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Eco-benign wet processing of leather: From dyeing to after treatment

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Abstract
Microbial colorants are gaining popularity in almost all the industrial sectors viz. Food, textile, paper, agriculture, pharmaceutical, and cosmetics. As compared to synthetic and natural dyeing, this technology is more commercial, reliable, scalable, predictable, and manageable. Leather dyeing industry is also seeking novel ways of green processing. As a solution, in this study, a microbial colorant namely *Penicillium minioluteum* producing maximum color under optimized conditions (medium-sabouraud; pH-5.6; temperature-15 °C; time-20 days; incubation-static) was used for dyeing wet blue goat nappa skin leather. Leather dyeing conditions were standardized (pH-2.0 altered after 30 min of dyeing, temperature-80 °C and time- 60 min) on the basis of highest color depth and percentage dye exhaustion. Dyed samples showed good rub fastness with moderate to remarkable fading to light and perspiration with no change in tear and tensile strength. The issue of poor light fastness was dealt with tannic acid and vitamin E-gum acacia emulsion. After treatment, improvement in light, perspiration, and rub fastness; tear and tensile strength; and color depth was noted. Darkening of color from red to brown was greatly appreciated as black and brown are popular leather colors. Additionally, a patch sensitivity test of dyed sample exhibited no allergy on human skin.

Keywords: *Penicillium minioluteum*; colorant; wet blue goat nappa skin; dyeing; fastness; patch test

1. Introduction
Dyeing is an important consideration for imparting color that is carried out in post-tanning operations. Widely synthetic dyes are used in leather dyeing, out of which 70% are acid dyes followed by direct dyes that hold about 20% of the total dye share (Hunger, 2002; Zengin *et al*., 2012) [10, 40]. Chemically all these dyes belong to azo, anthraquinone and triphenylmethane dyes (Hudson & Britten, 2008; Puntener, 2000) [9, 24]. German Ordinance on Materials and Articles has identified 20 carcinogenic aryl amines that have been reported to cause cancer and therefore are prohibited for use and manufacture of dyes. In a latest study, 22 amines have been identified and restricted for use by EU and REACH regulations (Sivakumar *et al*., 2009) [35]. It is believed that, more number of amines are likely to be added in this list if further toxicological tests are conducted on these types of dyes (Rao *et al*., 2002; Velmurugan *et al*., 2009) [27, 37]. These dyes are difficult to degrade and therefore are harmful as effluent. According to statistics, about 10–35% of dyes used for leather are lost in the effluent during the dyeing process (Rai *et al*., 2005; Rao, 2010) [25, 26]. Due to these environmental problems, health related issues and regulations with regard to synthetic dyes, an increase in demand for natural dyes for leather have been reported in many studies (Onem *et al*., 2011; Selvi *et al*., 2012; Sivakumar *et al*, 2009; Velmurugan *et al*., 2009) [22, 29, 35, 37]. This is because they are non-toxic, non-allergic, non-carcinogenic, biodegradable and higher compatibility with the environment (Rao *et al*., 2002) [27]. Several colors have been screened from different plant and animal based organic sources having moderate to good fastness properties (Musa *et al*., 2009; Rao, 2010; Selvi *et al*., 2012) [17, 26, 30]. However, they have not been commercialised due to their limited availability, instability, dependency on season, environmental conditions and restricted flora and fauna (Shahid *et al*., 2013) [32]. Secondly, these dyes are extremely costly, due to tedious and time consuming extraction procedures that yield very less dye which costs about USD 1/g and therefore used only for high-value-added natural-coloured garments (Siva, 2007; Velmurugan *et al*., 2009) [34, 37].

Recently, many studies have been carried out for exploring the color producing ability of various microbes like fungi, bacteria, yeast and algae. Microbial colorants are independent of season, geographical conditions, requires no land and controlled production is possible with predictable yield in large fermenters unlike plant based natural dyes (Shirata *et al*., 2000) [33]. When compared to petroleum based synthetic dyes they are found to be biodegradable, non-toxic, easy to dispose off and thus have higher compatibility with the environment (Poorniammal *et al*., 2013; Sengupta & Singh, 2003) [23, 31]. They also have wide color palette like red, blue, yellow, green, pink, orange, purple, black, brown, grey, creamish, bronze etc. which is not possible in case of natural dyes (Joshi *et al*., 2003) [11]. Most of these dyes have been reported to have good fastness properties. In a nutshell, this technology seems more scalable, reproducible and cost effective. Due to these listed advantages over natural and synthetic dyes, they have been considered important for different kinds of industries like food, pharmaceutical, cosmetic and textile industry (Dharmaraj *et al*., 2009; Venil *et al*., 2013) [5, 38]. However, their application has not been explored much where leather is concerned. Only Velmurugan *et al*. (2009) [37] studied the dyeing potential of five fungal pigments on pre tanned leather samples.

In this study, optimized colorant of *Penicillium minioluteum* was used to dye goat nappa leather. Conditions of dyeing were standardized and various after dyeing assessments were carried out. Poor light fastness was also improved using natural agents. Toxicity test was carried to ensure safety of the colorant used for dyeing.

2. Methodology

2.1 Cultivation of color

For production of color *Penicillium minioluteum* was cultured in haffkine flasks (3000 mL) having 1.5 L sabouraud dextrose broth (dextrose 20 g/L; peptone 10 g/L; pH 5.6). Aseptically ten to eleven purified mycelial disks (1 mm) bored from purified PDA plates were inoculated in liquid sabouraud dextrose medium. All culture flasks were then kept at 15 ºC ± 2 ºC for 20 days in static incubation. After incubation, the crude filtrate or supernatant was filtered using pre weighed Whatman GF/C microfiber filter paper (47 mm).

2.2 Leather dyeing and its standardization

Leather samples measuring 1 x 1 inch^2 were dyed in a static water shaker bath (NSW, India) using 50 mL of crude colorant to standardize the dyeing parameters. Before dyeing, samples were neutralized with 1% borax solution in water shaker bath set at 30 ºC for 30 min. The end point of neutralization was assessed by dropping bromocresol green indicator that turns the outside layers i.e. grain and flesh blue in color (pH 6.0) leaving the central layer greenish yellow (pH 4.0 to 4.5). Neutralized samples were washed at 45 ºC for 5 min to remove undesirable matter. After neutralization, dyeing was carried out at different pH viz. 2.0, 3.0 and 4.0 (altered after 30 min of dyeing using 85% formic acid (Molychem, India). After 30 min, dyeing at maintained pH was carried out for further 20 min. Standardized pH was later used to standardize time (20, 40 and 60 min) and temperature (60 °C, 70 °C and 80 °C).

For standardizing the pH, time, and temperature of dyeing, color depth (*K/S*) and color values (*L*, a*, b*, C* and H**) were recorded via computer color matching system (Macbeth, Color Eye 3100, USA). Dyeing parameters showing highest *K/S* value and percentage dye exhaustion (1) were considered together for dyeing.

$$E\,(\%) = \frac{O.D^1 - O.D^2}{O.D^1} \times 100 \qquad (1)$$

Here, $O.D^1$ represent the optical density of the dye liquor before dyeing, and $O.D^2$ represent the optical density of the spent dye liquor after dyeing recorded using spectrophotometer (Visible spectro 105, Systronic, India) at λ_{max} 490 ± 5 nm.

After dyeing all samples were washed at 60 °C for 5 min followed by treatment with 2% Coripol®DX-3080 (fatliquoring agent) at 60 ºC for 30 min. Samples were again rinsed at 60 ºC for 5 min.

2.3 Testing of dyed samples

Final dyed samples with standardized pH, time and temperature were subjected to different fastness tests like dry and wet rub fastness (SATRA TM 167: 2001), light fastness (ISO 105 BO2) and color fastness to perspiration (SATRA TM 335: 1994). Tensile strength (SATRA TM 43: 2000) and induced tear strength (SATRA TM 162: 1992) were also tested. All Testing was conducted at the physical laboratory of International Testing Centre, FDDI, Noida, India accredited by PFI Germany, BIS India and SATRA UK and certified ISO 17025 by Deutschen Akkreditierungs Rat (DAR) of Germany.

2.4 Improving light fastness of dyed leather using natural agents

Dyed leather was treated with tannic acid extract (prepared by boiling 2 gm tannic acid powder in 100 mL of distilled water) at 60 °C for 60 min in static water shaker bath. Tannic acid treated sample was later on padded three times using a laboratory padding mangle (Electronic & Engineering Company, India) with the prepared emulsion of vitamin E and gum acacia (10% vitamin E, 10% glycerol, 4.5% gum acacia powder). After employing both the methods, assessment of light fastness and other properties was carried out.

2.5 Patch Sensitivity test of dyed leather for contact allergy

Patch sensitivity test was carried out by placing 1 X 1 inch^2 of the dyed leather sample treated with tannic acid and Vitamin-E gum acacia emulsion on the upper back of 30 subjects with a ½ inch microporous surgical tape (Doctor's Choice, Indian Hospitex Private Limited sourced from Apollo Pharmacy). After sticking the samples the test site was marked with an indelible marker pen (Vikrant life sciences Pvt. Ltd., India). The test was conducted for 48 hours during which the subjects were asked to refrain themselves from bathing, swimming, showering, sunbathing and wearing pale colored clothing (to avoid permanent staining of the indelible ink) as suggested by British Association of Dermatologists. After completion of the test, patch was removed and the tested site was observed for signs and intensity of skin irritation (contact dermatitis) as recommended by the International Contact Dermatitis Research Group.

3. Results and Discussions

3.1 Standardized dyeing conditions

3.1.1 pH

According to Table 1, none of the dyed samples had pure red color, as *b** was showing positive values towards yellow.

Also, the color was light according to the values of *L**. However, according to *C** and *H**, saturation and shade of color was found to be more at pH 2.0 as compared to pH 3.0 and pH 4.0. This increase is due to higher exhaustion of color as a result of complete cationization of carboxylic groups while dyeing with pH 2.0 (Puntener, 2000; Tuck, 1949) [24], because of which it showed higher *K/S* as compared to other samples.

Table 1: Color values; color depth; $O.D^1$, $O.D^2$, and *E* (%) as mean of four samples ± standard deviation of samples dyed at different pH

pH	*L**	*a**	*b**	*C**	*H**	*K/S*	$O.D^1$	$O.D^2$	*E* (%)
2.0	82.186	9.779	5.441	11.191	29.080	2.02	1.014 ± 0.002	0.485 ± 0.006	52.16 ± 0.509
3.0	81.261	9.942	4.142	10.770	22.608	1.74	1.014 ± 0.002	0.563 ± 0.005	44.48 ± 0.435
4.0	81.945	8.855	4.715	10.032	28.023	1.47	1.014 ± 0.002	0.664 ± 0.004	34.52 ± 0.500

3.1.2 Time and temperature

Sample dyed at 80 °C for 60 min showed highest *K/S* and *E* (%). According to *H** values, it was found that samples dyed at 80 °C were darker as compared to other samples (Table 2). However, values of *L**, *a**, *b** and *C** were very close to each other. Therefore, no reasonable explanation could be drawn.

Table 2: Color values; color depth; $O.D^1$, $O.D^2$, and *E* (%) as mean of four samples ± standard deviation of samples dyed at different time and temperature

Time (min)	Temperature (°C)	*L**	*a**	*b**	*C**	*H**	*K/S*	$O.D^1$	$O.D^2$	*E* (%)
20	**60**	81.580	9.673	4.475	10.658	24.817	1.99	1.013 ± 0.002	0.485 ± 0.004	52.12 ± 0.518
40	**60**	81.168	10.350	4.218	11.176	22.164	2.03	1.013 ± 0.002	0.475 ± 0.005	53.11 ± 0.611
60	**60**	81.396	10.471	4.621	11.445	23.804	2.16	1.013 ± 0.002	0.446 ± 0.005	55.97 ± 0.433
20	**70**	81.168	10.351	4.216	11.177	22.161	2.03	1.013 ± 0.002	0.474 ± 0.004	53.21 ± 0.523
40	**70**	81.396	10.471	4.621	11.445	23.803	2.16	1.013 ± 0.002	0.445 ± 0.005	56.07 ± 0.509
60	**70**	81.357	11.033	4.693	11.990	23.034	2.34	1.013 ± 0.002	0.411 ± 0.004	59.43 ± 0.612
20	**80**	81.911	9.777	6.123	11.671	31.256	3.01	1.013 ± 0.002	0.320 ± 0.006	68.41 ± 0.523
40	**80**	82.381	9.875	6.237	11.680	32.263	3.10	1.013 ± 0.002	0.311 ± 0.005	69.30 ± 0.588
60	**80**	81.928	9.895	5.469	11.306	28.918	3.81	1.013 ± 0.002	0.253 ± 0.004	75.02 ± 0.511

3.2 Color fastness, tear and tensile strength of the dyed samples

No change in color and moderate staining (grade 3) was observed in rub fastness samples (Table 3). In general, moderate staining occurred in dyed leather and does not bring any change in the original color. On the contrary, samples tested for perspiration, and light fastness failed the criteria of acceptability as there was marked to moderate fading and staining in perspiration and very marked fading in light fastness samples. Furthermore, no change in strength was observed in any of the samples (Table 4).

Table 3: Color fastness of dyed samples

Fastness test			SDCE Grey scale ratings Color staining	Color change
Dry rubbing			3	5
Wet rubbing			3	5
Light fastness			-	1
Perspiration	Alkali	Material	2	2-3
	Acid	Material	2-3	2-3
	Water	Material	2-3	2-3

Table 4: Tensile and tear strength of dyed and undyed samples as mean of three samples ± standard deviation

Dyed wet blue goat NAPPA skin	Tensile strength (N/mm^2)		Tear strength (N/mm)	
	Direction A	Direction B	Direction A	Direction B
Undyed sample	41 ± 0.6	51 ± 0.6	4.91 ± 0.01	3.91 ± 0.01
Dyed sample	41± 0.6	51 ± 0.7	4.92 ± 0.01	3.90 ± 0.01

3.3 Improvement in light fastness of dyed leather using natural agents

Tannic acid treated sample was found to be darker with higher color depth i.e. 5.17 as compared to non-treated dyed samples. Fading due to light was recorded to be moderate (grade 2-3) for the sample treated with tannic acid. Tannic acid treatment has also improved tear and tensile strength as shown in Table 5, and perspiration fastness (color staining as 2-3 in alkali) of the dyed leather. Tannic acid is a polyphenolic agent that acts as a retanning agent. In general,

Table 5: Tensile and tear strength of control dyed and tannic acid treated dyed sample as mean of three samples ± standard deviation

Treatment	Tensile strength (N/mm^2)		Tear strength (N/mm)	
	Direction A	**Direction B**	**Direction A**	**Direction B**
Control dyed sample	41 ± 0.6	51 ± 0.6	4.92 ± 0.6	3.90 ± 0.6
Tannic acid	46 ± 0.6	59 ± 0.6	5.32 ± 0.6	4.20 ± 0.6

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 (NIIR Board of Consultants and Engineers, 2005; Albu *et al*., 2009; Samanta & Aggarwal, 2011) [19, 2, 28]. 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 (Gulcin *et al*., 2010; Albu *et al*., 2009) [7, 2]. 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 (Colak *et al*., 2014; Muthu, 2014) [4, 18].

Furthermore, application of vitamin E - gum acacia emulsion led to more increase in the light fastness rating (grade 3). 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. (Lui *et al*., 2009; Lui *et al*., 2010; Lui *et al*., 2011) [14]. Also, a coating of this emulsion with glycerol helped in overcoming the hardening effect of leather fibers due to the application of tannic acid. Furthermore, 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 (Yadav *et al*., 2007; Montenegro, 2012) [39, 16]. Thus, the triple action of vitamin E, gum acacia, and glycerol helped in suppressing photooxidation phenomenon and heat deterioration of color. Increase in color depth i.e. 12.00 was also noticed. 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*. (2002) [27] 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. 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.

3.4 Patch Sensitivity test of dyed leather for contact allergy

Tested dyed samples treated with tannic acid and vitamin E - gum acacia emulsion on 30 literate and healthy young adults showed no sign of skin allergy. All volunteers got 1 on the score card i.e. none of them got any signs of skin allergy or change in the contact skin color or texture as recommended by the International Contact Dermatitis Research Group. The reason behind this could be the non-pathogenic nature of this species that cause no harm to humans. Moreover, the possibility of allergens in extracellular colorant of *Penicillium minioluteum* like fungal spores was eliminated as the dyeing was carried out at 80 °C and according to Aneja (2005) [3] and Fallik and Lurie (2007) [6], fungal spores, vegetative cells, and conidia, all are killed at this temperature. Furthermore, Vitamin E and tannic acid are known antioxidants that have been reported to possess antibacterial, antiallergic, and anti-inflammatory properties (Albu *et al*., 2009; Gulcin *et al*., 2010; Gumrukcu & Ozgur, 2010) [2, 7, 8]. Externally, tannic acid has also been reported to fight skin ulcers and wounds (Aelenei *et al*., 2009) [1].

4. Conclusion

In a nutshell, unlike expensive and toxic synthetic dyes, this red colorant of *Penicillium minioluteum* is eco-benign and cost effective because of many reasons. Firstly, because the raw material of dye i.e. microbial culture is very cheap and easily available. Secondly, due to the presence of natural auxiliaries and tanning agents in the colorant because of which color was highly substantive and needed no additional chemicals. Thirdly, these natural agents also helped in decreasing the dyeing time that in turn lowers the production cost. Lastly, unlike synthetic dyes no costly chemicals are required to improve the after dyeing characteristics as the sample showed uniform dyeing with good color uptake and rub fastness. Collectively because of the listed reasons, the dye extracted from *Penicillium minioluteum* is significantly economical and better as compared to synthetic leather dyes. Moreover, if production of this colorant is carried out in bulk using bigger fermenters, the cost can be reduced further. Though there is a slight increase in dyeing cost after incorporation of certain agents for improving light fastness, yet they have been used because these agents can improve perspiration fastness, strength characteristics, rub fastness, and final shade from red to brown. As mentioned earlier also, 80% of manufactured leather garments and upper part of the shoes 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.

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