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Natural dyeing of fabrics using *Quercus robur* L. (fruit cups) dye and *Punica granatum* L. (peel) mordant

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Abstract

Investigation was carried out to study the dyeing quality of *Quercus robur* L. (fruit cups) and *Punica granatum* L. (peel) mordant for the dyeing of wool and cotton fabrics. The fabrics were dyed both excluding and including the mordant by adopting different mordanting methods. The efficiency of the dye and mordant combinations was evaluated in terms of percent absorption (%), Colour coordinates (CIELAB), Colour strength/ Relative colour strength (K/S) and fastness properties respectively. Absorption of the dye, colour coordinates, colour strength (K/S) by the wool fabric recorded higher values as compared to cotton fabric. The cotton fabric does not showed much affinity for the dye and mordant combinations and appeared with dull and poor colour shades with lower values of absorption, colour strength and retention grades. However, wool fabric showed beautiful and bright colour shades in different mordanting combinations.

Keywords: Natural dye, *Quercus robur, Punica granatum*.

Introduction

The production and usage of the synthetic dyes is related with carcinogenic, toxic, allergic effects on humans and to our environment. The textile industry consumes a substantial amount of water in manufacturing processes used mainly in the dyeing and finishing operations. In textile industry, up to 200, 000 tons of dyes are lost to effluents every year during the dyeing and finishing operations, due to the inefficiency of the dyeing process.[1] The wastewater from textile plants is classified as the most polluting of all the industrial sectors, considering the volume generated as well as the effluent composition.[2] The untreated wastewater is one of the biggest threats to the environment. Recalcitrant organic, coloured, toxicant, surfactant and chlorinated compounds and salts are the main pollutants in textile effluents.[2] The ingestion of water contaminated with textile dyes can cause serious damage to the human health and of other living organisms, due to the toxicity and mutagenicity of its components.[3] These chemicals cause different diseases like contact dermatitis, allergic dermatoses, respiratory diseases and asthma.[4] Workers in the textile industry have a two-fold increased risk of contracting bladder cancer compared to workers in other occupations like aviation, agriculture and construction.[5] Different tests conducted for mutagenicity, genotoxcity, carcinogenecity and teratogenecity reported adverse effects of textile dyes.[6] The global demand for natural dyed products is increasing in international market due to their less toxicity and harmful effects. The natural dyes are clinically safer than their synthetic analogues, in handling and use because of non-carcinogenic and biodegradable nature.[7] Natural dyes exhibit better biodegradability and generally have a better compatibility with the environment. They are less toxic, polluting, health hazardous, non-carcinogenic, easily available and renewable.[8] Though possess lower toxicity and allergic reactions than synthetic dyes however safety of natural dyes needs to be proved if they are used more widely and in commercial process.[9] The environmental pollution problems caused due to the harmful chemical dyes requires a dire need for the assessment of the synthetic dyes, which can be countered with the wide search and usage of the viable cheaper sources of dye and mordant.

Materials and Methods

Collection of Material

The fruit cups of *Quercus robur* L. were collected from Dachigam wild life sanctuary, Srinagar and material of *Punica granatum* L. (peel) for mordant was collected from university outskirts (Plate-1). Wool and cotton were purchased from Poshish (JKHDC) outlet at Srinagar (J&K) and Govt. silk weaving factory.

Quercus robur L. (fruit cups) *Punica granatum* L. (peel)

Plate 1: Selected materials for dye and mordant

Preparation of dyeing material

Quercus robur L. (fruit cups) were used as a source of natural dye. The material was dried and washed with distilled water and dried in tray drier at 80°C for 2 hours, finely powdered with the help of a grinding machine. The material was then passed through a standard test sieve (BSS-14).

Preparation of Mordant

The peel of *Punica granatum* L. was cut into small pieces followed by drying in tray drier and soaked in distilled water for four days. The mordant solution was prepared by using one liter of distilled water and 100 grams of the material. The mordant solution was then filtered and refrigerated for future usage.

Extraction of dye

The extraction of the dye was carried using soxhlet apparatus keeping distilled water as solvent. 1 L of distilled water was used for 100g of plant material. The material was kept for reflux for about 8 hrs at 80-85°C. Liquid extract was evaporated at 65°C in a rotary vacuum evaporator to one fourth of its original volume to obtain the final dyeing extract.

Scouring of fabrics

The test fabrics was cut into 5×6 cm, washed with 2% non-ionic soap (Labolene) and heated at 50 °C for 20 min, by maintaining the material-to-liquor ratio at 1:50. The test fabrics were washed thoroughly with plenty of tap water and dried at room temperature.

Dyeing of Fabrics

The scoured material was soaked in distilled water for 30 minutes prior to dyeing. Process of dyeing was carried out in a water bath maintaining material to liquor ratio 1:50. The test fabrics were dipped in 250ml beaker containing 100ml of dyeing solution and 4% dye (OWM) at room temperature and raised to 85^o - 90^oC with gentle stirring continued for 1 hour. The material was then removed and washed 2-3 times with 1% of detergent and water. Dyed samples were squeezed and dried at room temperature. Dyeing of the wool fabric was done at acidic pH by adding acetic acid (CH_3COOH) and cotton fabric was dyed at basic pH by adding Sodium carbonate (Na_2CO_3).

Mordanting

The mordanting was carried out by the following three methods, i.e. pre mordanting, simultaneous mordanting and post mordanting. The process of mordanting was performed by using 4% of the solution keeping the M:L ratio of 1:100. The mordanting of the samples was carried at 60-75^oC and continued for 1 hour.

Determination of percent absorption of dye

The dye uptake by the selected test fabrics was calculated by recording the optical density of the dye solution both before and after dyeing process. The ultraviolet-visible adsorption spectra (UV-VIS) was recorded on PC based double beam spectrophotometer (Systronics 2202) over the range of 200-800 nm. The percent absorption of natural dye was calculated by using the following equation.

$$\text{Percent absorption} = \frac{\text{O.D before dyeing - O.D after dyeing}}{\text{O.D before dyeing}} \times 100$$

Evaluation of CIE L*a*b* values of dyed fabrics

Colour coordinates (CIELAB) values of the dyed and non-dyed fabrics was determined by chromometer (Model CR-2000, Minolta, Osaka, Japan) equipped with 8 mm measuring head and AC illumination (6774 K) based on CIE system (International Commission on Illumination). The meter was calibrated using the manufacturer's standard white plate.

L*, a* and b* coordinates, Chroma (C*) and hue angle (h^o) values were calculated by the following equations.

$$\text{Chroma} = (a^{*2} + b^{*2})^{1/2}$$
$$\text{Hue} = (h = \tan^{-1} b^*/a^*)$$

Total colour change of the dyed fabrics was calculated from the L*, a* and b*coordinates by applying the following equation.

Total Colour change (ΔE):

$$(\Delta E) = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

Where,

$\Delta L^* = L^*$ sample - L^* standard
$\Delta a^* = a^*$ sample - a^* standard
$\Delta b^* = b^*$sample - b^*standard

Determination of Colour strength (K/S) value

The colour strength (K/S values) of both the non-dyed and dyed fabric samples was evaluated using JAYPAK 4802 colour matching system (Jay Instruments Ltd, Mumbai, India) at D65 illuminate/10 Deg observer. The reflectance of the samples was measured at 360-760 nm. The colour strength value in the visible region of the spectrum (400-700 nm) was calculated based on the Kubelka-Munk equation.

$$\frac{K}{S} = \frac{(1-R\lambda)^2}{2\times R\lambda}$$

Where, K is the coefficient of absorption, S is the scattering coefficient and R is the surface reflectance value of the sample at a particular wavelength, where maximum absorption occurs for a particular dye/colour component.

Relative colour strength

Relative colour strength (K/S values at maximum wavelength) was determined by adopting the following equation.

$$\text{Relative colourstrength} = \frac{\text{(K/S) Extracted}}{\text{(K/S) Raw}}$$

Evaluation of colour fastness properties

The retention of the dye by the test fabrics were recorded on the basis of Colour fastness tests carried out as per ISO 105-B02 for light, ISO 105 X-12 for rubbing and ISO 105-C01 for washing respectively. Grading for colour change and colour staining were evaluated as per ISO 105-AO2 and ISO 105-A03.

Result and Discussion

Percent absorption

The overall mean of percent absorption for wool and cotton are 25.7 and 14.38 respectively. The uptake of dye by the wool fabric recorded higher values than cotton fabric where, mordanted samples recorded higher values than unmordanted samples. Among the methods post mordanting method shows the highest uptake of the dye. Wool has higher percent absorption than cotton fabric (Table-1). The wool fibre contains equal amount of amino and carboxyl groups which ionize and form zwitter ion. At low pH the hydrogen ions are absorbed by carboxyl groups present in wool. At high pH the protein losses hydrogen ions leaving behind ionized groups. Thus wool absorbs maximum dye in acidic medium.[10] Dyeing of the cotton fabrics with the combination of the mordants did not show much effect on absorption which may be due to weak and low ability of cotton to form coordination complexes with dye molecules. This low coordination tendency of cotton with the dyes and mordants resulted in low dye absorption [11] and also reported lesser dye ability of cotton than that of the wool.

Table 1: Percent absorption the dyed fabrics

Fabric	Without mordant	Pre mordanting	Simultaneous mordanting	Post mordanting	Mean
Wool	25.01	26.51	26.11	25.19	25.7
Cotton	13.73	14.88	14.94	13.97	14.38

Colour coordinates (CIELAB) values

All dyed samples showed variation in L*, a*, b*, C* and h^o values Table-2, confirmed by the variation in total colour change (ΔE) values. The lightness values of both the test fabrics show coloured samples. Both wool and cotton fabric recorded positive values of a* and b*. The colour of the test fabrics showed dark and light brownish and yellowish shades, with beautiful colour tones and hues as depicted by the L*, a*, b* & h^o values. Light yellowish shades with low chroma were recorded in dyed cotton fabrics. The cotton fabric showed higher L* and low a*, b*, C*, h^o and ΔE values than wool fabric. The chromaticity (C*) of the dyed fabrics showed brighter and dark shades. Whereas, the colour of the cotton fabric sowed light and dull tones and colour saturation. The total colour change of unmordanted samples for wool and cotton fabrics are 31.16 and 18.17 respectively (Table-2). Among the two fabrics the wool fabric shows the best colour as compared to the cotton fabric. For both the test fabrics the methods adopted were found to be significant. In wool fabric post mordanting method showed best result as depicted by its colour values. Similarly for cotton fabric simultaneous mordanting method showed best result as depicted by its colour values (Table-3). The tone of samples were much yellowish and less reddish as indicated by values of a* and b*. These changes could be attributed to resonating structures of dyes.[12] Chroma value of all the dyed fabrics recorded highest representing the bright colours of dyed fabrics.[13] There is pronounced difference among the dyed samples. This could be correlated with complex forming ability of the metal ions with dye molecules on the fabric. In mordanting some of the mordant is stripped out in the dye bath, which subsequently forms an insoluble complex with dye molecules in solution. Thus simultaneous mordanting showed less depth in shade.[14]

Table 2: Average colour coordinates of test fabrics

Methods \ Colour coordinates	L*	a*	b*	C*	h^o	Δ E
Wool Fabric						
Without Mordant	73.07	4.375	31.22	31.53	82	31.16
Pre mordanting	64.4	7.72	27.42	28.49	74.3	27.80
Simultaneous mordanting	60.97	6.95	36.86	37.51	79.3	29.32
Post mordanting	48.94	4.29	20.76	21.20	78.3	34.97
Cotton Fabric						
Without Mordant	80.44	4.505	19.73	20.24	77.1	18.17
Pre mordanting	78.88	1.86	25.6	25.67	85.8	23.54
Simultaneous mordanting	73.82	0.21	33.33	33.35	89.6	32.61
Post mordanting	83.79	0.48	23.41	23.41	88.8	18.87

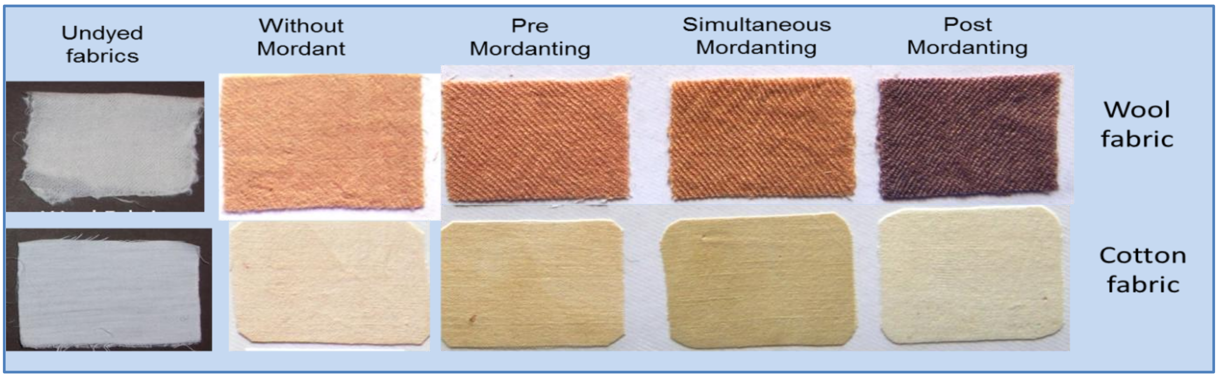

Plate 2: Dyed and undyed fabrics of wool and cotton

Colour Strength of the dyed fabrics (K/S)

The colour strength (K/S) is a single numerical value related to the amount of light-absorbing material (colourant) contained in the sample usually based on spectral data. The calculation of colour strength (K/S) value of a sample is based on the reflectance values of the dyed sample and Kubelka-Munk equation is used for calculating the K/S value. The average K/S for wool and cotton fabrics was 0.615 and 0.531 respectively. The colour strength for unmordanted samples shows best results in wool fabric as compared to cotton fabric. Among all the methods adopted for mordanting wool fabric shows best results except in simultaneous mordanting method. Similarly, for cotton fabric all the methods adopted shows best results except post mordanting method with reference to the unmordanted sample (Table-3). The relative colour strength of the wool fabric shows best result as compared to the cotton fabric as depicted by its average values (1.64 & 1.12) respectively (Table-54). Among all the methods adopted for wool fabric, Pre mordanting method (2.06) shows the best result as compared to other methods with respect to relative K/S. Similarly, for cotton fabric simultaneous mordanting method (1.22) gives best results as compared to other adopted methods with respect to relative K/S (Table 4). The difference in the K/S values of the test fabrics in different methods is due to the stripping out of the dye and formation of coordination complexes in the dye bath, which subsequently forms an insoluble complex with dye molecule in solution.[14] The higher colour strength of the mordanted fabrics may be due to their ability of forming coordination complexes with dye molecules.[15] The increase in colour strength of dyed wool may be due to fiber swelling and the breakdown of the dye molecule aggregates in the solution became more, thus the diffusion of the dye molecules to the fiber became easier causing increase in colour strength value of the wool fabric.[7] Cotton by its nature is negatively charged in water, thus exhibiting poor absorption for natural dyes due to repulsion effect causing poor colour strength.[17]

Table 3: Colour strength (K/S) of the selected dyed fabrics

Fabric	Without mordant	Pre mordanting	Simultaneous mordanting	Post mordanting	Mean
Wool	25.01	26.51	26.11	25.19	0.615
Cotton	13.73	14.88	14.94	13.97	0.531

Table 4: Relative colour strength (K/S) of the selected dyed fabrics

Fabric	Without mordant	Pre mordanting	Simultaneous mordanting	Post mordanting	Mean
Wool	1.54	2.06	1	1.97	1.64
Cotton	1.1	1.21	1.22	0.97	1.12

Fastness properties of dyed fabrics

The colour fastness grade is equal to the grey scale step which is judged to have the same colour or contrast difference.[15] All the dyed samples recorded acceptable fastness grades. The fastness grades of the dyed fabrics in terms of washing, light and rubbing recorded efficient dye retention. However the grades of the mordanted samples in all the retention tests recorded efficient grades with good quality and retention. The mordant and mordanting method affected the retention quality of the dyed fabrics in all the tests performed. The washing fastness grades of the wool fabric recorded Fair to Good (3/4), Good (4), Good to Excellent (4/5) and Excellent (5) grades in colour change, whereas in colour staining Good to Excellent (4/5) and Excellent (5) grades were recorded. Light fastness of the wool fabric recorded Good to Excellent (4/5) and Excellent (5) grades. The rubbing fastness both dry and wet in staining and fading of the wool fabric recorded Good (4), Good to Excellent (4/5) and Excellent (5) grades in colour change, whereas in colour staining Good to Excellent (4/5) and Excellent (5) grades. In cotton fabric washing fastness grades of color change and colour staining recorded Good (4), Good to Excellent (4/5) and excellent (5) grades. Light fastness grades recorded good (4) and excellent (5) grades. However, grades of rubbing fastness both in staining and rubbing recorded good (4), good to excellent (4/5) and excellent (5) grades (Table-5). Cotton is a cellulosic fibre and cotton lacks affinity for the natural dyes.[18] The increase in the fastness properties of the dyed fabrics due to mordants may be attributed to increase in size of dye molecules when connected to tannin molecules into the fibre.[19] The colour fastness of natural dyes not only depends on chemical nature and type of natural colourant, but also on chemical nature and type of mordants being used.[20] The washing fastness of the dye is influenced by the rate of the diffusion of the dye and state of the dye inside the fibre.[21] Good light fastness is due to the formation of complex with the mordant which protects chromatophore from photolytic degradation.[22]The lower grade of light fastness implies that metal ligand chealates formed by the mordant are not much resistant to photo degradation as by other mordants having Excellent (5) grades.[23] The higher grades of the wet rub fastness than dry rub fastness may be to the dissolving of water soluble dye molecules by the water which make them easier to be removed from the fibre by rubbing.[23] The satisfactory results of in mordanted samples may be due to the mordants which chelate several dye molecules together, thus creating a larger complex and providing a link between the dye and the fibre.[24]

Table 5: Fastness grades of fabrics dyed with *Quercus robur* L. (fruit cups) and *Punica granatum* L. (peel) adopting different methods

Method	Washing fastness		Light fastness	Rubbing fastness			
				Staining		Fading	
	CC	CS		Dry	Wet	Dry	Wet
Wool							
Without mordant	4	4/5	4/5	4/5	4/5	5	4/5
Pre mordanting	¾	5	4	5	5	4/5	4
Simultaneous mordanting	4/5	5	5	4/5	5	4/5	4
Post mordanting	4	5	5	4/5	4	5	5
Cotton							
Without mordant	4/5	4/5	4	5	5	5	4/5
Pre mordanting	5	5	4	5	4/5	5	4/5
Simultaneous mordanting	5	5	5	5	4/5	5	5
Post mordanting	4	5	5	4	4	5	4/5

Conclusion

The natural dye and mordant was successfully extracted and applied on wool and cotton fabric. The dye in isolation and in combination produced varied beautiful shades of colour with different shades and tones. The natural dye applied with different mordanting methods produced different shades in case of wool fabric. However, cotton fabric does not showed much affinity for the natural dye and mordant and produced light and dull shades. The natural mordant applied increased the dye uptake, colour strength and fastness properties with varied shades in wool fabric. *Quercus robur* (fruit cups) dye in combination with *Punica granatum* (peel) is suggested as an effective alternative substitute to chemical dyes for their usage in textile industries for wool fabric.

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References

1. Ogugbue, C.J., Sawidis, T. Bioremediation and Detoxification of Synthetic Wastewater Containing Triarylmethane Dyes by *Aeromonas hydrophila* Isolated from Industrial Effluent. Biotechnology Research International 2011; DOI 10.4061/2011/967925.

2. Ben, M.H., Houas, I., Montassar, F., Ghedira, K., Barillier, D., Mosrati, R. Ghedira, L. Alteration of *in vitro* and acute *in vivo* toxicity of textile dyeing waste water after chemical and biological remediation. Environmental Science and Pollution Research International 2012; DOI 10.1007/s11356-012-0802-7.

3. Prado, A.G.S., Torres, J.D., Faria, E.A.,Dias, S.C.L. Comparative adsorption studies of indigo carmine dye on chitin and chitosan. Journal of Colloid and Interface Science2004; 1(1): 43-47.

4. Thoren, K., Meding, B., Nordlinder, R.,Belin, L. Contact Dermatitis and Asthma from Reactive dyes. Contact Dermatitis1980; 15(3): 186.

5. Gonzales, C.A., Riboli, E., Lopez, A.G. Bladder Cancer among workers in the textile industry, results of a Spanish case-control study. American Journal of Industrial Medicine1988; 14 (6): 673-680.

6. Kaisa, K., John, P., Atte, V.W., Jyrki, L., Pirjo, L.S. Evaluating the toxicity of reactive dyes and dyed fabrics with the Hepa-1 cytotoxicity test. Autex Research Journal2007; 7(3): 224-228.

7. Aminoddin., Haji. Functional dyeing of wool with natural dye extracted from *Berberis vulgaris* wood and *Rumex hymenosepolus* root as biomordant. Iranian Journal of Chemistry and Chemical Engineering2010; 29 (3): 55-60.

8. Adeel, S., Ali, S., Bhartti, I.A., Zsila, F. Dyeing of cotton fabric using Pomegranate (*Punica granatum*) aqueous extract. Asian Journal of Chemistry 2009; 21 (5): 3493-3499.

9. Kumar, V., Bharti, B.V. Eucalyptus yields dye. The Indian Textile Journal1998; 10: 18-20.

10. Mathur, J.P., Bhandari, C.S.Use of beet sugar as wool colourant. Indian Journal of Fibre and Textile Research2001; 26: 313-316.

11. Tiwari, H.C., Singh, P., Mishra, P.K., Srivastava, P. Evaluation of various techniques for extraction of natural colourants from pomegranate rind-Ultrasound and enzyme assisted extraction. Indian Journal of Fibre and Textile Research2010; 35: 272-276.

12. Montazer, M., Parvinzadeh, M.Colourimetric properties of wool dyed with natural dyes after treatment with ammonia. Colouration Technology2004; 120(4): 161-166.

13. Almela, L., Javaloy, S., Fernendez, L.J.A., Lopez, R.J.M. Comparison between the tristimulus measurements Yxy and L*a*b* to evaluate the colour of young red wines. Food Chemistry 1995; 35: 321-327.

14. Deo, H.T., Desai, B.K. Dyeing of cotton and jute with tea as a natural dye. Journal of the Society of Dyers &Colourists 1999; 115: 224-227.

15. Kumaresan, M. Comparison of fastness properties and colour strength of dyed cotton fabrics with Eco friendly natural dyes. International Journal of Science and Technology2013; 8(3) : 483-489.

16. Baishya, D., Talukdar, J., Sandhya, S. Cotton dyeing with natural dye extracted from flower of Bottle brush (*Callistemon citrinus*). Universal Journal of Environmental Research and Technology2012; 2 (5): 377-382.

17. Kampeerapappun, P., Phattararittigul, T., Jittrong, S., Kullachod, D.Effect of Chitosan and mordants ion dyeability of cotton fabrics with *Ruellia tuberosa* Linn. Chiang Mai Journal of Science2010;38(1): 95-104.

18. Prabhu, K.H., Bhute, A.S. Plant based natural dyes and mordants: A review. Journal of Natural Product and Plant Researches2012;2(6): 649-664.

19. Haji, A. Functional dyeing of wool with natural dye extracted from *Berberis vulgaris* wood and *Rumex hymenosepolus* root as Biomordant. Iranian Journal Chemistry and Chemical Engineering2010;29(3): 55-59.

20. Samanta, A.K.,Agarwal, P. Application of natural dyes on textiles. Indian Journal of Fibre and Textile Research 2009; 34: 384-399.

21. Jothi, D. Extraction of Natural dyes from African marigold flower (*Tagetes erecta* L.) for Textile colouration. AUTEX Research Journal2008;8(2): 74-79.

22. Kulkarni, S.S., Gokhale, A.V., Bodake, U.M., Pathade, G.R. Cotton dyeing with natural dye extracted from Pomegranate (*Punica granatum*) Peel. Universal Journal of Environmental Research and Technology 2011; 1(2) : 135-139.

23. Gupta, D., Gulrajni, M.L., Kumari, S. Light fastness of naturally occurring anthraquinone dyes on nylon. ColourationTechnology2004;120: 205-212.

24. Cardon, D. Natural dyes: Sources, tradition, technology and science. Archetype Publications: London 2007.