

# Biocolorant for Leather Dyeing Applications: An Eco-benign Evaluation of Natural Coloring Agent

by

C. Kurinjimalar,<sup>1</sup> Gladstone Christopher Jayakumar,<sup>2</sup> A. Tamil Selvi,<sup>3\*</sup> R. Venba,<sup>4</sup> Malathy Jawhar,<sup>4</sup> and Swarna V. Kanth<sup>1</sup>

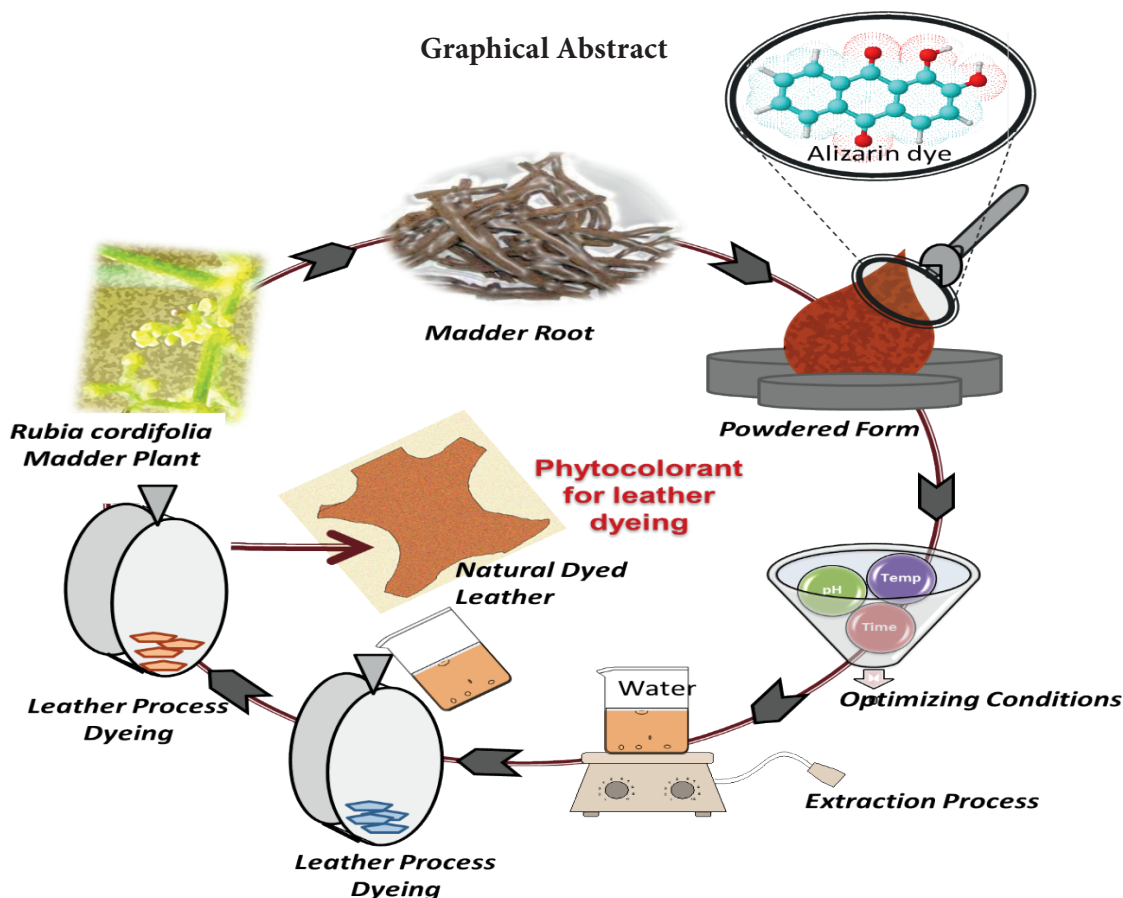
<sup>1</sup>Centre for Human and Organizational Resources Development,

<sup>2</sup>Centre for Academic and Research Excellence,

<sup>3</sup>Unit for Science Dissemination

<sup>4</sup>Leather Process Technology Department

CSIR- Central Leather Research Institute, Adyar, Chennai 600020



Exploration of biocolorant in leather industry is explored widely owing to its environmental limitation. Besides, employing synthetic dyes in leather process requires high end of pipe treatment due to their complex chemical structure. Therefore, an attempt has been made on exploiting madder root dye (*Rubia cordifolia* L.) for leather dyeing application. The effect of varying pretreatment regimen on madder colorant extraction, chemical characterizations (including UV-Vis, IR, particle size, zeta potential

value, and thermal studies) and optimum operating leather dyeing conditions are studied. The results revealed dissolving medium pH 5, 100°C, and 60 min duration of extraction is optimum. Thus, obtained dye characteristics showed maximum absorption peak at 460 nm, with an average particle size of 166 nm. The optimum leather dyeing is found at leather pH 5.5, 10% dye concentration and 4 h duration. At optimum dyeing parameters it shows good fastness, perspiration, organoleptic properties without affecting the physical characteristic. Novelty of the present research would lead to develop eco-dyeing method in leather manufacture. Moreover,

\*Corresponding author email: tamilselvi@clri.res.in

Manuscript received August 7, 2020, accepted for publication April 8, 2021.

the study unravels a new application of eco-benign dye to achieve sustainable process.

## Introduction

Leather sector is one of the highest contributors to the Indian economy. Leather processing involves tanning with pre- and post-tanning operations, with dyeing as one of the post-tanning processes.<sup>1</sup> Dyeing is carried out to impart color to the substrate which is a vital unit activity in leather, textile, and allied industries to enhance aesthetic value.<sup>2</sup> During dyeing, reactive groups of dye molecules react with collagen fibers in the leather substrate by possible adsorption and slow diffusion through the pores.<sup>3</sup> Generally, dyes are chemical structures with attached chromophore conjugate which produce color. The chromophores are diverse based on the functional group such as azo, nitro, carbonyl, anthraquinone, etc.<sup>4</sup> On considering the aesthetic value, several emerged synthetic dyes are employed in leather processing due to their high fastness and lower price. However, using synthetic dyes is prone to serious alarming pollution load and treatment constraints and ultimately toxic to all levels of life forms.<sup>5</sup> Therefore, to combat these paradigms, efficient natural dyes and pigments are emerging as research output to alternate synthetic dyes.

A eco-friendly and renewable dye source is needed in all dyeing industries, including food, textile, and leather sectors. Besides, some plant products possess biological properties, including anti-cancer, anti-oxidant, anti-microbial, anti-viral and larvicidal activity.<sup>6-8</sup> The source of coloring chemical compound is from different plant parts including whole plants, roots, leaves, flowers and fruits.<sup>9-12</sup> Plant metabolite products such as quercetin and lutein was reported as a possible substitute for synthetic dyes by Gulzar et al. (2015) and Adeel et al. (2017), respectively.<sup>13,14</sup>

In the current study, an industrial dye crop plant madder (*Rubia cordifolia*, L.) is used to obtain vibrant reddish colorant towards sustainable leather dyeing process.<sup>15</sup> The vibrancy of madder red can surpass synthetic red color which contains principal coloring component alizarin (1, 2-dihydroxy anthraquinones), an anthraquinone in its root.<sup>16,17</sup> Moreover, recently burgeoning environmental conditions, toxic nature of synthetic dyes and growing awareness on sustainability has posed towards revival of natural dye applications as the success and promises encountered in textile field. Therefore, natural dyes are gaining popularity in other fields with pre-requisite for dyeing process. Many studies pertained to show characterization of natural dyes and chemistry of its dyeing in many non-leather applications. Especially many have been reported for possible utility in applications such as food, textile and health sectors towards eco-benign approach due to their non-toxic nature. Several native plant derived dyes in textile dyeing have been reported extensively and have long been utilized since ancient

times.<sup>18,19</sup> A few studies on leather dyeing using plant metabolites are reported by Mohammed et al. (2017); Sivakumar et al. (2009); Musa et al. (2009); Velmurugan et al. (2016); (2017); Tamil Selvi et al. (2013); Vedaraman et al. (2017).<sup>20-24</sup> Considering utilization of natural dye in a large industrial scale operation standardized extraction condition must be optimized to obtain quality of dyeing in leather.

The commercial feasibility of madder dye in the leather application is addressed in this study to increase the demand for natural dye, which is not only beneficial to the environment but also increases the economic feasibility. The main objective is the optimization of madder colorant extraction, chemical characterization, and leather application under optimum fixation condition. The dyeing of leather is optimized at different dye concentrations, initial leather pH value, duration, mordants and analysed the color values. The dyed leather properties, such as color fastness, physical strength, and organoleptic properties were studied.

## Materials and Methods

### Materials

The madder root powder was purchased from a local buyer, Tindivanam, Tamil Nadu. Undyed chrome-tanned goat crust leather (1.00 mm thickness) was used in the experimental trials. All other chemicals used were of commercial grade.

### Optimization on madder dye extraction

An aqueous solution of 1% madder root powder was used for optimizing the extraction and UV-Vis spectrum analysis. The effect of dye extraction at different regimens of temperatures (50, 60, 70, 80, 90 and 100°C) and pH (4, 5, 6, 7, 8 and 9) for 60 min were carried out. Similarly, different time periods (15, 30, 45, 60 and 120 min) on extraction was analyzed for maximum absorption peak and compared.

### Preparation and characterization of madder dye

Aqueous dye extraction was carried out at pH 5.0, 80°C for 1 h. The obtained dye extracts were filtered and concentrated to 15-20% solid content. Later, the aqueous extract was dried using a spray dryer apparatus adjusted at a range of 160-170°C and 80-90°C as an inlet and outlet temperature, respectively. The extracted dye was stored at ambient temperature for further characterization.

### Spectral characteristics

The extracted dye was scanned for absorption maxima between 200-800 nm using a UV-Vis spectrophotometer. Vibrational spectroscopy was used to determine the functional groups between 4000-400 cm<sup>-1</sup> wavenumber (JASCO FTIR 4700). Furthermore, the particle size and stability were analyzed using Malvern Zetasizer Nano Instrument.

### Thermal property analysis

Thermal stability and its behavior of extracted dye were analyzed from thermograms of TGA (Thermogravimetric analyzer) and DSC (Differential Scanning Calorimetry), respectively. In TGA analysis samples were heated between 25 and 800°C with an increasing temperature of 20°C/min under N<sub>2</sub> atmosphere (TA instruments, Q-50). For DSC analysis samples were heated between 25 to 300°C with an increasing temperature of 10°C/min under N<sub>2</sub> atmosphere (TA Instruments, DSC Q200).

### Leather dyeing application and analysis

The dyeing efficiency of dye was evaluated on chrome tanned crust leather as given in Table I. Leather trials were carried out with different parameters such as dye concentrations (2, 5, 10, 15 and 20%), pH (4.0, 4.5, 5.0, 5.5 and 6.0) and durations (2, 4 and 6 h). To understand the mordanting effect on leather dyeing, hence, mordants such as aluminium sulfate, ferrous sulfate and calcium carbonate were used. After dyeing the leathers were subjected to color measurements using reflectance spectrophotometer (Milton Roy ColorMate HDS instrument) and morphological evaluation using optical microscope. The same experimental formulation was used for pre-mordanting experimental trials using 1% aluminium sulfate, ferrous sulfate and calcium carbonate.

To understand the influence of dyeing on leather characteristics rub fastness, perspiration fastness, tear strength, tensile strength, elongation at break and grain crack strength were studied.<sup>25-29</sup> In addition to physical characterization, organoleptic properties such

as dye uniformity, dye penetration, grain smoothness, and softness were assessed by four experienced leather tanners.

## Results and Discussion

Eco-benign and sustainability are the two critical parameters to assess for the use of chemicals in leather processing. Natural and renewable chemicals are the major characteristic to attain bio-driven processing. Several bio-driven chemicals are exploited for use in leather manufacture. Dyeing is one of the important unit processes in leather making which add aesthetic value to the products for the end use. Natural dyes are exploited as an alternate to synthetic dyes to achieve eco-sustainable and thereby reducing the pollution at the end of pipe treatment. In the present study, dye prepared using madder root was used to dye leather and characterized to understand its possible intervention as a dyeing agent.

### Optimization on madder dye extraction

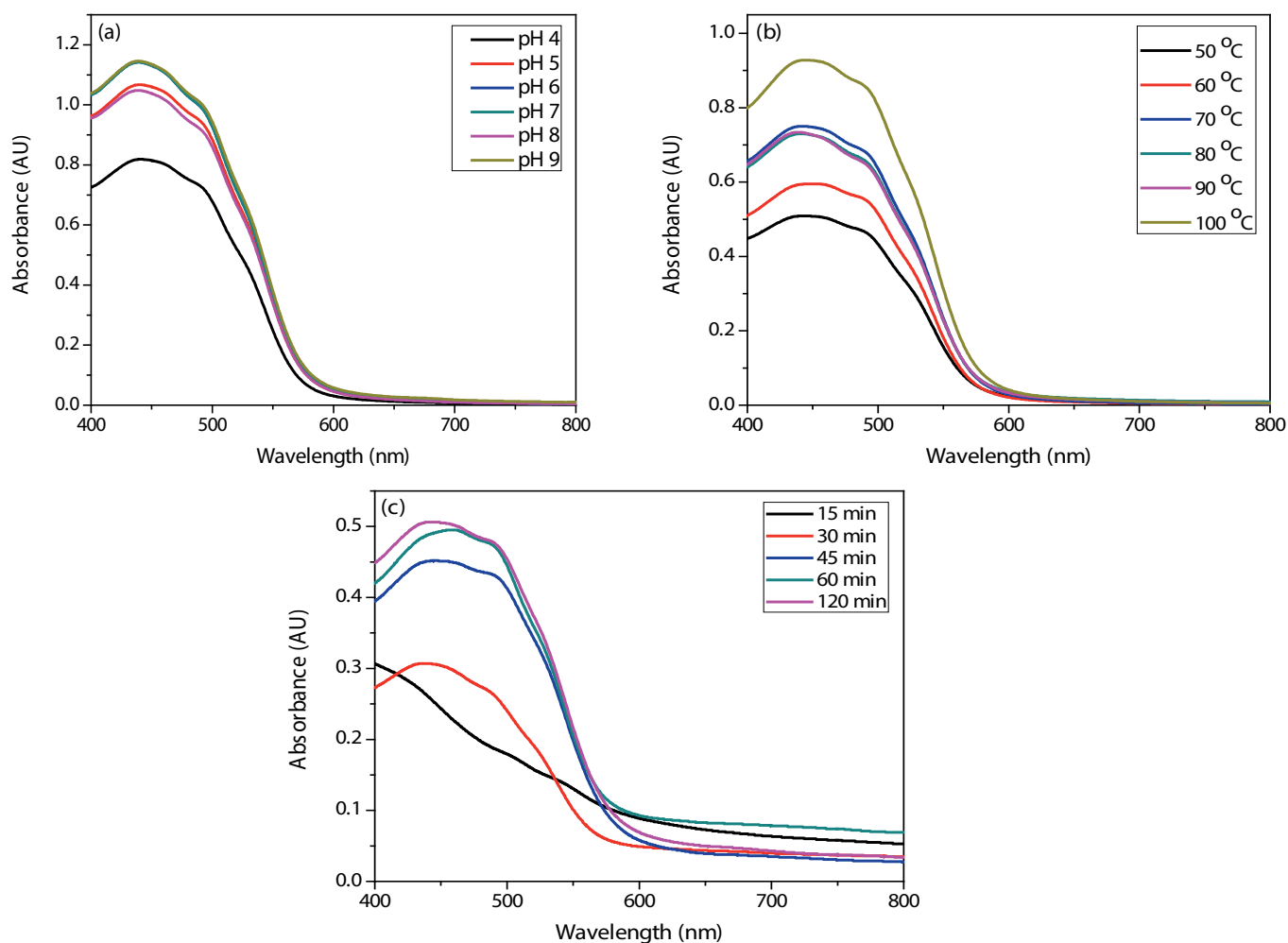
The dyes of natural origin must be extracted from plant material by an eco-friendly manner, which is highly susceptible to degradation, and is majorly influenced by pH, temperature, light, metals, etc.<sup>30</sup> The influence of temperature, pH, and duration of physical disruption factor plays a significant role in the colorant extraction. The absorption spectra of madder dye extracted at different temperatures are shown in Figure 1a. From this data it can be inferred that maximum absorption value is at 100°C. Thus, result showed a hyperchromic shift with increasing temperature. A strong hyperchromic shift is inferred when the temperature increased above 70°C, therefore, dye is extracted at 100°C.

**Table I**  
Post-tanning procedure for dyeing using madder dye

Process	Chemicals	%	Duration	pH adjustment
Wetting back	Water	300	Overnight	
	Wetting agent	1.0		
	Ammonia solution	0.2		
Washing	Water	300	30'	
Neutralization	Sodium formate	1.0	3 × 10'	Different pH***
	Sodium bicarbonate	0.5		
Dyeing	Water	100	15'	Penetration check
	Madder dye	Different percentage*	Different time interval**	
Fixation	Formic acid	1.5	3 × 10'	pH 3.8 - 4.0

Leathers piled overnight, hooked to dry, staked, trimmed and buffed before analysis

\* % of dye - 2 to 20; \*\* Time duration - 2 to 6h; \*\*\* pH - 4 to 6

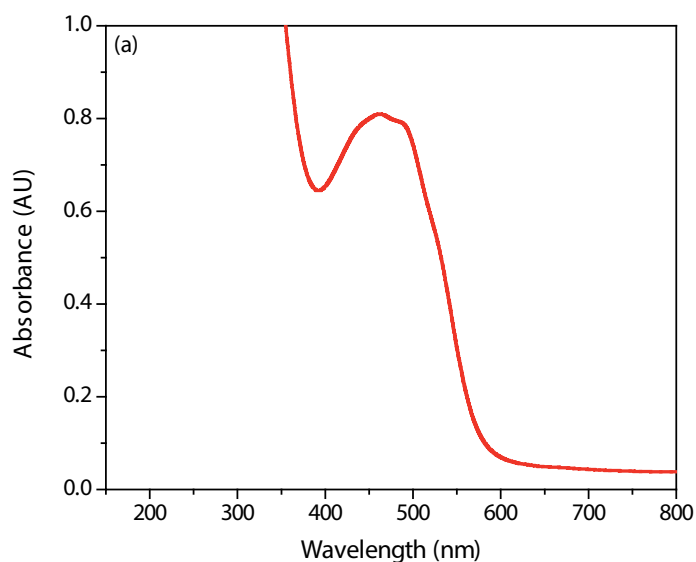


**Figure 1.** Absorption maximum analysis of dye extracted at different (a) Temperatures, (b) pH, (c) Durations

The absorption spectra of madder dye at different pH levels are shown in Figure 1b. Comparatively, a high pH value towards basic condition has significantly improved the dye extraction process. Thus, dye extracted from the biomass above pH 5 shows maximum peak value. This is a significant hyperchromic shift in absorbance peak value. The absorption spectra of madder dye extracted at different durations is shown in Figure 1c. From this data it can be inferred that the maximum dye extraction has been observed between 30-to-60-minute duration. Therefore, optimum duration for dye extraction is 60 minutes with a hyperchromic shift (Figure 1c). Thus, the overall optimization result shows 60 minutes of extraction duration under 100°C, and pH 5 showed significantly improved colorant extraction. Similarly, Berhanu and Ratnapandian (2017) reported natural dye extracted from *Cassia singueana* at temperature of 95°C and 60 minutes of duration as the optimum dye extraction condition for leather dyeing application.<sup>31</sup>

#### Spectral characteristic analysis

The UV-Vis spectra of madder dye extract shows a maximum absorption wavelength at 460 nm (Figure 2a). As previously reported alizarin chromophore prominently shows maximum



**Figure 2a.** UV-Vis spectrum of madder dye

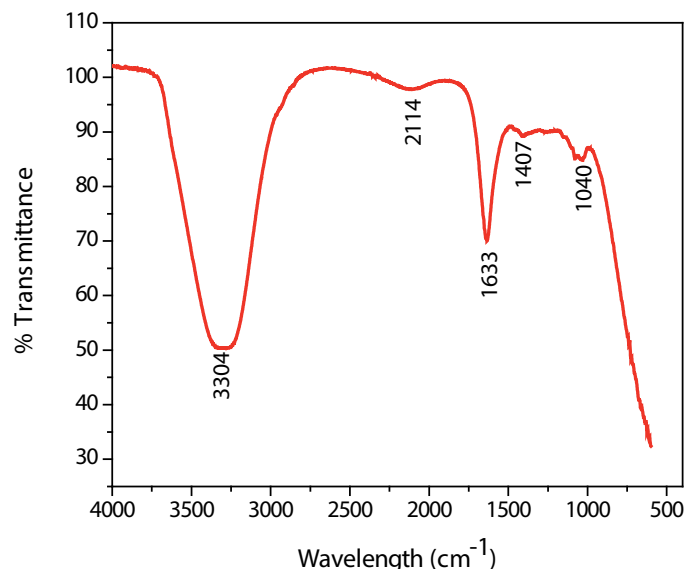


Figure 2b. FT-IR spectrum of madder dye

absorption spectrum at 459 nm.<sup>32</sup> The FT-IR spectra of madder dye extract shows the presence of characteristic peaks at 3300, 2114, 1633, 1407, 1077  $\text{cm}^{-1}$  corresponding to OH, C=O, C=C, C-H and C-C group, respectively (Figure 2b). Thus, the vibrant red color of anthraquinone molecule with chromophore can be exploited for leather dyeing applications.

#### Particle size and stability analysis

The hydrodynamic diameter or particle size of madder dye is measured using DLS method. The result revealed that the distribution range is 166 nm (Figure. 2c). Therefore, madder dye component alizarin within this particle will lead to uniform dye penetration. In an earlier report by Tamil Selvi et al. (2013) and Mohammed et al. (2017), the reported particle size of natural plant dye of *Bixa orellana* and mekmeko dye extract showed good dye penetration in the leather substrate.<sup>3,24</sup> As reported in the previous report, leather dyeing using madder extract shows good penetration through leather pores due to smaller particle size. The obtained colorant showed a zeta potential value of -5.31 (negative) and was found to be highly stable (Figure 2d). The anionic dye property influences the adsorption on the cationic leather surface due to the electrostatic force of attraction. Thus, madder dye is feasible for leather dyeing application.

#### Thermal stability analysis

The TGA of madder dye shows a weight loss of colorant which indirectly reveals the dye's thermal stability towards increasing temperature (Figure 3a). The colorant decomposing at the high-temperature profile shows a drop in the curve, indicating a loss of sample mass. The TGA curve shows degradation occurs in two distinct regions. Thus, madder dye can be heated up to 100°C as

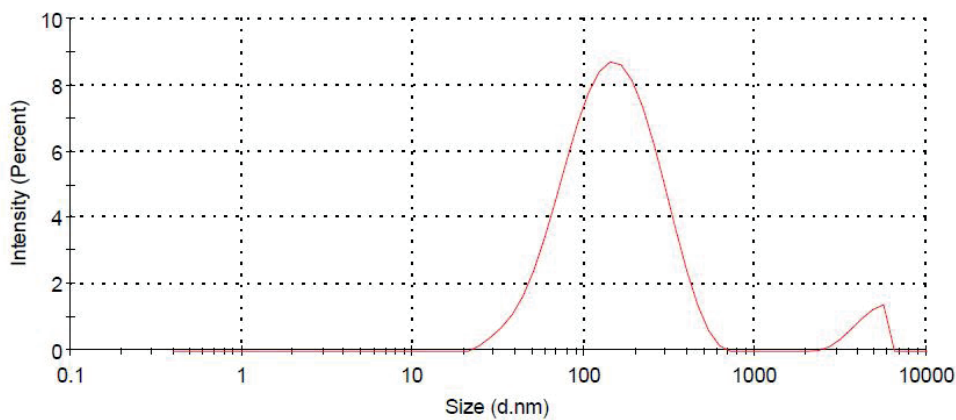


Figure 2c. Particle size spectrum of madder dye

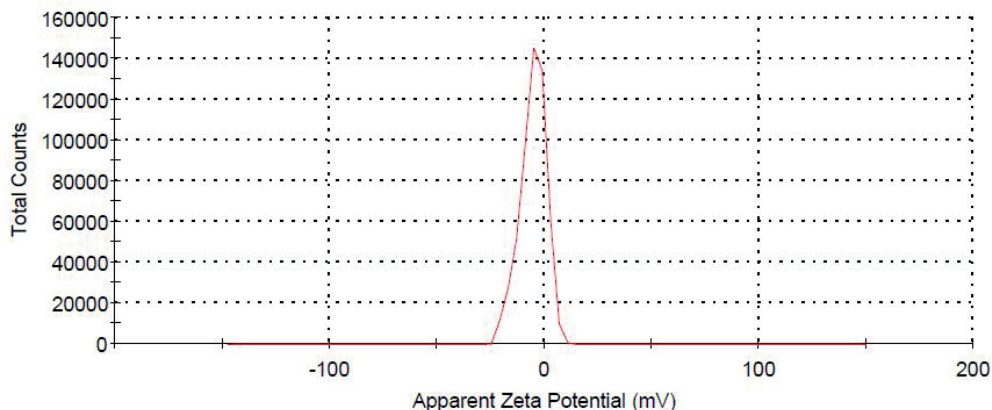


Figure 2d. Zeta potential spectrum of madder dye

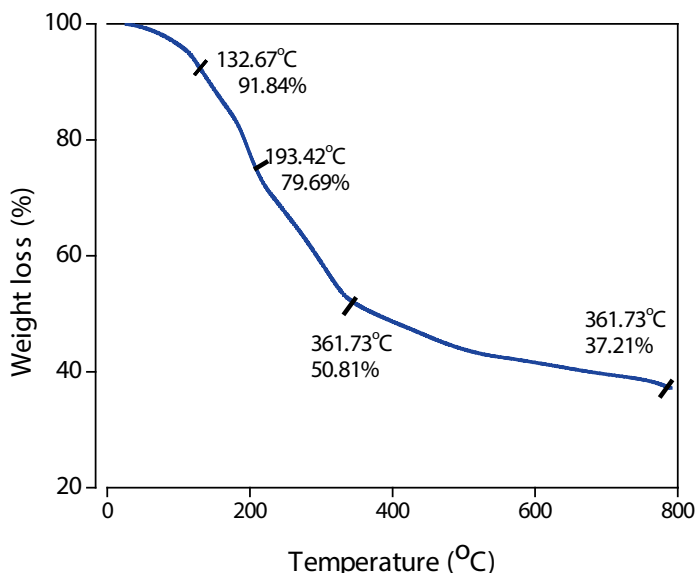


Figure 3a. TGA thermogram of madder dye

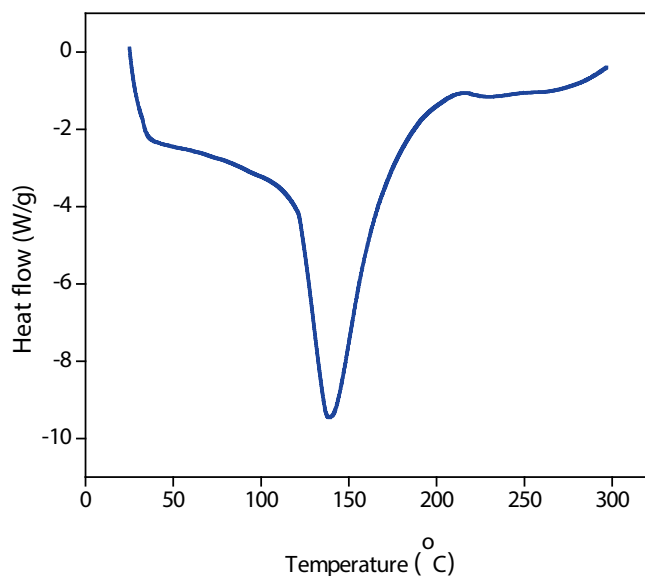


Figure 3b. DSC thermogram of madder dye

revealed in pre-treatment processing. Figure 3b shows the DSC thermogram of madder dye extract. The endothermic reaction at 139.05°C is beyond 100°C due to less moisture content. This indirectly reveals the high heat stability.

#### Leather dyeing optimization trials

In the following experiments, madder dye was used for wet blue crust leather dyeing at different processing conditions and analysed for the color values.

#### Effect of concentration (Trial 1)

Color values of different concentrations of dye are given in Table II a. With the increase in the concentration of dye, there is an increase in color values towards the darker shades. From the  $L^*$ ,  $a^*$ ,  $b^*$  values obtained, it is observed that there is increased darkness towards high dye concentration. Similarly, the more positive values and only marginal difference in  $a^*$ ,  $b^*$  values show slightly more redness and yellowness. Higher color values are obtained with 10% and 20% dye concentration, but the difference in color values is only marginal; therefore, 10% is taken as an optimized concentration taken for further study.

#### Effect of pH (Trial 2)

Color values of varied pH leathers were studied and the results given in Table II b. It is observed that pH 5.5 is optimum for high dye uptake by leather. The  $L^*$ ,  $a^*$ ,  $b^*$  color values at different pH values shows significant changes above pH 5.5 compared to others (Table II b). High fixation at pH 5.5 is due to surface charge alteration

towards basic pH, which is influenced by high dye uptake and increased darkness value. Therefore, appropriate surface charge alteration in the leather substrate enhanced the dye fixation. Dye uptake and fixation onto the leather at pH 5.5 were higher than at acidic pH.

#### Effect of time (Trial 3)

Color values of varied dyed leather at different time intervals is tabulated in Table II c. It is observed that dye uptake increased with increased dyeing time. Thus, optimal duration for dye penetration in the leather substrate is observed at 4 h time duration (Figure 4c). Interestingly color values ( $L^*$ ,  $a^*$ ,  $b^*$ ) in different period trials show significant changes observed between different fixed durations (Table II c).

#### Effect of Mordants (Trial 4)

Impact of mordants on leather dyeing is given in Table II d. The dyeing effects are varied with different selected mordants and we selected the one which imparts more redness for further studies. In addition, the dye uptake onto leather increased when pre-treated with all mordants with vivid coloration and good penetration. The result showed a significant difference in color values ( $L^*$ ,  $a^*$ ,  $b^*$ ) in the presence of aluminium sulfate mordant. The results show that compared to selected mordants, 1% of alum has more red shade and less saturated compared to control (non-mordanted). This result shows that bio-colorant applied on mordant pre-treated leather is an alternate to different color shades in par with synthetic dye.

**Table II**  
Color value analysis of crust leather dyed using madder dye

<b>a. Effect of concentration</b>			
	<b>L*</b>	<b>a*</b>	<b>b*</b>
2.0%	58.638	20.321	9.815
5.0%	56.383	22.629	10.388
10.0%	54.236	23.632	9.495
15.0%	54.018	23.743	9.968
20.0%	52.657	20.495	12.189
<b>b. Effect of pH</b>			
	<b>L*</b>	<b>a*</b>	<b>b*</b>
pH 4.0	64.173	17.903	10.559
pH 4.5	60.017	20.732	11.897
pH5.0	55.456	23.875	7.495
pH 5.5	59.622	20.602	10.948
pH 6.0	59.663	19.741	9.037
<b>c. Effect of time duration</b>			
	<b>L*</b>	<b>a*</b>	<b>b*</b>
2h	62.654	12.777	9.433
4h	48.986	15.308	11.731
6h	41.398	30.958	14.069
<b>d. Effect of mordants</b>			
	<b>L*</b>	<b>a*</b>	<b>b*</b>
Dyed without mordant	62.19	11.17	5.01
Aluminium sulfate	40.43	31.39	13.87
Ferrous sulfate	57.29	18.65	9.48
Calcium carbonate	53.42	15.17	9.98

#### Grain Surface Analysis

The optical images of dyed crust leather surface imaging were analysed for topographical changes due to dyeing (Figure 4 a-d). From the surface image, it can be ascertained that there was no significant changes in the surface. The dyed leather samples are similar to undyed crust leather samples having compact grain tightness and without any morphological changes. Rather a significant change in color strength is observed prominently.

#### Characterization of dyed leather

The preliminary studies revealed that 10% of dye concentration, pH 5.5, the period of 4 h, and pre-mordanted with alum yields high coloration and dye penetration.

#### Color fastness analysis

Wet rub, dry rub, and perspiration results of leathers are given in Table III. The testing results show that color fastness characteristic are better and in good acceptable range. From the result, it is evident that rubbing fastness of the bio-colorant dyed leather is good, which is one of the important factors for commercializing the madder dye for leather application.

#### Organolectic properties analysis

The organoleptic properties such as dye uniformity, dye penetration, grain smoothness, and grain softness values of the experimental leathers are given in Table III. The visual assessment of the leathers was improved and dyeing was found to have no impact on the leather quality.

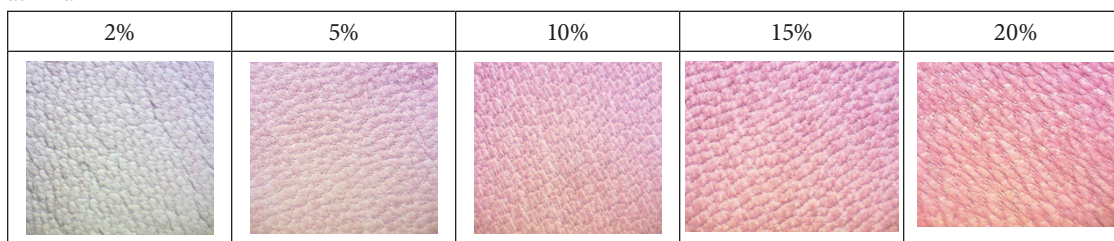
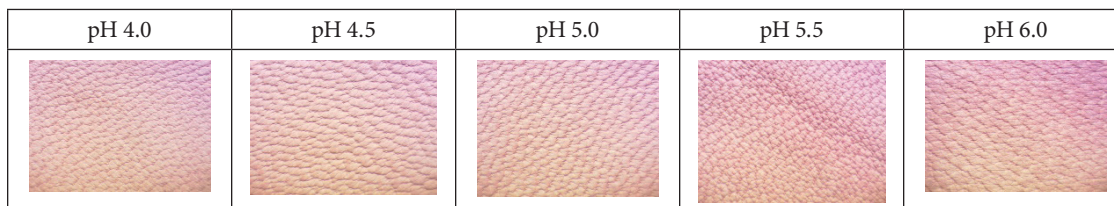
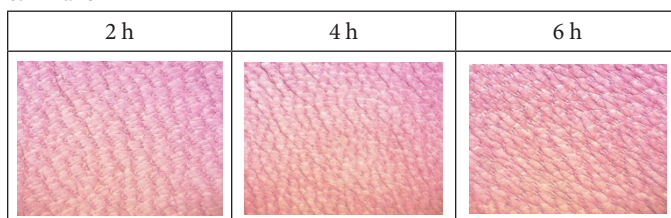
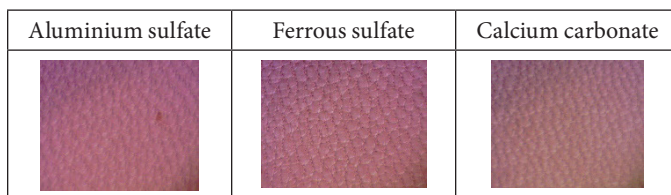
**a. Trial 1****b. Trial 2****c. Trial 3****d. Trial 4**

Figure 4. Optical images of different trials

**Table III**  
Organoleptic and fastness properties of crust leather dyed using madder dye

S. No.	Properties		Color change values of madder colorant-dyed leather	Recommendation
i	Color fastness to rubbing	Dry 150 rubs	4/5	Min 3
		Wet 50 rubs	4/5	
	Color fastness to perspiration	Cellulose acetate	4/5	Min 3
		Bleached cotton	4/5	
		Spun nylon	4/5	
		Spun polyester	4/5	
		Spun acrylic	4/5	
ii	Organoleptic	Wash spun wool	4/5	
		Dye uniformity	9/10	
		Dye penetration	9/10	
		Grain smoothness	8/10	
		Grain softness	9/10	

## Conclusions

The present study focused on developing eco-dyeing from plant wastes. Utilization of plant wastes into a high value product has been presented. The optimum leather dyeing has been optimized at pH 5.5 with 10% dye concentration and required minimum of 4 h duration. Mordants have been used to enhance the dyeing characteristics and the color shades can be varied based on the choice of mordants. The physical characteristics of the dyed leathers met the standard norms. Application of madder root dyes in leather manufacture would be a new insight to achieve sustainable leather products. Moreover, the madder roots are known for biomedical applications. This study could lead to develop medicated properties in leather products. From the preliminary studies, it can be concluded that madder root dyes could be a potential eco-dyeing agent for leather manufacture.

## Acknowledgements

Authors would like to thank The Director, CSIR-CLRI and CLRI-CATERS for facilitating the testing facilities. Authors also acknowledge the financial support from CSIR funded project MLP2004 with communication number A/2020/USD/CLRI/1416.

## References

- Covington, T.; Tanning Chemistry. The science of leather, Cambridge: The Royal Society of Chemistry, 2009.
- Morshed, A.M.A., Rahman, M.M.; A review on the physico-chemical studies of dyeing progress and dyeing kinetics using natural dyes. *JPTE*. **2**, 71-75, 2015.
- Mohammed, S.A., Panda, R.C., Madhan, B., Demessie, B.A.; *Rumex abyssinicus* (mekmeko) extract as cleaner approach for dyeing in product manufacture: Optimization and modeling studies. *Asia-Pac. J. Chem. Eng.* doi.org/e2165.https://doi.org/10.1002/apj.2165, 2017.
- Labarthe, F.L., Bruneel, J.L., Buffeteau, T., Sourisseau, C.; Chromophore Orientations upon Irradiation in Gratings Inscribed on Azo-Dye Polymer Films: A Combined AFM and Confocal Raman Microscopic Study. *J. Phys. Chem.* **108**, 6949–6960. 2004.
- Sun, S.S., Xing, T., Tang, R.C.; Simultaneous Coloration and Functionalization of Wool, Silk, and Nylon with the Tyrosinase-Catalyzed Oxidation Products of Caffeic Acid. *Ind. Eng. Chem. Res.* **52**, 8953–8961, 2013.
- Nakanishi, F., Nagasawa, Y., Kabaya, Y., Sekimoto, H., Shimomura, K.; Characterization of lucidin formation in *Rubia tinctorum* L. *Plant Physiol. Biochem.* **43**, 921-928. 2005.
- Shahid-ul-Islam, Mohammad, S., Mohammad, F.; Perspectives for natural product based agents derived from industrial plants in textile applications - a review. *J. Clean. Prod.* **57**, 2-18, 2013.
- Ozen, E., Yeniocak, M., Goktas, O., Alma, M.H., Yilmaz, F.; Preservation with natural colorant. *Bioresources* **9**, 1998-2009, 2014.
- Sivakumar, V., Lakshmi Anna, J., Vijayeeswarri, J., Swaminathan, G.; Ultrasound assisted enhancement in natural dye extraction from beetroot for industrial applications and natural dyeing of leather. *Ultrason. Sonochem.* **16**, 782-789, 2009.
- Velmurugan, P., Kamala-Kannan, S., Balachandar V., Lakshmanaperumalsamy, P., Chae, J.C., Oh, B.T.; Natural pigment extraction from five filamentous fungi for industrial applications and dyeing of leather. *Carbohydr. Polym.* **79**, 262-268, 2010.
- Punrattaanasin, N., Nakpathom, M., Somboon, B., Narumol, N., Rungruangkikrai, N., Mongkholrattanasit, R.; Silk fabric dyeing with natural dye from mangrove bark (*Rhizophora apiculata* Blume) extract. *Ind. Crop. Prod.* **49**, 122-129, 2013.
- Yusuf, M., Shahid, M., Ibrahim Khan., Ahmad Khan, S., Ali Khan, M., Mohammad, F.; Dyeing studies with henna and madder: A research on effect of tin (II) chloride mordant. *J. Saudi. Chem. Soc.* **9**, 64-72, 2015.
- Gulzar, T., Adeel, S., Hanif, I., Rehman, F., Hanif, R., Zuber, M., Akhtar N.; Eco-Friendly Dyeing of gamma ray induced cotton using natural quercetin extracted from acacia bark (*A. nilotica*). *J. Nat. Fibers.* **12**, 494-504, 2015.
- Adeel, S., Gulzar, T., Azeem, M., Saeed, M., Hanif, I., Iqbal, N.; Appraisal of marigold flower based lutein as natural colorant for textile dyeing under the influence of gamma radiations. *Radiat. Phys. Chem.* **130**, 35-39, 2017.
- Jahan, N., Datta, E.; A Comparative Study on Dyeing of Cotton and Silk Fabric Using Madder as a Natural Dye. *JPTE*, **2**, 5-11, 2015.
- Derksen, G.C.H., van Beek, T.A.; In: Atta-ur-Rahman (Ed.), Studies in Natural Products Chemistry, vol. 26, Elsevier, Amsterdam, p. 629, 2002.
- Agnhage, T., Perwuelz, A., Behary, N., Towards sustainable *Rubia tinctorum* L. dyeing of woven fabric: How life cycle assessment can contribute, *J. Clean. Prod.* doi: 10.1016/j.jclepro.2016.09.183, 2016.
- Gupta, V.K.; Fundamentals of natural dyes and its application on textile substrates. IntechOpen, doi.org/10.5772/intechopen.89964, 2019.
- Samanta, P.; A review on application of natural dyes on textile fabrics and its revival strategy. IntechOpen, doi.org/10.5772/intechopen.90038, 2020.
- Musa, A.E., Madhan, B., Madhulatha, W., Rao, J.R., Gasmelseed, G.A., Sadulla, S.; Coloring of leather using henna—natural alternative material for dyeing. *JALCA* **104**, 183-190, 2009.
- Velmurugan, P., Shim, J., Seo, S.K., Oh, B.T.; Extraction of Natural Dye from *Coreopsis tinctoria* Flower Petals for Leather Dyeing – An eco-friendly approach. *Fiber. Polym.* **17**, 1875-1883, 2016.
- Velmurugan, P., Kim, J.I., Kim, K., Park, J.H., Lee, K.J., Chang, W.S., Park Y.J., Cho M., Oh B.T.; Extraction of natural colorant from purple sweet potato and dyeing of fabrics with silver nanoparticles for augmented antibacterial activity against skin pathogens. *J. Photochem. Photobiol. B.* **173**, 571-579, 2017.
- Tamil Selvi, A., Aravindhan, R., Madhan, B., Raghava Rao, J.; Studies on the application of natural dye extract from *Bixa orellana* seeds for dyeing and finishing of leather. *Ind. Crop. Prod.* **43**, 84-86, 2013.

24. Vedaraman, N., Sandhya, K.V., Charukesh, N.R.B., Haribabu, K., Sridharan, M.R., Nagarajan, R.; Extraction of natural dye from *Rubia Cordifolia*, optimisation using response surface methodology (RSM) and comparison with artificial neural network (ANN) model and its dyeing properties on different substrates. *Chem. Eng. Process.* doi.org/10.1016/j.cep.2017.01.008, 2017.
  25. Indian standards (IS6191-LF:10). Determination of color fastness to rubbing (crocking test). p.48, 1971.
  26. Indian standards (IS6191-LF:7). Determination of fastness of colored leather to perspiration. p.40, 1971.
  27. IUP 6. Measurement of tensile strength and percentage elongation. *JSLTC* **84**, 317, 2000.
  28. IUP 8. Measurement of tear load-Double edge tear. *JSLTC* **84**, 327-332, 2000.
  29. IUP 9. Measurement of distension and strength of grain by the ball burst test, Official methods of analysis, *JSLTC* 1996.
  30. Markakis, P.; Anthocyanins as Food Colors. Academic Press, London, 1982.
  31. Berhanu, T., Ratnapandian, S.; Extraction and Optimization of Natural Dye from Hambo Hambo (*Cassia singueana*) Plant Used for Coloration of Tanned Leather Materials. *Adv. Mater. Sci. Eng.* doi:org/10.1155/2017/7516409, 2017.
  32. Marzec, A., Szadkowski, B., Rogowski, J., Maniukiewicz, W., Szyrkowska, M.I., Zaborski, M.; Characteristics of Hybrid Pigments Made from Alizarin Dye on a Mixed Oxide Host. *Materials*, **12**, doi.org/10.3390/ma12030360, 2019.
-