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Compatibility of binary mixture of natural dyes for developing compound shades for cotton khadi fabric

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The compatibility rating of any two natural dyes applied together for obtaining compound shade has been determined. The natural dyes selected for compatibility study are, babool (BL), pomegranate rind (PR), madder or manjistha (MJ), red sandal wood (RSW), tesu flower (TF) and catechu (CT) based on their maximum commercial use. The dyes have been extracted in aqueous medium under optimized conditions and their binary mixtures in different proportions are used to dye cotton khadi fabric for developing varying compound shades on 15% overall concentration of myrobolan (harda) and aluminium sulphate (75:25) in sequence double pre-mordanted cotton khadi fabric. After dyeing with binary mixtures of natural dyes , dyed cotton fabric samples are subjected to evaluation of *K*/*S*, colour differences (ΔE), colour difference index (CDI) values; changes in hue /chroma, brightness index (BI), metamerism index (MI) etc; and also colour fastness to washing, light, rubbing and perspiration. The compatibility of these binary pairs of natural dyes has been assessed conventionally (Δc *vs* ΔL and *K*/*S* *vs* ΔL), as well as using an unique and simple novel method of compatibility test applied for assessing relative compatibility rating (RCR) of each binary pairs of natural dyes, by evaluating colour difference index [(ΔE x ΔH) / (ΔC x MI)] for application of different proportion of two dyes in each binary pair. The results of this novel simple method are found mostly in well agreement with the findings of compatibility test by conventional methods. Finally, the order of relative degree of compatibility of these binary pairs of natural dyes is found to be BL: MJ > BL: RSW > BL: CT > BL: PR > BL: TF.

Keywords: Cotton khadi, Dye extraction, Mordanting, Natural dyes

1 Introduction

Growing consciousness for environment-friendliness of textile products has led most of the consumers for using natural fibre-based textiles dyed with natural dyes. Production of synthetic dyes are dependent on non-renewable petrochemical source, produce toxic intermediates during their synthesis and may contain toxic / carcinogenic amines and are not eco-friendly. Contrary to this, most of the natural dyes with few exceptions are based on vegetable plant origin and are renewable, biodegradable, energy-efficient and eco-friendly having some medicated applications as well[1]**.** Hence, dyeing with natural dyes on natural fibre based textiles are being revived now a days due to consumers' growing environmental concern for different chemical hazards and toxic effects of synthetic dyes during its synthesis, application on textiles and use as synthetic dyed textiles[1-4]. But natural dyeing of textiles is still restricted in small to medium sector for hand dyeing and has not achieved wide acceptability in organized large scale sector, due to lack of standardized procedures of dyeing, hazards in extraction, limited availability, limited shades, difficulty in reproducibility and matching as well as lack of information on compatibility between any two natural dyes if applied together in a mixture. If these drawbacks of natural dyes can be overcome and be eliminated, its revival may be rapid for adopting eco-friendly dyeing of textiles. The present work is an endeavour towards study of compatibility issue of any selected pair of natural dyes to be applied on cotton khadi fabric.

There are many reports on dyeing of different textiles with different natural dyes[4-8]. But a few and discrete studies are only available in literature describing application of mixture of natural dyes on cotton and other textiles for study of their compatibility[9-12], reporting the colour interaction parameters including resultant colour strength and metameric effects. Some studies on compatibility of

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binary and tertiary mixtures of synthetic dyes [13-18] are also widely available in literature, whereas such studies with even binary mixture of natural dyes for obtaining compound shades on cotton or other natural fibre-based textiles are scanty and sporadic[12,19-21].

Therefore, to obtain newer compound shade with selected binary mixture of natural dyes along with acceptable colour fastness rating with uniform and reproducible shade following the standardized dyeing procedures, determining of degree of compatibility between any two selective natural dye pair is essential and justified.

Compatibility of dyes[13-18] is a relative measure of similarities and dissimilarities in dyeing rate/colour build up to produce progressive depth of shade, when any two natural or synthetic dyes are used in a mixture of binary pair for obtaining compound shade. But all these methods are cumbersome and tedious for determining compatibility of any two natural dyes. So, without knowing the actual compatibility rating of selected pair of natural dyes, when applied together in a binary mixture for developing compound shades, it is not possible to obtain rightly anticipated/desired shade depth/colour build up to obtain desired tone.

Hence, in the present study, compatibility of the few selected binary pair of two natural dyes has been assessed using two different methods to obtain correct compound shade/colour build up. Conventionally, the compatibility between two dyes has been determined through the plots of ΔC *vs* ΔL and /or *K*/*S* *vs* ΔL. A very simple novel method is used to determine relative compatibility rating (RCR) in numerical rating from the results of differences in CDI values[10-12]. Finally, the results of compatibility study by conventional methods and by the newer simpler methods are compared and reported.

2 Materials and Methods

2.1 Materials

2.1.1 Cotton Khadi Fabric

Plain weave khadi cotton fabric (73 Nm warp, 70 Nm weft, 76 ends/inch, 53 picks/inch, 73.5 g/m^2 fabric areal density and 0.075mm fabric thickness), bleached with 3% H_2O_2 (30%), was obtained from Gram Sewa Mandal, Gopuri, Wardha for the present study.

2.1.2 General Chemicals, Dyes and Mordants

Commercial grade acetic acid, common salt, sodium carbonate and non-ionic soap; and laboratory reagent (LR) grade aluminium sulphate were obtained from local suppliers.

Cetrimide (Loba Chem-India) was used under acidic *p*H (with acetic acid) as cationic dye fixing agent for improving wash fastness.

The following selected natural materials and natural dyes were used for the study:

- Harda/myrobolan (*Terminalia chebula*) —having chebulinic acid + ortho-hydroxyl + carboxylic acid
- Red sandal wood (RSW) or raktachandan (*Pterocarpus santalinius*) —having Santalin A + Santalin B + Deoxysantalin[10]
- Manjista (MJ) or madder *(Rubia cordifolia*) —having purpurin + manjisthin + purpuroxanthin + pseudo-purpurin + nordamncanthal + alizarin[22]
- Babool/babla (BL) (*Acacia nilotica*) —having catechin + epi-catechin + gallic acid + decatechin quercetin + leuco-cyanidin-gallate[23]
- Tesu flower (TF) (*Butea monosperma frondosa*) —having butein[24]
- Catechu (CT) (*Acacia catechu*) —having catechin + tannic acid[25]

2.2 Methods

2.2.1 Extraction and Purification of Colorant from Natural Dyes

Pre-cut and dried chips of selected plant materials of corresponding natural dyes were initially dried and crushed to powder in a locally made mechanical pulveriser cum grinder machine, and then it was subjected to aqueous extraction under the optimized conditions as reported earlier (Table 1).

All the above aqueous extracts of corresponding optimized concentration of natural dyes were double filtered and the filtrate was used as dye solution. However, as per requirement the corresponding optimised concentration of the filtrates was further concentrated by additional heating in water bath to obtain higher dye concentration or to obtain semi solid dry mass of corresponding dye. Dye concentration percentages were taken on the basis of dry weight of solid source material for each dye. To obtain purified dye powder from semi-solid dye mass, the said semi-solid dye mass was subjected to repeated distillation with soxleht apparatus using ethyl alcohol as solvent to obtain purified dye powder.

2.2.2 Mordanting

Bleached cotton fabrics were pre-mordanted using overall 15% myrobolan (75%) followed by aluminium sulphate (25%) in sequence at optimized concentration and conditions as reported earlier[23].

Table 1 — Optimised parameters of aqueous extraction of dye

Natural dye	Dye conc.[a], %	MLR	Temperature, °C	Time, min	*p*H	Ref.
Red sandal wood	40	1:40	80	15	10	10
Manjistha	30	1:30	60	30	5	22
Babool bark	30	1:30	60	45	6	23
Tesu flower	30	1:20	90	60	11	24
Catechu	40	1:20	90	30	12	25
Pomegranate rind	30	1:50	80	45	7	26

[a]Based on the dry weight of solid source of dye materials.

The mordanting was done using the following method in sequence with double mordents.

Myrobolan 'gel' prepared by soaking myrobolan in water overnight (12 h) was diluted in an appropriate concentration (15% w/w) and filtered. Bleached cotton fabrics were then first mordanted with 11.25% (i.e 75% of 15%) myrabolan solution using 1:20 MLR at 80°C for 30 min. After the treatment, the fabric was dried in air without washing to make it ready for second mordanting.

The above myrobolan treated cotton fabrics were then treated with 3.75% (i.e, 25% of 15%) aluminium sulphate at 80°C for 30 min using 1:20 MLR. After the second mordanting, the fabric samples were finally dried in air without washing to make them ready for subsequent dyeing.

2.2.3 Method of Natural Dyeing

Above double pre-mordanted cotton khadi fabrics were dyed by following method. In this method, the pre-mordanted cotton fabrics were dyed with aqueous extracts of either single or selected binary pairs of natural dyes in varying proportion (100:0, 75:25, 50:50, 25:75, and 0:100), applying overall 30% (owf) concentration of selected dyes (based on the dry weight of the amounts of source material) at 65°C for 60 min, maintaining MLR 1:30, *p*H 5 and 5% sodium chloride[23]. Hence, no further optimization of dyeing concentrations was felt necessary. In each case, the dyed samples were repeatedly washed with hot and cold water and finally dried in air. Finally, the dyed samples were subjected to soaping with 2g/L soap solution at 60^0C for 15 min, followed by water wash and drying in air.

2.2.4 Measurement of Colour Strength and Related Colour Interaction Parameters

The *K/S* values of the dyed cotton fabric were determined by measuring their surface reflectance using X-rite (Gretag Macbeth) portable spectrophotometer followed by calculating the *K/S* values using following Kubelka Munk equation[27].

Other colour parameters like change in hue (ΔH), change in chroma (ΔC), change in darkness/lightness (ΔL) and total colour difference (ΔE) were carried using CIE-Lab 1976 standard formula[27].

General metamerism index (MI) was calculated employing Nimeroff and Yurow's equation[27] of determining metamerism index, which is as follows: -

$$MI = \frac{\sum (\Delta RX_o)^2}{X^2} + \frac{\sum (\Delta RY_o)^2}{Y^2} + \frac{\sum (\Delta RZ_o)^2}{Z^2}$$

where X_o, Y_o and Z_o are the tri-stimulus values of a standard white surface of MgO (or equivalent surface of standard white tile); and X, Y and Z are the tri-stimulus values of the corresponding samples. ΔR values refers to the difference in reflectance values between two pieces of the same fabric sample measured at two different wavelengths.

Brightness index (BI) was measured using following relationship ISO-2469 and 2470 method[28]:

$$\text{Brightness index} = \frac{\text{Reflectance value of sample at 457nm}}{\text{Reflectance value of standard diffuser (white tile)at457 nm}} \times 100$$

2.2.5 Test of Colour Fastness

Colour fastness to washing[29] of the dyed samples was determined as per the IS: 764-1984 method following IS -3 (equivalent to ISO-III) wash fastness method using Megatech Overseas India Launder-O-Meter and relevant grey scale.

Colour fastness to rubbing[29] (dry and wet) was assessed as per the IS: 766-1984 method using an electronic crock meter and relevant grey scale. Colour fastness to light [29] was determined as per IS: 2454-1984 method using Microsal Fade-O-Meter and eight blue wool standards with known light fastness grade 1-8. Perspiration fastness tests for dyed cotton khadi fabric samples were carried out as per IS: 971-1983: RA 2009 method[29] at two different *p*H levels (5.5 and 8) using freshly prepared perspiration liquor as per standard recipe and method (as human perspiration may be acidic or alkaline in nature depending on one's metabolism).

2.2.6 Compatibility Tests for Selected Binary Pairs of Natural Dyes

2.2.6.1 Conventional Method

Following selected binary pairs of natural dyes in equal proportion (50:50) were applied on the pre-mordanted cotton fabrics using overall 30% (owf) of the respective extracts:

- M1 – Babool + Pomegranate rind (BL & PR)
- M2 – Babool + Madder (BL & MJ)
- M3 – Babool + Red sandal wood (BL & RSW)
- M4 – Babool + Tesu flower (BL & TF)
- M5 – Babool + Catechu (BL & CT)

For compatibility tests, pre-mordanted cotton fabric was dyed in two different sets (Set I and Set II) of progressive depth of shade.

Set I — The progressive depth of shade was developed by varying dyeing time and temperature. For each pair of dyes (M1-M5), nine separate small pre-mordanted cotton fabric samples were dyed using laboratory model beaker dyeing machine (Megatech Overseas India make) at varying dyeing temperature (40 - 65^{0}C @ 5^{0}C difference) and varying dyeing periods (10-60 min @ 10 min interval). The samples were taken out from the dye bath at the intervals of 5 min from 40^{0}C onwards, maintaining the heating rate of 1^{0}C/min. The penultimate sample was taken out after 50 min at 65^{0}C and the last one at the end of the dyeing process after 60 min.

Set II — The progressive depth of shade was developed by varying total concentration of dye mixture (5-30% @ 5% differences). For each pair of dyes, seven separate pre-mordanted cotton fabric samples were dyed by applying 5-30% (owf) each pair of dye at 65^{0}C for 60 min.

For both Set I and Set II dyeing, all the dyed fabrics were subjected to normal washing, soaping and rinsing before final air drying. The differences in the CIE Lab coordinates, namely ΔL, Δa, Δb and Δc, for all the dyed fabrics were obtained using the above-mentioned X-rite (Gretag Macbeth) portable spectrophotometer. The compatibility of a selective pair of dyes by conventional method can be judged[13-18] by observing the degree of closeness and overlapping of curves of the two sets of dyeing (ΔC *vs* ΔL or *K/S vs* ΔL).

2.2.6.2 Novel Method of Compatibility Test

An alternative simple method of assessing compatibility of binary pairs of natural or synthetic dyes has been established recently[9,10,30]. After the application of different proportions of binary pairs of dyes on the same fabric, the magnitudes of the respective ΔE, ΔC, ΔH and MI values, irrespective of their sign and direction, may be utilized to obtain colour difference index (CDI) values using the following proposed empirical relationship[9]:

$$\mathrm{CDI} = \frac{\Delta E \times \Delta H}{\Delta C \times \mathrm{MI}}$$

Proposed numerical relative compatibility rating (RCR) was represented as per earlier work [10].

3 Results and Discussion

It has been reported earlier work[23] that the pre-mordanting using 15% overall myrobolan followed by aluminium sulphate in 75:25 ratio is the most suitable system for dyeing bleached cotton khadi fabric with bark of baboon dye. Hence, the same system of pre-mordanting of cotton khadi fabric has been used for this study.

3.1 Colour Strength and Related Parameters

Table 2 shows the k/s values at a common wavelength (λmax 420 nm) for pre-mordanted cotton khadi fabrics dyed individually and with selected binary pairs of dyes in different proportions (75:25, 50:50 and 25:75) sequentially. Data are also given for total colour differences (ΔE), changes in hue (ΔH), changes in chroma (ΔC), metamerism index (MI) and brightness index (BI). The data for total colour difference show the minimum ΔE values for the combination M4, irrespective of the proportions of the mixture of each selected pair of dyes.

In case of dyeing with individual dye (100:0 and 0:100 combination) the results are found as those of selective dye used.

Comparison of the negative values for change in chroma (ΔC) (Table 2) shows that the changes in chroma values for the combination M4 are always lower or minimum, while a maximum change in the same is observed for M1 among all the dye mix studied.

The values for change in hue angle (ΔH) are found to be negative for all the combinations. Irrespective of negative or positive signs, the increasing orders of magnitude for ΔC and ΔH values of each binary pairs of dyes in equal proportion (50:50) are:

ΔC – BL: RSW< BL: TF< BL: CT< BL: MJ< BL: PR
ΔH – BL: PR< BL: TF< BL: RSW< BL: MJ< BL: CT

The minimum MI values are observed for the combination M3 for all the three proportions of dyes

Table 2 — Effects of selective double pre-mordanting on dyeing of cotton khadi fabric with aqueous extract of 30 % babool bark

Mordant	*K/S* at λmax	ΔE	ΔL	Δa	Δb	ΔC	ΔH	BI	MI	CDI	CV% of *K/S*
Control fabric[a]	0.115	-	-	-	-	-	-	69.13	-	-	-
Harda+ $Al_2(SO_4)_3$ (15% Combination)											
0:100	1.69	0.34	0.32	0.09	-0.06	0.18	-0.11	26.74	0.27	0.77	5.36
25:75	2.78	2.04	-1.84	0.61	-0.63	-0.35	-0.80	20.94	0.29	16.13	2.45
50:50	5.04	1.07	0.29	-0.61	0.83	0.60	0.84	16.29	0.36	4.16	11.02
75:25	5.44	0.59	0.06	-0.20	-0.55	-0.59	-0.03	15.11	0.12	0.25	16.78
100:0	3.05	1.20	-1.10	0.47	0.12	0.33	-0.35	17.00	0.21	6.08	8.61

[a] After dyeing with 30% Babool bark extract at *p*H 11.
K/S - surface colour strength, ΔE-Total color difference, ΔL- Lightness /darkness, Δb- blueness/yellowness, ΔH-change in hue, ΔC-change in chroma, BI- brightness index, MI- metamerism index, CDI-colour difference index, and CV%- coefficient of variation .

mixture. Irrespective of the proportions of pair of dyes, the order of increasing MI is as follows:

BL:RSW< BL: TF< BL: MJ < BL: CT < BL: PR

Brightness index (BI) is another important colour parameter for dyed fabrics, being considerably dependent on surface lustre and specular reflectance. Brightness index values for these binary pairs of dyes (50:50) are found to reduce in the following increasing order:

BL:PR< BL: CT< BL: RSW< BL: TF < BL: MJ

Brightness index values for the binary pairs of dyes (75:25) are found to increase in the following order:

BL: CT < BL: PR< BL: MJ < BL: TF < BL: RSW,

The same values for binary pairs of dyes (25:75) are also found to reduce in the following increasing order:

BL: CT< BL: PR< BL: RSW< BL: TF < BL: MJ.

Reflectance value of dye and its orientation along the fibre axis after fixation is mainly dependant on brightness index of dyed products. As reported earlier[26] for anar and other natural dyes, there is an appreciable reduction in brightness index after pre-mordanting followed by dyeing with natural dyes, which is also found true in the present case for babool and other binary mixed natural dyed cotton khadi fabric, irrespective of the mordant type or binary ratio and dyeing conditions used. However, it may be noted that at lower concentration of harda mordanting assistant, the reduction in brightness index is lower than that observed at higher concentration of harda (Table 3). Expectedly, as explained earlier[23,26] due to increased disorientation of dye molecules in case of higher dye concentration, the reductions in brightness index are found to be higher in each case.

3.2 Colour Fastness

Table 4 shows the colour fastness data for selected binary pairs of dyes applied to pre-mordanted cotton khadi fabrics. The binary pairs M1, M2, M3 and M5 for combinations 75:25 and M2 for combination 25:75 show better fastness to washing without after treatment [loss of depth (LOD) 4 and staining 4 or 4/5]. Binary pairs M1, M2 and M3 for combinations 50:50 and M1 & M5 for combination 25:75 show the fastness to washing for LOD as one unit lower and it may be improved to a measurable extent by the use of any of the cationic fixing agents. Fastness of the binary pair M4 for both 25: 75 and 50: 50 combinations is, however, totally unsatisfactory with or without after treatment, except in the case of M3 (25: 75), M4 (75:25) and M5 (50: 50) combinations, which show better fastness as compared to M4, irrespective of the proportions of binary pair of dyes.

The data for fastness to light indicate that the binary pairs M1 (75: 25) and M2 (50: 50) show better fastness to light followed by M3 & M4 in both 75: 25 and 50:50 combinations, and all other binary pairs show unsatisfactory results of light fastness.

In all cases, the fastness to dry rubbing is between 4-5 and 4, except for the binary combination M2 and hence need no special treatment for its further improvement. Fastness to wet rubbing for the binary pair M1 (75: 25) and M2, M3 & M4 (25: 75) is found to be at 4 and hence need no special treatment for its further improvement. For other combinations, it is between 3 and 3-4 and hence need some treatment for improvement of wet rubbing fastness. Good rub fastness indicates that there are no unfixed dyes left on the fibre surface after soaping and washing and that these dyes have penetrated well inside the fibre voids and probably got fixed well by ionic interaction

Table 3 — Dyeing properties of pre-mordanted cotton fabrics dyed with selected binary pairs of natural dyes [Dye concentration 30%,15% Harda +$Al_2(SO_4)_3$ (75:25 ratio)]

Dye combination	*K/S*	ΔE	ΔL	ΔC	ΔH	MI	BI	CDI
Controlled mordanted fabric	2.58	0.00	0.00	0.00	0.00	0.00	19.68	0.00
For 100:0 Proportion								
M1	5.84	46.39	39.59	23.65	5.03	7.60	10.60	1.29
M2	5.84	46.39	39.59	23.65	5.03	7.60	10.60	1.29
M3	5.84	46.39	39.59	23.65	5.03	7.60	10.60	1.29
M4	5.84	46.39	39.59	23.65	5.03	7.60	10.60	1.29
M5	5.84	46.39	39.59	23.65	5.03	7.60	10.60	1.29
For (75:25) Proportion								
M1	9.24	46.82	37.75	27.51	3.27	7.89	9.94	0.70
M2	4.21	42.52	35.21	23.20	5.47	7.38	13.85	1.35
M3	4.13	40.91	34.45	21.53	4.79	6.98	14.35	1.30
M4	4.24	41.22	34.79	21.66	4.40	6.93	13.98	1.20
M5	5.81	49.53	43.89	22.12	6.12	7.50	9.07	1.82
For (50:50) Proportion								
M1	12.68	49.35	38.00	31.38	2.69	8.25	8.61	0.51
M2	3.47	39.75	30.20	25.31	5.25	7.26	16.53	1.13
M3	4.52	42.38	35.60	22.52	4.70	7.02	13.17	1.25
M4	3.84	39.99	32.07	23.51	4.24	7.05	15.12	1.02
M5	5.98	50.69	44.03	24.21	6.69	8.01	8.75	1.74
For (25:75) Proportion								
M1	12.49	48.52	35.56	32.94	2.20	8.18	9.23	0.39
M2	4.12	41.24	34.00	22.78	5.08	7.12	14.58	1.30
M3	4.06	41.09	33.55	23.31	4.41	6.88	14.18	1.12
M4	3.90	41.59	30.63	27.79	4.41	7.52	14.41	0.87
M5	7.26	53.34	47.27	23.74	6.89	7.87	7.34	1.96
For (0:100) Proportion								
M1	13.72	49.01	32.06	31.62	1.74	49.01	8.61	0.33
M2	2.72	37.17	30.82	19.69	6.65	7.09	19.10	1.77
M3	3.45	46.50	41.10	20.60	6.99	6.85	11.22	2.30
M4	2.42	31.74	24.84	19.59	2.58	5.76	12.29	0.72
M5	1.30	25.63	21.98	12.83	3.03	4.49	19.13	1.84

M1-(Babool: Anar), M2-(Babool: Madder), M3-(Babool: RSW), M4-(Babool: Tesu) and M5-(Babool:Catechu).

Table 4 — Colour fastness data for pre-mordanted cotton fabrics dyed with selected binary pairs of natural dyes in different proportion [15% Harda +$Al_2(SO_4)_3$ (75:25 ratio)]

Dye	Fastness to						
	Washing		Light	Rubbing		Perspiration	
	Loss of depth	Staining		Dry	Wet	Acidic	Alkali
For100:0 Proportion							
M1	4/5	4	4/5	3/4	3	3/4	4
M2	4/5	4	4/5	3/4	3	3/4	4
M3	4/5	4	4/5	3/4	3	3/4	4
M4	4/5	4	4/5	3/4	3	3/4	4
M5	4/5	4	4/5	3/4	3	3/4	4
For 75:25 Proportion							
M1	4	4	4/5	4/5	4	4	4
M2	4	4/5	1/2	3/4	3	4	4
M3	4	4/5	3	4	3/4	4	4

(*Contd.*)

Table 4 — Colour fastness data for pre-mordanted cotton fabrics dyed with selected binary pairs of natural dyes in different proportion [15% Harda +$Al_2(SO_4)_3$ (75:25 ratio)] — (*Contd*.)

Dye	Fastness to						
	Washing		Light	Rubbing		Perspiration	
	Loss of depth	Staining		Dry	Wet	Acidic	Alkali
For 75:25 Proportion							
M4	3	4/5	3	4/5	3/4	3/4	4
M5	4	4/5	2/3	4	3/4	3	4/5
For 50:50 Proportion							
M1	3/4	4/5	1/2	4	3	4/5	4/5
M2	3/4	4	4/5	4	3/4	3	3
M3	3/4	4/5	3	4	3/4	4/5	4/5
M4	2/3	4/5	3	4/5	3/4	3/4	4
M5	3	4/5	2/3	4/5	3	2/3	4/5
For 25:75 Proportion							
M1	3/4	4/5	1/2	4	3	4/5	4/5
M2	4	4	4/5	4/5	4	3/4	4
M3	3	4/5	3	4/5	4	4/5	4/5
M4	2	4/5	2	4/5	4	2	4/5
M5	3/4	4/5	2/3	4/5	3/4	2/3	4/5
For 0:100 Proportion							
M1	4/5	4	4/5	4/5	3/4	4/5	4/5
M2	3	4	3/4	4	3/4	2/3	3
M3	3/4	4	4/5	4/5	4	4	4
M4	2	3/4	3/4	4/5	3/4	1/2	3
M5	3/4	3/4	4/5	3/4	3	3/4	4

or hydrogen bonding or coordinated complex formation with the mordants or with the functional groups of cotton fibre, as the case may be.

The data for fastness to perspiration indicate that the binary pairs M1, M2 & M3 (75: 25) and M1 & M3 (50: 50 and 25: 75) have better fastness followed by M4 and M5 (75: 25); M2 & M4 (50: 50) and M2 (25: 75). However, M5 (50: 50) and M4 & M5 (25: 75) show unsatisfactory results of perspiration fastness.

It is observed that in case of combination with tesu, the colour fastness to wash and light are inferior; and hence, with increase in proportion of tesu, the colour fastness grades are drastically reduced. This may be due to less anchoring of tesu on cotton for less number of hydroxyl/ phenoxy groups in the dye structure of tesu, while other dyes like manjistha, babool, catechu and red sandal wood, have some tannin content in it besides large number of phenoxy/ hydroxyl group. Hence, the affinity and anchoring power in the said dye-fibre-mordant system is much higher for the above-said manjistha, babool, catechu and red sandal wood dyes than that for tesu with different mordant system. This is more effective for iron based mordants also, with deepening of colour due to self-colour of iron salt mordant[31] like self-colour of harda also.

3.3 Compatibility Tests

Binary pairs of dyes vary considerably in their response to dyeing processes. A given pair of dyes may exhibit compatibility under one set of dyeing conditions but it may be incompatible under another set of condition. Regular build-up of the individual dye on a particular fibre does not always guarantee similar behaviour when applied together. Two different methods of test for compatibility of binary pairs of dyes have been used in the present work. In the conventional method, the closeness and degree of overlap have been compared between two sets of curves in the plots ΔC *vs* ΔL or *K/S* *vs* ΔL for two sets of progressive depth of shade[13-16, 10, 24, 30, 32] produced using the Set I and Set II dyeing methods. However, it is felt highly essential to test the compatibility of different pairs of natural dyes by quantitative numerical rating (grading) scale to be expressed as relative compatibility rating (RCR), so that it will help the natural dyers in selecting or rejecting specific natural dyes in specific binary pairs, to obtain a targeted compound shade to match.

As per simpler newer method of compatibility test[10,30,32], the closer the difference in CDI values for dyeing with different proportions (75:25, 50:50, 25:75) of the dyes in binary pairs under the same dyeing conditions, the higher is the compatibility rating for that pair of dyes. To test the degree of fitness of this proposed method, the results of the compatibility between the two methods (conventional and proposed) has been compared.

Figure 1 shows the plots of *K/S vs* ΔL (plots a – e) and ΔC *vs* ΔL (plots a' – e') for two sets (Set I & Set II) of dyed materials for 5 separate pairs (M1-M5) of natural dyes.

In case of binary pair M1, plots of *K/S vs* ΔL show that the curves for Set I and Set II run similarly with only slight separation, whereas plots ΔC *vs* ΔL show that the curves for Set I and Set II are bit spaced and run parallel to each other. In the proposed RCR system, the pairs of dyes exhibit grade 3 (average) relative compatibility rating (Table 5), showing predominantly closer similarity with the behaviour in the *K/S vs* ΔL plots [Fig. 1 (a) and (a')].

In case of binary pair M2, the two curves for Sets I and II do show similar build-up behaviour in both the plots [Fig. 1 (b) and (b')]. This is indicative of 'Very good' compatibility for this binary pair of dyes. In the RCR system, this binary pair also exhibits grade 5 (excellent) relative compatibility rating (Table 5). Thus, the conventional and the proposed methods show very similar results.

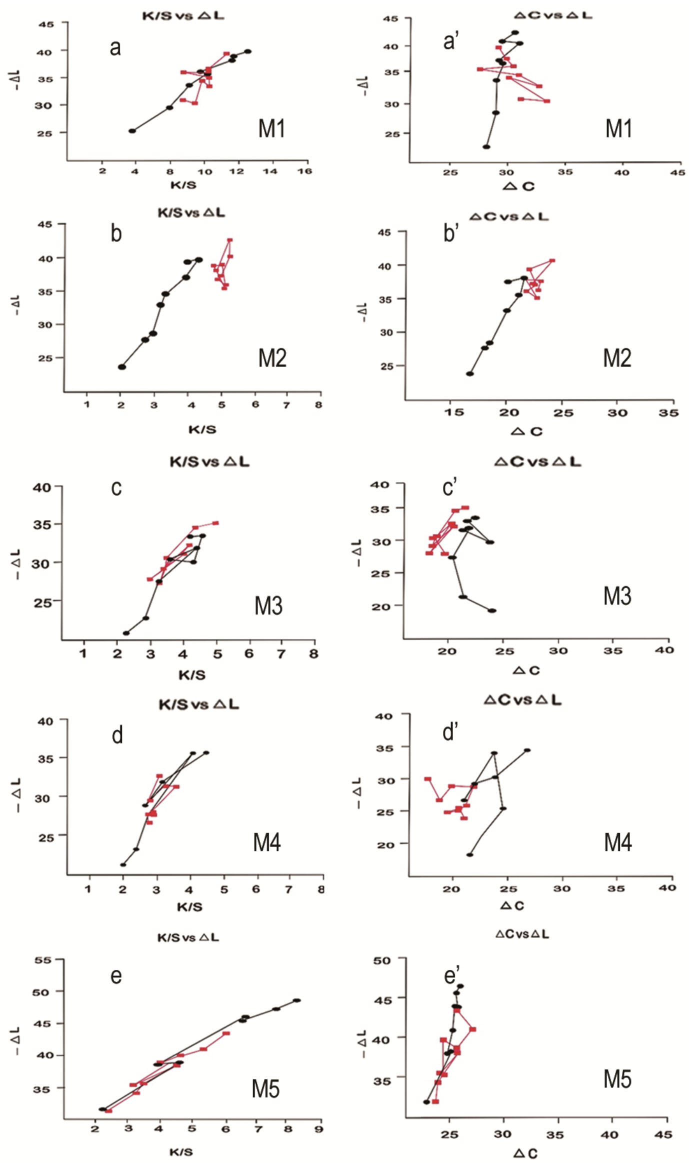

Fig. 1 — Plots of *K/S vs* ΔL (a-e) and ΔC *vs* ΔL (a'-e') for dyeing of five binary pairs of natural dyes on pre-mordanted cotton fabrics [M1 a & a'; M2 b and b'; M3 c'; M4 d and d'; M5 e and e' (●) Set I method of dyeing and (■) Set II method of dyeing]

Table 5 — Colour Difference Index (CDI) and relative compatibility rating (RCR) for application of selected binary pairs of natural dyes

Dye	CDI					CDI_{max}	CDI_{min}	RCR	Compatibility grade
	100:0	75:25	50:50	25:75	0:100				
M1	1.29	0.70	051	0.39	0.33	0.70	0.39	0.31	Average
M2	1.29	1.35	1.31	1.30	1.77	1.35	1.30	0.05	Excellent
M3	1.29	1.30	1.25	1.12	2.30	1.30	1.12	0.18	Good
M4	1.29	1.20	1.02	0.87	0.72	1.20	0.87	0.33	Average
M5	1.29	1.82	1.74	1.96	1.84	1.96	1.74	0.22	Moderate

In case of binary pair M3, the plots *K/S vs* ΔL [Fig. 1 (c) and (c')] show that the two curves for Sets I and II run similarly with only slight separation, indicating good degree of compatibility showing rating of 4 (good) (Table 5).

In case of binary pair M4, the plots *K/S vs* ΔL [Fig. 1 (d)] show that the two curves for Sets I and II show slight deviation, indicating a fair degree of compatibility. In the corresponding plots ΔC *vs* ΔL (Fig. 1 d'), however, the curves for Set I and set II show a significant separation from one another, indicating an average degree of compatibility between these dyes. In the proposed RCR method, this binary pairs of dyes exhibits grade 3 (average) relative compatibility rating (Table 5).

In case of binary pair M5, the plots *K/S vs* ΔL [Fig. 1 (e) and (e')] show that the two curves for sets I and II overlap, indicating fair degree of compatibility. In the proposed RCR method, this binary pairs of dyes exhibit grade 3-4 (moderate) relative compatibility rating (Table 5).

4 Conclusion

4.1 A variety of browner shades are thus possible to obtain on cotton using binary mixture of babool with pomegranate rind, madder, red sandal wood, tesu flower, etc after suitable mordanting and dyeing, both under un optimized conditions.

4.2 The binary pairs M1, M2, M3, M5 for combinations 75:25 and M2 for combination 25:75 show better fastness to washing without after treatment. For binary pair M1, M2 & M3 for combinations 50:50 and M1 & M5 for combination 25:75, the fastness to washing is satisfactory and may be improved by the use of any cationic fixing agents. Fastness of the binary pair M4 for both 25: 75 and 50: 50 combinations is, however, totally unsatisfactory with or without after treatment, except in the case of M3 in 25: 75, M4 in 75:25 and M5 in 50: 50 combinations which show better fastness as compared to M4, irrespective of the dye proportions in binary pair.

4.3 The data for fastness to light indicate that the binary pairs M1 for 75: 25 combination and M2 for 50: 50 combination show better fastness to light followed by M3 & M4 in both 75: 25 and 50:50 combinations. All other binary pairs show unsatisfactory results of light fastness.

4.4 In all cases, the fastness to dry rubbing is between 4-5 and 4, except for the binary combination M2, and hence need no special treatment for its further improvement. Fastness to wet rubbing for the binary pair M1 for 75: 75 combination and for the binary pair M2, M3 & M4 in 25: 75 combination is at 4, and hence need no special treatment for its further improvement. For other combinations, it is between 3 and 3-4, and hence need some treatment for improvement of wet rubbing fastness.

4.5 Data for fastness to perspiration indicate that the binary pairs M1, M2 & M3 for 75: 25 combination, M1 & M3 for 50: 50 & 25: 75 combination show better fastness followed by M4 and M5 for 75: 25 combination, M2 & M4 for 50: 50 combination and M2 for 25: 75 combination. However, M5 for 50: 50 combination and M4 & M5 for 25: 75 combination show unsatisfactory results of perspiration fastness.

4.6 The results for test of compatibility by the proposed newer system of relative compatibility rating of dyes are in good agreement with the results of the conventional compatibility test based on the analysis of *K/S vs* ΔL and ΔC *vs* ΔL plots. According to the newer RCR system, the order of relative degree of compatibility of selected pairs of dyes is:

BL: MJ > BL: RSW > BL: CT > BL: PR > BL: TF

Thus, this easy and simpler newer method of the relative compatibility rating method is found to be useful to identify compatible binary pairs of natural dyes for dyeing cotton khadi fabric with babool bark with other natural dyes as binary mixture in different proportions.

4.7 The simple colorimetric method of relative numerical grading of relative compatibility rating (RCR) to identify and select proper compatible natural dyes to get different compound shades with improved wash and light fastness for cotton khadi fabric products by eco-friendly natural dyeing using compatible binary mixture of selective natural dyes.

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