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Eco friendly dyeing of Silk and Pashmina fabrics with *Quercus robur* L. as dye and *Punica granatum* L. as mordant

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Abstract

An experiment was setup to study the dyeing efficiency of *Quercus robur* L. (fruit cups) and *Punica granatum* (Peel) mordant applied on silk and pashmina fabrics. Dyeing was performed both excluding and including the mordant adopting different methods. Colour quality was assessed in terms of dye absorption (%), Colour coordinates (CIELAB), Colour strength (K/S), and fastness properties in terms of washing, light and rubbing. Unmordanted dyed samples showed light colour and tones than mordanted samples. A percent absorption and colour strength value of dye by selected fabrics was efficient in both the fabrics. Colour quality of the silk and pashmina fabric recorded efficient values with low values of lightness and colour changes values (ΔE) with beautiful shades and colour tones. Fastness grades in terms washing, light and rubbing recorded excellent grades most of the mordanted samples.

Keywords: Eco friendly, *Quercus robur*, *Punica granatum*, Silk, Pashmina.

Introduction

Environmental problems arising after industrialization of textiles by the dyeing, when traditional natural dyes substituted by synthetic dyes. Synthetic dyes are persistent to the environment and are designed to resist chemicals, and improve the quality of the product. The sources of synthetic dyes are cheap petroleum, easily dyed, superiority in fastness, available widely at an economical prices and variety colours and shades are produced [1]. To produce synthetic dyes the chemicals used for the process are highly toxic, carcinogenic, allergic, explosive and dangerous to work with. Many violent reactions involved in the production of synthetic dyes are considered to be health hazardous [2]. The textile industries commonly utilize reactive dyes for dyeing different types of fibres, producing effluents comprising of several types of chemicals like dispersants, leveling agents, acids, alkalis, carriers etc. [3]. The dyeing industry releases untreated wastewater which is threat to environment. The coloured wastewater which is produced from industries have high organic load and can enormously contributed to the surface water pollution and treatment plants if not properly treated before disposal into the water resources.

Textile wastewaters are characterized by extreme fluctuations in many parameters such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), pH, colour and salinity. The discharge of highly coloured synthetic dye effluents into inland and coastal waters is an environmental problem of growing concern [4]. Pollution by dye wastewater is becoming increasingly alarming and is of great environmental concern [5]. Even presence of very small amounts of dyes (<1 mg/L for some dyes) in the water, which are nevertheless highly visible, seriously affect the aesthetic quality and transparency of water bodies like lakes, rivers leading to damage to the aquatic environment [6]. During the dyeing process loss of colourants to the environment can reach 10-50 % [7]. Some dyes are highly toxic and mutagenic, and also decrease light penetration and photosynthetic activity, causing oxygen deficiency and limiting beneficial uses such as recreation, drinking and irrigation [8]. The global demand for natural dyes is about 10,000 tonnes, which is equivalent to 1 % of the world synthetic dye consumption [9]. However, demand for natural dyed products is increasing in international market. Natural dyes are excellent for long endurance and retain great beauty and charm. They create very harmonious combinations with various natural mordants. Manufacturing of natural dyes offers a rich and varied source providing a source of income through sustainable harvest and sale.In view of advancements in technology and urban development, there is dire need to assess the environmental pollution problems caused due to synthetic dyes. Considerable research work is being conducted throughout the world to search out new cheaper dye sources and extraction methods for producing sufficient quantities of viable safe natural pigments and dyes.

Materials and Methods

Collection of Material

The material of *Quercus robur* L. (fruit cups) as dye and *Punica granatum* L. (Peel) as mordant was collected from Dachigam wild life sanctuary and SKUAST-K, Shalimar, Srinagar, respectively. Silk were purchased from Govt. silk weaving factoryat Rajbaghand Pashmina was purchased from F.S. Shawls, Eidgah Srinagar (J&K).

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 natural dye source and shade dried fruit cups were washed with water to remove unwanted materials followed by drying in tray drier at 80 °C for 2 hours, powdered with the help of a crunching machine. The material was then passed through a standard test sieve (BSS-14).

Preparation of Mordant

The material (peel) of Pomegranate (*Punica granatum* L.) was cut into small pieces, dried and poured in distilled water for 4 days. For making the solution of mordant, 1 L of distilled water was used for 100 gm of peel which was then filtered and kept under refrigeration for further usage.

Extraction of dye

The dyeing material was extracted using Soxhlet apparatus using distilled water as solvent. 1 L of distilled water was used for 100g of plant material and the material was kept for reflux for about 8 hours at 80-85^{o}C. Liquid extract was evaporated at 65^{o}C in a rotary vacuum evaporator to one fourth of its original volume to obtain the final dyeing extract.

Scouring of fabrics

Silk and Pashmina fabric was cut into 5×6 cm, followed by washing with 2% non-ionic soap (Labolene) at 50^{o}C for 20 min, maintaining the material-to-liquor ratio at 1:50. The scoured material was then washed thoroughly with plenty of tap water and dried at room temperature. The scoured material was soaked in distilled water for 30 minutes prior to dyeing.

Dyeing of Fabrics

Process of dyeing was carried out in a water bath maintaining material to liquor ratio 1:100 for silk fabrics and 1:60 for Pashmina fabric. The scoured and washed fabric was dipped in 250ml beaker containing 100ml of dyeing solution and 4% dye (OWM) at room temperature and raised to 85^{o} - 90^{o}C with gentle stirring continued for one 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 silk and pashima fabrics was done at acidic pH by adding acetic acid (CH_3COOH).

Mordanting

The mordanting was carried out by the following three methods, i.e. pre mordanting, simultaneous mordanting and post mordanting.

Recipe of mordanting

Mordant	*Punica granatum* L. (Peel)
Concentration (%)	4
Temperature (^{o}C)	60-75
Material to Liquor ratio (MLR)	1:100 for Silk and 1:60 for Pashmina
Time (hrs)	1

Determination of percent absorption of dye

The absorption of the natural dye by recording the optical density of the dye solution both before and after dyeing of selected fabrics was recorded. 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

CIE L*a*b* values of the dyed and undyed 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 K/S value (colour strength) of the un-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 and the colour strength value in the visible region of the spectrum (400-700 nm) was calculated based on the Kubelka-Munk equation.

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

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.

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

Evaluation of colour fastness properties

The Colour fastness tests of the dyed fabrics were 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 absorption of the dye by the fabrics is an important parameter to determine the dyeing quality of the fabric. In all the test fabrics absorption of the dye is affected by the usage of the mordant and adopting of the mordanting method. Percent absorption of the Pashmina fabric recorded higher than silk. The highest value of absorption in silk fabric (26.92) was recorded in simultaneous mordanting method. However, pashmina fabric recorded higher value (28.24) by adopting pre mordanting method. The absorption of the dye in the adopted methods varied significantly (Fig. 1). The absorption of the dye by the fabrics is due to electro-potential forces, temperature and agitation which drive dye molecules towards the fibre surface [10]. Since the dye used is a water soluble dye containing anionic groups would interact ionically with the protonated terminal amino groups of the silk fibres at acidic pH via ion exchange reaction. This ion attraction would increase the dye ability of the fibre.The Pashmina wool protein (-NH2,-OH,-COOH) provides a bridge between the dye and the pashmina wool resulting in increase of the percent absorption than the other fabrics [11].

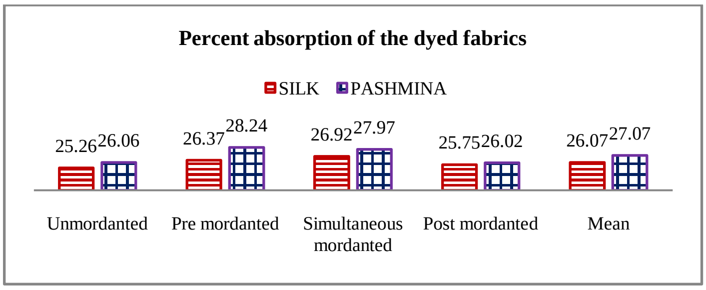

Fig. 1: Percent absorption of the selected fabrics

Colour coordinates (CIELAB) values of test fabrics dyed

Highest L* (68.29) was recorded in silk fabric following pre mordanting method. However, in pashmina fabric highest L* (61.73) was recorded adopted pre mordanting method. The positive values of a* & b* justifies the reddish and yellowish dyed samples with different shades and tones of colour, which varied in each sample by adopting different mordanting methods. The values of the chroma represented the bright and darkcoloured samples which gotvisible in pashmina fabric followed by the silk fabric. The hue value of the dyed samples represented the tonacity of the colour which marked the different shades of the coloured fabrics. The fabrics of silk showed beautiful shades of light yellow, light brown, brown and dark brownish shades. Whereas, pashmina fabric showed brightest light and dark brown shades. The unmordanted dyed samples of silk and pashmina showed light shades than mordanted samples. The total colour change (ΔE) of the dyed fabrics represented the change in the colour of the samples with referenceto fabrics which varied in each samples in all the methods of the mordanting. Chroma value of all the dyed fabrics recorded highest representing the bright colours of dyed fabrics [12]. The change in the colour of the dyed samples may be attributed to the resonating structures of dyes [13]. There difference among the dyed samples 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]. The difference in the shade of dyed fabrics with different mordants and mordanting methods may be due to individual metal ions and different techniques, exhibiting unique complex formation resulting in different shade of the dyed fabrics [15].

Table 1: Average colour coordinate values of different fabrics treated with *Quercus robur* L. fruit cups dye using *Punica granatum* L. peel as mordant.

Colourcoordinates / Methods	L*	a*	b*	C*	h°	Δ E
Silk Fabric						
Without Mordant	65.81	4.84	28.98	29.39	80.5	30.03
Pre mordanting	68.29	6.51	21.58	22.54	73.2	23.54
Simultaneous mordanting	48.68	3.72	24.74	25.02	81.4	42.59
Post mordanting	54.48	5.29	26.16	26.69	78.6	37.73
Pashmina Fabric						
Without Mordant	55.71	4.34	25.53	25.9	80.3	26.95
Pre mordanting	61.73	5.51	37.60	38.01	81.7	28.97
Simultaneous mordanting	42.09	5.56	29.78	30.29	79.4	41.27
Post mordanting	41.47	4.39	26.45	26.81	80.6	40.78

Plate 2: Test fabrics dyed with combination of dye and mordant

Colour strength (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. Better results of colour strength and relative colour strength of the dyes and mordants were observed in pashmina fabric followed by silk fabric. Both the silk and pashmina fabric recorded excellent colour strength and relative colour strength values. The highest value of colour strength (K/S) (0.848) with relative K/S of 2.18 in both the fabrics was recorded in post mordanted pashmina fabric. In silk fabric highest colour strength value (K/S) was recorded in simultaneous mordanted dyed sample with relative K/S of 2.3 (Fig. 2&3). All the mordanted samples showed higher K/S values when compared with the unmordanted except in pre mordanted silk sample (0.534) with relative K/S of (1.67) (Fig. 2&3). Better colour strength results depend on the mordant used [16]. The higher colour strength of the mordanted fabrics may be due to their ability of forming coordination complexes with dye molecules [17]. The higher colour strength value of pashmina fabric may be due to formation of coordinate complex between dye and mordant and their aggregation inside the fibre leading to linear increase in colour. The increase in colour strength (K/S) of the silk fabric may be due to formation of additional linkage of mordants with dye molecules compared to the silk samples dyed without any mordant strength of the pashmina fabric [18].

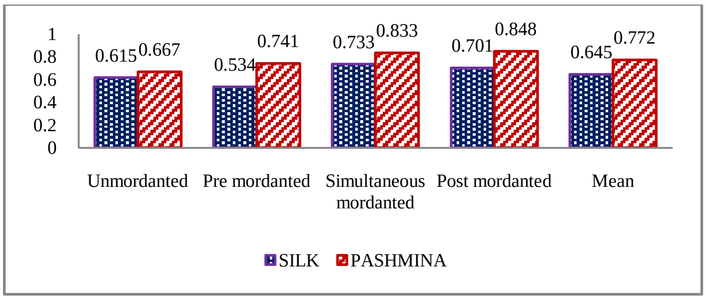

Fig-2: Colour strength of the dyed test fabrics

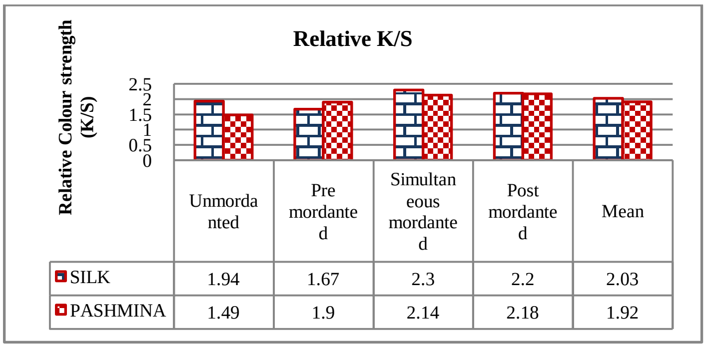

Fig-3: Relative colour strength (K/S) of the selected test fabrics

Colour fastness properties of the dyed samples (Washing, light and rubbing).

Among all types of colour fastness properties, light fastness, washing fastness and rubbing fastness are considered generally for any textile [19]. The colour fastness grade is equal to the grey scale step which is judged to have the same colour or contrast difference [20]. The fastness requirements are largely determined by the end use of dyed fabrics. The colour fastness and retention of the dye by the selected fabrics in terms of washing, light and rubbing tests recorded best quality of the colour in both the silk and pashmina fabrics (Table-2). The colour fastness grades in silk fabric recorded Good to Excellent (4/5) to Excellent (5) grades in washing and rubbing fastness tests and Good (4), Good to Excellent (4/5) to Excellent (5) in light fastness tests in both dry and wet tests in terms of the colour change and colour staining. The grades of the pashmina fabric also recorded Good (4), Good to Excellent (4/5) and Excellent (5) grades in washing, light and rubbing tests. The wet fastness grades in washing and rubbing tests recorded higher than dry test grades (Table-2). Thus the overall grades recorded determine the efficient fastness quality of the dyed fabrics in the performed tests. The pashmina and silk are amphoteric and can absorb both acids as well as bases. Pashmina wool protein (-NH2, -OH, -COOH) provide the bridge between dye and wool. The cochineal-aluminium complex inside the pashmina wool fibre matrix is probably stable and witnesses the satisfactory fastness results [21]. 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 [22]. 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 [22].

Table 2: Fastness grades of fabrics dyed with *Quercus robur* L. (fruit cups) and *Punica granatum*. (peel) adopting different mordanting methods

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

CC: Colour change
CS: Colour staining

Conclusion

The fabrics dyed with *Quercus robur* L. (fruit cups) dye and *Punica granatum* L. (peel) mordant both in isolation and in combination with the mordant showed the best affinity and colour quality of the extracted materials on the fabrics. Beautiful colour shades and tones of the dyed fabrics were produced. The dyeing material produced beautiful colour and shades when applied on the fabrics. However, the colour quality of the mordanted samples was observed to be much efficient with better quality and retention. The extracted material can be recommended as a viable source for their utilization in dyeing industries and can be exploited commercially both in national and international market.

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Conflict of interest statement

We declare that there is no conflict of interest.

References

1. Aminoddin, Haji. Functional dyeing of wool with natural dye extracted from Berberis vulgaris wood and RumexHymenosepolusroot as biomordant. Iranian Journal of Chemistry and Chemical Engineering 2010; 29(3):55-60.

2. Wilkinson SM, Mcgechaen K. Occupational Allergic contact Dermatitis from Reactive dyes. Contact Dermatitis 1996;35(6): 376-378.
3. Cooper P. Colour in dye house effluent. Society of Dyers and Colourists, Bradford 1995;3(8): 97-101.
4. Padmavathy S, Sandhya S, Swaminathan K, Subrahmanyam YV, Chakrabarti T, Kaul SN. Aerobic decolourization of Reactive Azo dyes in presence of various co substrates. Chemical Biochemical Engineering 2003;17(2):147-151.
5. Moreira TA, Viacava C, Gladys V. Fed batch decolourization of Poly R-478 by Trametesversicolour.Braz. Arch. Biol. Technol. 2004;47(2):137-165.
6. Wijetunga S, Li X, Jian C. Effect of organic load on decolourization of textile wastewater containing acid dyes in upflow anaerobic sludge blanket reactor.Journal of Hazardous Materials 2010;177(1-3):792-798.
7. Ben MH, Houas I, Montassar F, Ghedira K, Barillier D, Mosrati R, Ghedira L. Alteration of in vitro and acute *in vivo* toxicity of textile dyeing wastewater after chemical and biological remediation.Environmental Science and Pollution Research International 2012.DOI 10.1007/s11356-012-0802-7.
8. Hubbe MA, Beck KRO, Neal WG, Sharma YC. Cellulosic substrates for removal of pollutants from aqueous systems: a review. 2. Dyes. Dye biosorption: Review. Bio Resources 2012;7(2):2592-2687.
9. Sachan K, Kapoor VP. Optimization of extraction and dyeing conditions for traditional Turmeric dye.Indian Journal of Traditional Knowledge 2007;6(2):270-278.
10. Trotman ER. Dyeing and Chemical Technology of Textile Fibres. 6th Ed. Sevenoaks: Edward Arnold, 1990;pp. 272-278.
11. Temani P, Shakyawar DB. Standardization of dyeing condition of Cochineal extract on pashmina yarn. Journal of the Textile Association, 2011;pp. 96-98.
12. Almela L, Javaloy S, Fernendez LJA, Lopez RJM. Comparison between the tristimulus measurements Yxy and L*a*b* to evaluate the colour of young red wines.Food Chemistry 1995;35 : 321-327.
13. Montazer M, Parvinzadeh M. Colourimetric properties of wool dyed with natural dyes after treatment with ammonia. Colouration Technology 2004;120(4) : 161-166.
14. Deo HT, Desai BK. Dyeing of cotton and jute with tea as a natural dye. Journal of the Society of Dyers & Colourists 1999;115 : 224-227.
15. 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 Science 2010;38(1) : 95-104.
16. Kamel MM, Helmy HM, Hawary NSE. Some studies on dyeing properties of cotton fabrics with *Crocus sativus* (saffron) (flowers) using an ultrasonic method. AUTEX Research Journal 2009;9(1) : 29-35.
17. 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 Technology 2012;2(5) : 377-382.
18. Baker, Temani P, Shakyawar DB. Standardization of dyeing condition of Cochineal extract on pashmina yarn. Journal of the Textile Association,2011; pp. 96-98.
19. Samanta AK, Agarwal P. Application of natural dyes on textiles. Indian Journal of Fibre and Textile Research 2009;34 : 384-399.
20. Kumaresan M. Comparison of fastness properties and colour strength of dyed cotton fabrics with Eco friendly natural dyes. International Journal of Science and Technology 2013;8(3) : 483-489.
21. Stintzing FC, Carle R. Cactus stems (Opuntiaspp): A review on their Chemistry, Technology and uses. Molecular Nutrition and Food Research 2005; 49: 175-194.
22. 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 Engineering 2010;29(3) : 55-59.