mixture was allowed to stand for 15 min after which it was strained using Whatman® qualitative filter paper, Grade 1.	17
Coffee seed	2	Same as catechu	9
Tannic acid (Merck, India)	2	The extract was prepared by boiling 2 g tannic acid powder in 100 mL distilled water using a 250 mL beaker (Borosil, India) until a clear solution was obtained. The prepared extract was then strained using Whatman® qualitative filter paper, Grade 1.	18, 15

Table II

Procedure for preparation of natural antioxidant extract.

Antioxidant	Amount (%)	Preparation of extract or solution	References
Pomegranate rind	2	Fresh pomegranate rind pieces were separated from the fruit, dried in an oven (Ambassador, India) at 40°C and converted into powder using pastel and mortar. The extract was prepared by boiling 2 g of rind powder in 100 mL distilled water for 1 h after which it was strained using Whatman® qualitative filter paper, Grade 1.	15, 19, 16
Orange rind	2	Similar procedure as given above was employed for obtaining orange rind powder. While, the extract was prepared by keeping 2 g powdered rind in 100 mL distilled water in a 150 mL conical flask (Borosil, India) for 24 h in a rotary shaker (Orbitek, Scigenics Biotech Pvt. Ltd., India) at 150 rpm. After an hour of shaking, solution was strained using Whatman® qualitative filter paper, Grade 1.	20

24 h after which they were stirred again for 2 h. Application of emulsion was carried out by spraying and padding method. In spraying method, the emulsion was sprayed twice over the samples using an electric spray gun (Arrow Textile Spot Cleaning Gun CM-16, India). While in padding method, dyed samples were padded three times with the prepared emulsion using a laboratory padding mangle (Electronic & Engineering Company, India). After employing both the methods, assessment of light fastness and other properties was carried out and compared.

Results

Treatment with Tannins and Antioxidants

Treated sample with tannic acid before dyeing showed a significant increase in color depth (K/S) i.e. 5.20 as compared to the color depth of the control dyed sample that was recorded as 3.80 as shown in Table III and Figure I. Further, after exposure to ATLAS Ci 3000+ Weather-Ometer and Fade-Ometer, an improved light fastness i.e. moderate fading (grade 2-3) was recorded as compared

Table III

K/S of samples treated with tannins, antioxidants, and vitamin E - gum acacia emulsion.

Name of agent		Treatment	Color depth (K/S)
Control dyed sample			3.80
Tannins	Catechu	Before dyeing	3.90
		After dyeing	3.88
	Tea leaves	Before dyeing	3.99
		After dyeing	3.96
	Coffee seed	Before dyeing	3.98
		After dyeing	3.98
	Tannic acid	Before dyeing	5.20
		After dyeing	5.17
Antioxidants	Pomegranate rind	After dyeing	3.82
	Orange rind	After dyeing	3.80
	Vitamin C	After dyeing	3.79
Vitamin E - Gum acacia emulsion	10% vitamin E + 10% glycerol + 1.5% gum acacia	Spraying	5.68
		Padding	6.98
	10% vitamin E + 10% glycerol + 3% gum acacia	Spraying	7.23
		Padding	9.03
	10% vitamin E + 10% glycerol + 4.5% gum acacia	Spraying	10.01
		Padding	12.00

to other samples (Table IV). Perspiration fastness was also seemed to be improving with the application of tannic acid before dyeing. While dry and wet rub fastness remained unchanged for all the tannin treated samples (Table IV). Also, tannic acid treated sample before dyeing showed a marked improvement in tensile and induced tear strength as compared to the control dyed and other tannin treated samples (Table V). Apart from tannins, when antioxidant extracts were applied, no significant change in any of the properties was observed (Table III, VI and V).

Treatment with Vitamin E - Gum Acacia Emulsion

Tannic acid treatment before dyeing showed improved fastness on the dyed sample. However, the fastness rating was not appropriate to be accepted according to international norms. Therefore, further treatment of tannic acid treated and dyed sample was carried out with a modified emulsion of vitamin E with gum acacia that originally was emulsified with sodium dodecyl sulfate (SDS) for improving color fading in a study by Liu *et al.*[14]

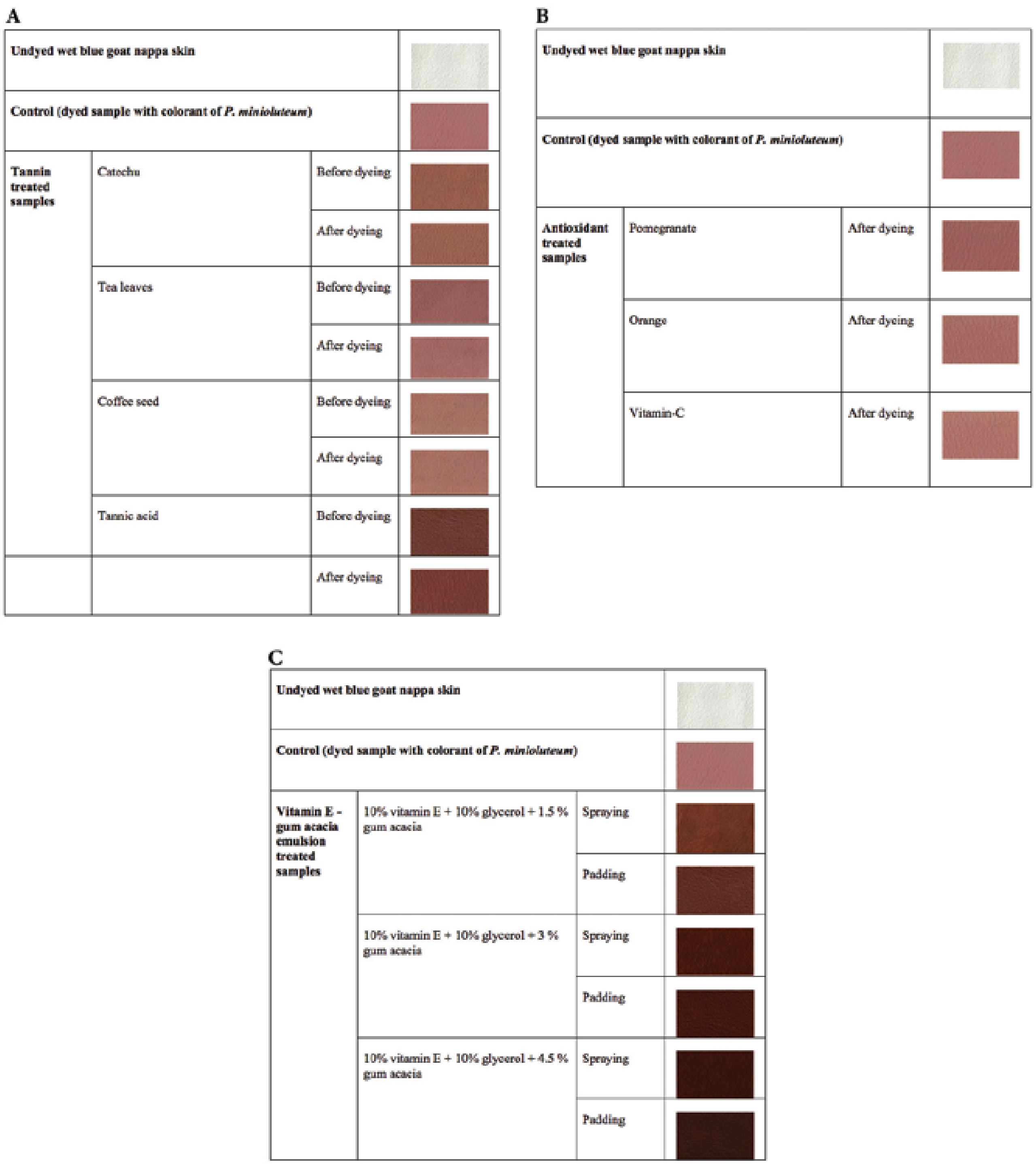

Figure 1. Wet blue goat nappa samples treated with (a) tannins, (b) antioxidants, and (c) vitamin E - gum acacia emulsion.

Table IV
Fastness of tannin treated wet blue goat nappa skin samples.

Type of fastness		Treatment		Control dyed sample[a]	Tannins[a]			
					Catech seed	Tea leaves	Coffee seed	Tannic acid
Light		Before dyeing		-	1-2	1	1	2-3
		After dyeing		1	1-2	1-2	1	2
Rub	Dry	Before dyeing	Color change	-	5	5	5	5
			Color staining	-	3	3	3	3
		After dyeing	Color change	5	5	5	5	5
			Color staining	3	3	3	3	3
	Wet	Before dyeing	Color change	-	5	5	5	5
			Color staining	-	3	3	3	3
		After dyeing	Color change	5	5	5	5	5
			Color staining	3	3	3	3	3
Perspiration	Alkali	Before dyeing	Color change	-	2-3	2-3	2-3	2-3
			Color staining	-	2	2-3	2	3
		After dyeing	Color change	2-3	2-3	2-3	2-3	2-3
			Color staining	2	2	2	2	2-3
	Acid	Before dyeing	Color change	-	2-3	2-3	2-3	2-3
			Color staining	-	2-3	2-3	2-3	3
		After dyeing	Color change	2-3	2-3	2-3	2-3	2-3
			Color staining	2-3	2-3	2-3	2-3	2-3
	Water	Before dyeing	Color change	-	2-3	2-3	2-3	3
			Color staining	-	2-3	2-3	2-3	3
		After dyeing	Color change	2-3	2-3	2-3	2-3	2-3
			Color staining	2-3	2-3	2-3	2-3	2-3

[a] These ratings are based on SDCE grey scale having 1 to 5 ratings including half steps for assessing change in color (A02) and color staining (A03)

Table V

Tensile and tear strength of tannins and antioxidants treated samples.

Treatment		Tensile strength (N/mm^2)		Tear strength (N/mm)	
		Direction A	Direction B	Direction A	Direction B
Control dyed sample		41	51	4.92	3.90
Catechu	Before dyeing	41	51	4.92	3.90
	After dyeing	41	51	4.93	3.91
Tea leaves	Before dyeing	41	51	4.93	3.92
	After dyeing	41	51	4.92	3.90
Coffee seed	Before dyeing	41	51	4.92	3.91
	After dyeing	41	51	4.91	3.92
Tannic acid	Before dyeing	46	59	5.32	4.20
	After dyeing	42	57	5.01	4.00
Pomegranate rind	Before dyeing	41	51	4.92	3.91
Orange rind	Before dyeing	41	51	4.92	3.90
Vitamin C	Before dyeing	41	51	4.91	3.91

Table VI

Fastness of antioxidant treated wet blue goat nappa skin samples.

Type of fastness			Control dyed sample[a]	Antioxidants[a]		
				Pomegranate rind	Orange rind	Vitamin C
Light			1	1-2	1	1
Rub	Dry	Color change	5	5	5	5
		Color staining	3	3	3	3
	Wet	Color change	5	5	5	5
		Color staining	3	3	3	3
Perspiration	Alkali	Color change	2-3	2-3	2-3	2-3
		Color staining	2	2	2	2
	Acid	Color change	2-3	2-3	2-3	2-3
		Color staining	2-3	2-3	2-3	2-3
	Water	Color change	2-3	2-3	2-3	2-3
		Color staining	2-3	2-3	2-3	2-3

[a]These ratings are based on SDCE grey scale having 1 to 5 ratings including half steps for assessing change in color (A02) and color staining (A03)

Table VII
Fastness of samples treated with vitamin E - gum acacia emulsion.

Type of fastness		Application method		Emulsion[a]		
				10% vitamin E + 10% glycerol + 1.5% gum acacia	10% vitamin E + 10% glycerol + 3% gum acacia	10% vitamin E + 10% glycerol + 4.5% gum acacia
Light		Spraying		2-3	2-3	2-3
		Padding		2-3	2-3	3
Rub	Dry	Spraying	Color change	5	5	5
			Color staining	3	3	3
		Padding	Color change	5	5	5
			Color staining	3	3	4
	Wet	Spraying	Color change	5	5	5
			Color staining	3	3	3
		Padding	Color change	5	5	5
			Color staining	3	3	4
Perspiration	Alkali	Spraying	Color change	2-3	2-3	3
			Color staining	3	3	3
		Padding	Color change	2-3	3	3
			Color staining	3	3	3
	Acid	Spraying	Color change	2-3	3	3
			Color staining	3	3	3
		Padding	Color change	2-3	2-3	3
			Color staining	3	3	3
	Water	Spraying	Color change	3	3	3
			Color staining	3	3	3
		Padding	Color change	3	3	3
			Color staining	3	3	3

[a] These ratings are based on SDCE grey scale having 1 to 5 ratings including half steps for assessing change in color (A02) and color staining (A03)

Table VIII
Tensile and tear strength of treated samples with vitamin E - gum acacia emulsion.

Emulsion	Application method	Tensile strength (N/mm^2)		Tear strength (N/mm)	
		Direction A	Direction B	Direction A	Direction B
10% vitamin E + 10% glycerol + 1.5% gum acacia	Spraying	46	59	5.31	4.21
	Padding	46	59	5.31	4.21
10% vitamin E + 10% glycerol + 3% gum acacia	Spraying	46	59	5.32	4.20
	Padding	46	59	5.32	4.21
10% vitamin E + 10% glycerol + 4.5% gum acacia	Spraying	46	59	5.32	4.20
	Padding	46	59	5.32	4.20

According to them, application of strong anionic detergent like SDS causes damage to the protein structure of collagen fibrils by the action of negatively charged sulfate groups, thereby decreasing the protective action of antioxidant and humectant mixture. Therefore, they have suggested the use of more eco-friendly emulsifiers like gum acacia that cause no harm to the leather structure.

Out of the three percentages of gum acacia powder, only higher percentage i.e. 4.5% applied using padding method was found to be increasing the light fastness rating to grade 3 (Table VII). Furthermore, Vitamin E emulsion having 4.5% of gum acacia showed remarkably high color depth i.e. 12.00 even more than tannic acid treated sample (Table III and Figure I). Rub fastness was also improved (grade 4) and perspiration fastness was recorded as moderate (grade 3). However, no further improvement in strength was reported after application of this emulsion (Table VIII). On the contrary, samples treated using spraying method yielded no fruitful results.

Discussion

Dyed leather with the colorant of *Penicillium minioluteum* showed poor light fastness because of two reasons. Firstly, due to the nature of leather itself. Most of the leather substrates exhibit poor light fastness when dyeing is carried out with acid dyes. However, this problem is not there in case of textile protein fibers. Textile fibers like wool have sulfide linkages that act as radical scavengers that help in stopping the mechanism of auto-oxidation. Whereas, in leather, auto-oxidation occurs as a mechanism that is initiated majorly by energy-rich UV radiations and sometimes due to visible light and IR radiations from the sun. This process is catalyzed by chemicals or impurities present in the environment that acts as radical initiators. In the presence of these energy-rich radiations, chemical compounds split to form free radicals. Free radicals are extremely reactive and thus, combine with atmospheric oxygen to create peroxide radicals. These peroxide radicals then react with organic constituents of leather such as fat liquors, finishing agents, colorants or dyes, and results into the deterioration of color by yellowing or bleaching the color. Even the tanning agent and tanned collagen can be destroyed if exposed for a longer duration. Apart from this, dry and moist heat have also been considered to cause fading and ageing in leather. Leather requires high moisture content i.e. 15% as compared to other protein fibers like wool that requires only 8% of moisture content. Substrates requiring high moisture content are always prone to fading when exposed to heat, as heat cause thermal deterioration in such cases.[21, 22, 23]

The second reason is the physical state of the dye that affects fading. If the dye molecule is smaller and finely dispersed within the fiber, like *Penicillium minioluteum* colorant, fading will be faster as compared to larger molecules of dye. As only a small surface area of a dye having larger aggregates is exposed to air and sunlight.[11] Due to these underlined reasons, different agents were employed in the present study to improve the light fastness characteristics of dyed wet blue goat nappa skin with the colorant of *Penicillium minioluteum*.

Treatment with Tannins and Antioxidants
As a result of tannin treatment before and after dyeing, the original shade of dyed leather was found to be changed a little

bit. According to NIIR Board of Consultants and Engineers[15] tanning agents are ones that help in retanning and coloring the leather substrate. However, the significant color change i.e. from red to reddish brown was only observed on tannic acid treated samples before dyeing. Not only change in color was maximum, light fastness, perspiration fastness, and strength characteristics were also greater in the tannic acid sample treated before dyeing as compared to others.

Tannic acid is a polyphenolic agent that acts as a retanning agent. In general, retanning agents are applied before dyeing especially in the case of acid dyes to yield good color uptake. Studies have revealed application of tannins to increase the color depth and light fastness of many natural dyes.[15,16,24] Tannic acids have been reported to possess antioxidant and radical scavenging properties that help in preventing or delaying oxidation of dye chromophore by inhibiting the propagation of oxidizing chain reactions.[24, 25] Apart from prevention to oxidation, retanned leather using tannic acid have been found to be effective in maintaining the harmful chromium VI and free formaldehyde levels that form on leather during processing. Additionally, improvement in some physical characteristics like tear and tensile strength was also reported in studies on tannic acid.[26, 27]

Hence, it is can be concluded that this commercial tannin is not only helpful in improving light fastness properties of microbial dyed leather but also useful in enhancing the color depth, physical characteristics, and suppresses the phenomenon that helps in decreasing the formation of harmful components during leather processing.

Treatment with Vitamin E - Gum Acacia Emulsion

Further improvement in light fastness was carried out with vitamin E - gum acacia emulsion to make this technology more acceptable. As a result, an emulsion having 4.5% of gum acacia powder applied using padding method helped in increasing light fastness to an internationally accepted grade. This increase was attributed to the presence of Vitamin E or α-tocopherol that has been found to be an excellent antioxidant agent for improving the light fastness of dyed leather. It has also been reported to prevent damage to leather strength or aging that occurs due to UV radiations and heat. Further, the addition of glycerol helped in preventing over-drying of leather as it was acting like a humectant. It, in turn, assisted in maintaining the moisture of leather required for preventing color damage by heat. Moreover, it also improved UV and heat resistance that protected wet blue goat nappa skin from aging.[14, 22, 23] Also, a coating of this emulsion with glycerol helped in overcoming the hardening effect of leather fibers due to the application of tannic acid. Besides, gum acacia in addition to emulsification assisted in stabilizing the emulsion for longer. It also considered as natural biopolymer that possess antioxidant properties helpful in preventing fading against the light.[28, 29] Thus, the triple action of vitamin E, gum acacia, and glycerol helped in suppressing photooxidation phenomenon and heat deterioration of color.

Additionally, darkening of color from reddish brown to brown was also observed probably due to the extra coating of oily Vitamin E, and gum acacia over tannic acid treated and dyed sample that helped in darkening the color shade. According to Rao *et al.*[30] around 80% of manufactured leather garments and upper leathers are dyed with either black or brown color. Therefore, in a way it is good, as the treated leather with improved properties will be highly acceptable in the market. Further testing revealed an increase in perspiration rating with a slight improvement in rub fastness.

Conclusion

In the present study, naturally eco benign agents have been tried to improve the light fastness property of a leather namely wet blue goat nappa skin dyed with an eco friendly colorant obtained from *Penicillium minioluteum*. Out of all tannins and antioxidants, only tannic acid treated sample before dyeing showed moderate light fastness with improved color depth, perspiration, tear, and tensile strength. Further improvement in light fastness (grade 3) was recorded when tannic acid treated and dyed sample was padded with vitamin E - gum acacia emulsion (10% vitamin E, 10% glycerol, 4.5% gum acacia powder). Here, improvement in color depth, perspiration, and rub fastness was also noticed.

With the moderate to good fastness towards light, rub, and perspiration, chances of acceptability of this naturally dyed leather have made increased for the leather industry. Altogether, it can be concluded that these agents are eco-friendly multifunctional agents that are capable of improving after dyeing properties including the color of the dyed leather. Therefore, the use of these agents should be carried out and explored more for even better application on leather.

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