Studies on Compatibility of Binary Mixture of Natural Dyes for Developing Compound Shades for Khadi Cotton Fabric

Hanamantagouda Sinnur¹, Dileep Kumar Verma¹, Ashis Kumar Samanta²,³

¹Khadi & Textile Division, Mahatma Gandhi Institute for Rural Industrialization, Wardha, India
²Department of Jute and Fibre Technology, University of Calcutta, Kolkata, India
³Khadi and Textiles Division, Wardha, India

Email address
hdsinnur.gouda@gmail.com (H. Sinnur), dileephone@gmail.com (D. K. Verma), ijtaksamanta@hotmail.com (A. K. Samanta)

Citation

Received: March 1, 2018; Accepted: April 2, 2018; Published: May 18, 2018

Abstract: The main objective of this part of the present work was to develop and verify an easy method of determining compatibility rating of any two dyes to be used in pair in combination for dyeing of cotton khadi fabric with natural dyes for obtaining compound shades. Each of the natural dyes taken here e.g. Madder or Manjistha (MJ), Pomegranate rind (PR), Babool (BL), Red Sandal Wood (RSW), Tesu Flower (TF) and Catechu (CT) were extracted in aqueous medium at optimized conditions and their binary mixtures in different proportions were then applied on cotton khadi fabric for developing varying compound shades. Varying proportion of binary mixtures of aqueous extracts of Madder or Manjistha (MJ) with each of the above said other natural dyes taken, have been used to dye bleached cotton khadi fabric after pre-mordanted with 15% myrobolan and potash aluminium sulphate (at optimized concentration and conditions of mordanting for dyeing cotton with madder (manjishtha). After dyeing so, dyed cotton fabric samples were subjected to evaluation of variation in depth of shade/hue/chroma, etc in terms of surface colour strength (K/S value) and its coefficient of variation, brightness index (BI), change in hue (ΔH), metamerism index (MI), total colour differences (ΔE) and also test of colour fastness to washing, light, rubbing and perspiration. The compatibility of these binary pairs of natural dyes has been assessed conventionally by rate of dyeing of each natural colour and also by the analysis of ΔC vs ΔL and K/S vs ΔL plots as well as by applying varying concentrations of the binary pairs of dyes taken in 50:50 ratio. In this paper, an unique and simple method of assessing relative compatibility rating of pairs of natural dyes has been assessed by evaluating colour difference index [(ΔE x ΔH) / (ΔC x MI)]. The results of this newer CDI calculation based simple and unique system of determining compatibility rating of binary pair of natural dyes are found mostly in well agreement with the results of compatibility test by conventional methods of ΔC vs ΔL and K/S vs ΔL plots analysis for progressive development of shades. Finally, the order of relative degree of compatibility of these binary pairs of natural dyes is MJ:BL >> MJ:TF >> MJ:RSW >> MJ:CT >> MJ:PR.

Keywords: Cotton Khadi, Dye Extraction, Compatibility, Compound Shade, Mordanting, Natural Dyes

1. Introduction

Khadi cotton fabric as being produced from hand spun yarn and woven in handloom sector, it assumes special interest in developing countries like India and its Asian subcontinent for generating huge employment for their livelihood that too in underdeveloped rural sector. In the present market, there is a huge and special demand for Khadi cotton fabrics due to its handcrafted look and produced from a eco friendly natural fibres providing support to village economy and some of the quality are considered also as Indian heritage made by hand spun yarn and woven in handlooms of rural sector. The value of this fabric may further be enhanced, if it is dyed with natural dyes replacing synthetic dyes to make it completely eco friendly and certified by GOTS standard.

Application of natural dyes has not achieved wide acceptability like synthetic dyes due to limited availability of
pure natural dye extract/powder as a ready dye, lack of viability of standard procedures of dyeing, difficulty in reproducibility and matching as well as shade limitation due to lack of sufficient scientific knowledge on compatibility between any two natural dyes if applied together in mixture and their chemical interaction/mechanism of absorption and rate of dyeing and related chemistry of dyes and technology of dyeing and more less knowledge on dyeing kinetics of each natural dyes applied on different types of textiles, for such binary mixture of natural dyes particularly to be used to get variety of compound shades using binary or ternary mixture of natural dyes.

There are only a few and discrete studies available in literature describing application of mixture of natural dyes on cotton textiles [1, 2] reporting the colour interaction, resultant colour strength and metamerism effects. Some studies on compatibility of binary and tertiary mixtures of synthetic dyes [3-8] are widely available in literature, whereas such studies with mixture of natural dyes on cotton or any other textiles are scanty [1, 2] and sporadic.

For successful ready commercial use of natural dyes for any particular fibres, the appropriate and standardized recipe and techniques for dyeing a particular fibre-natural dye system need to be available in hand to be adopted easily. Therefore to obtain newer shade with acceptable colour fastness behaviour, reproducible colour yield and production of compound shades using binary or ternary mixture of natural dyes, along with appropriate scientific and standardized dyeing techniques/procedures, an easy method of determining compatibility of between any two natural dyes (to be applied in mixture for dyeing) is to be established/verified and standardized for use it by regular practicing dyers of natural dyes.

Compatibility of a pair of dyes can be judged by different methods, such as, subjective visual assessment of the degree of on-tone build up by a series of dyeing or theoretical prediction of compatibility by comparison of rates of dyeing (time of half dyeing) and dyeing kinetics (diffusion coefficients) for each individual dye to derive V numbers or Z values which are usually specific to the textile substrate and dyeing conditions or quantitative assessment of change in hue angle (ΔH) or comparing and plotting ΔC vs ΔL or K/S vs ΔL values for two sets of progressive shades (20-100% with 10-20 point differences) developed and obtained by dyeing particular fabric with varying total dye concentration of mixture of respective two dyes in a pair, taking each in 50:50 ratio and in another set of dyeing varying profile of dyeing time and temperature taking fixed amount of two dyes taken in 50:50 ratio as a popularly known conventional method [3] or quantitative compatibility rating for the mixtures of more than two dyes by colorimetric analysis of actual colour strength development (not on the basis of dye absorbed). But all these methods are cumbersome and tedious for determining compatibility of any two natural dyes, when applied in pair of binary mixture, but without knowing compatibility of two dyes to be used in combination as a pair for developing compound shades, it is not possible to obtain rightly anticipated/desired shade depth/colour build up.

So, in the present work, compatibility of each of the few selected two natural dyes have been assessed to be used as a pair of binary mixture of varying proportion for dyeing cotton khadi fabric to obtain correct compound shade/colour build up desired/expected. For this purpose, in this part of our present work, two different methods of determining compatibility of a binary mixture as a selected single pair of natural dyes (manjistha with other natural dyes as few selected pair) were used and compared. Conventional method is used in which a plotting of ΔC vs ΔL or K/S vs ΔL for two sets of dyeing with varying concentration of total dye (taking two dyes in equal proportion) as a dye mixture and varying time and temperature profile of another set of dyeing having fixed dye concentration. Non-Conventional method used in the present work relates very recently reported newer method [9] to determine relative compatibility rating for other binary pairs of natural dyes has been used as an unique and simple method of assessing relative compatibility rating of a pair of binary mixture of natural dyes based on evaluating colour difference index [9] or CDI values [(ΔE x ΔH) / (ΔC x MI)] for application of different proportion of two dyes in a pair and determining differences of CDI values therein.

So, the main objective of this part of the present work is to develop and verify an easy method of determining compatibility rating of any binary mixture of natural dyes to be used as a single pair in combination for obtaining compound shades, as a continuation of our earlier published work on natural dyeing of cotton khadi fabric. Each of the natural dyes taken here e.g, Madder or Manjistha (MJ), Pomegranate rind (PR), Babool (BL), Red Sandal Wood (RSW), Tesu Flower (TF) and Catechu (CT) were extracted in aqueous medium at earlier optimized conditions and their binary mixtures in different proportions were then applied on cotton kahdi fabric for developing varying compound shades. Varying proportion of binary mixtures of aqueous extracts of Madder or Manjistha (MJ) with each of the above said other natural dyes taken, have been used to dye bleached cotton khadi fabric after pre-mordanted with 15% myrabolan and potash aluminium sulphate (at optimized concentration and conditions of mordanting for dyeing cotton with madder (manjistha). After dyeing with varying proportion of binary mixture of each pair of two natural dyes, dyed cotton fabric samples were subjected to evaluation of variation in shade depth/hue/chroma, etc in terms of surface colour strength (K/S value) and its coefficient of variation, brightness index (BI), change in hue (ΔH), metamerism index (MI), total colour differences (ΔE) and also test of colour fastness to washing, light, rubbing and perspiration.

2. Experimental

Materials used: 3% H2O2 (30%) bleached, plain weave khadi cotton fabric (73 Nm warp, 70 Nm weft, 76 ends per inch, 53 picks per inch, 73.5 gsm fabric area density and 0.075mm fabric thickness) obtained from Gram SewaMandal, Gopuri, Wardha was used for this study.
Chemicals used: Commercial grade acetic acid, common salt, sodium carbonate and non-ionic soap from local suppliers were used. Laboratory Reagent (LR) grade potash aluminium sulphate and the natural mordant myrobolan (hartaki or harda, TerminaliaChebula) powder, both obtained from local suppliers was used.

Dyes used: The following selected natural dyes were used for the study:

i. Red Sandal Wood (RSW) or Raktachandan (PterocarpusSantalinius) – The main colour components in red sandal wood are Santalin A, Santalin B and Deoxyxysantalin; Santalin A is the main colour component [10-12]


iii. Babool (BL) or Babla (Acacia Nilotica)[16]- Several polyphenolic coloured components have been identified in the bark or woody part of babool tree. These are mainly catechin, epicatechin and gallic acid along with minor amount of decatechin, quercetin and leucocyanidingallate.

iv. Tesu Flower (TF) (Buteamonospermafrondosa) – The main colour component of tesu extract has been identified earlier [17] as butein, a chalcone of yellowish red/orange colour.

v. Catechu (CT) (Acacia Catechu) - The main colour component of catechu has been identified earlier [18] as catechin, also called catechuic acid and peculiar tannic acid called catechu-tannic acid.

vi. Pomegranate rind (PR) (Punicagranatum L) - The rind of pomegranate contains a considerable amount of tannin, about 19% with pelletierine [19]. The main colouring agent in the pomegranate peel is granatinone. This compound gives colour to the dye.

2.1. Evaluation Methods

2.1.1. Extraction and Purification of Colorant from Natural Dyes

Pre-cut and dried chips of selected natural dyes were initially crushed to powder form and then subjected to aqueous extraction under optimized conditions as shown in Table 1 below:

<table>
<thead>
<tr>
<th>Natural dye</th>
<th>Initial MLR</th>
<th>Temp. during extraction, °C</th>
<th>pH</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red Sandal Wood [9]</td>
<td>1:40</td>
<td>80</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Manjistha [15]</td>
<td>1:30</td>
<td>60</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>Babool bark [16]</td>
<td>1:30</td>
<td>60</td>
<td>6</td>
<td>45</td>
</tr>
<tr>
<td>Tesu Flower [17]</td>
<td>1:20</td>
<td>90</td>
<td>11</td>
<td>60</td>
</tr>
<tr>
<td>Catechu [18]</td>
<td>1:20</td>
<td>90</td>
<td>12</td>
<td>30</td>
</tr>
<tr>
<td>Pomegranate rind [19]</td>
<td>1:50</td>
<td>80</td>
<td>7</td>
<td>45</td>
</tr>
</tbody>
</table>

The aqueous extracts of corresponding natural dyes were filtered and then concentrated by evaporation in water bath to a desired concentration level for final application.

For chemical characterization, the concentrated aqueous extracts of the selected natural dyes were filtered and the filtrates were evaporated to a semi-solid mass under water bath. The semi-solid mass was then put in a cage of wrapped filter paper and further subjected to in soxhlet apparatus using 1:1 ethyl alcohol/ benzene mixture for 10 cycles at 70°C for 2 hours.

The alcohol-benzene extract of the colour component was finally subjected to evaporation in a water bath at 50°C to get semi-dry mass of the pure colour component. Finally, this dry mass of the colour component was washed with acetone followed by methyl alcohol and finally dried in air to obtain the dry powder of the pure colour component.

2.1.2. Mordanting

Bleached cotton fabrics were pre-mordanted using myrobolan followed by potash aluminium sulphate in sequence using the procedure given here under.

Bleached cotton khadi fabrics were pre mordanted with overall 15% myrobolan and potash aluminium sulphate (using 75:25 ratio) i.e using overall 15% concentration taking 75% harda/ myrobolan and 25% potash aluminium sulphate at optimized concentration and conditions of mordanting from earlier work for dyeing cotton with madder (manjistha) and other natural dye mixture for test of compatibility. The above said pre-mordanting is done as per our earlier study on the same published elsewhere [15] for optimization of mordant and dyeing conditions etc, for madder as natural dye applied on cotton khadi fabric. The mordanting was done by following method in sequence for applying the said double mordants given below:

Myrabolan ‘gel’ prepared by soaking myrobolan in water overnight (12 hours) was diluted an appropriate concentration (15% w/w) and filtered. Bleached cotton fabrics were then first mordanted with 11.25% (i.e 75% of 15%) myrobolan 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 myrobolan treated cotton fabrics were then treated with 3.75% (i.e 25% of 15%) potash 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.

2.1.3. Method of Natural Dyeing

Pre-mordanted cotton fabrics were dyed by two methods – In the first 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 20% (owf) concentration of selected dyes (based on the dry weight of the amounts of source material) dyeing temperature 80°C for time 60 min, MLR 1:20 and 10 g/l Sodium Chloride as per the work done on optimization in our earlier work published elsewhere [15]. 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°C for 15 min, followed by repeated water wash and atmospheric drying under sun.

2.1.4. 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 [20], equation with the help of relevant computer aided colour measurement software:

\[ K/S_{\lambda_{\text{max}}} = \frac{(1 - R_{\lambda_{\text{max}}})^2}{2R_{\lambda_{\text{max}}}} = \alpha C_D \]

Where K is the coefficient of absorption; S, the coefficient of scattering; R_{\lambda_{\text{max}}} is the Reflectance value at maximum absorbance wavelength, C_D is concentration of dye and \( \alpha \) is the constant for a particular textile substrate and dye system.

Other colour parameters like change in hue (\( \Delta H \)), change in chroma (\( \Delta C \)), change in whiteness and darkness (\( \Delta L \)) and total colour difference (\( \Delta E \)) were carried as CIE-Lab 1976, standard formula [20].

General metamerism index (MI) was calculated employing Nimeroff and Yurow’s equation [20] of determining metamerism index, which is as follows:

\[ MI = \frac{\sum (\Delta R_x)^2}{X^2} + \frac{\sum (\Delta R_y)^2}{Y^2} + \frac{\sum (\Delta R_z)^2}{Z^2} \]

Where, X, Y, and Z 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. \( \Delta R \) values refers to the difference in reflectance values between two pieces of the same fabric sample measured at two different wavelengths (under two viewing conditions i.e wavelength conditions of viewing illuminant used in the measurement).

Brightness Index (BI) was measured using following relationship ISO-2469 and 2470 method [21].

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

2.1.5. Test of Colour Fastness

Colour fastness to washing [22] of the dyed samples was determined as per the IS: 766-1984 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 [22] (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 [22] 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 method 971-1983: RA 2009 method [22] at two different pH levels i.e, pH – 5.5 and pH -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).

2.1.6. Methods of Compatibility Tests for Selected Binary Pairs of Natural Dyes

i. Conventional Method

Following selected binary pairs (50:50) of natural dyes were applied on the pre-mordanted cotton fabrics using overall 20% (owf) of the respective extracts:

1. M1 – Manjistha + Pomegranate rind (MJ & PR)
2. M2 – Manjistha + Babool wood (MJ & BL)
4. M4 – Manjistha + Tus Flower (MJ & TF)
5. M5 – Manjistha + Catechu (MJ & CT)

In compatibility tests of binary pairs, pre-mordanted cotton fabric samples were dyed in two different sets (Set I and Set II) of progressive depth of shade for each selected binary pair of dyes taken in equal proportions (50:50).

In set I, the progressive depth of shade was developed by varying dyeing time and temperature profile during dyeing. For each pair of dyes (M1-M5), nine separate small pre-mordanted cotton fabric samples were dyed using Megatech Overseas India make laboratory atmospheric pressure beaker dyeing machine with temperature controller for different dyeing periods (5-60 min). The samples were taken out from the dye bath at the intervals of 5 min from 40°C onwards, maintaining the heating rate of 1°C/min. The penultimate sample was taken out after 50 min at 80°C and the last one at the end of the dyeing process after 60 min.

In set II, the progressive depth of shade was developed by varying total concentration of dye mixture from 5% to 40%. For each pair of dyes, seven separate small pre-mordanted cotton fabric samples were dyed using Megatech Overseas India make laboratory atmospheric pressure beaker dyeing machine with temperature controller for different dyeing periods (5-60 min). The samples were taken out from the dye bath at the intervals of 5 min from 40°C onwards, maintaining the heating rate of 1°C/min. The penultimate sample was taken out after 50 min at 80°C and the last one at the end of the dyeing process after 60 min.
K/S data observing the degree of closeness and overlapping of the two sets of curves i.e. AC vs ΔL or K/S vs ΔL observed using the two sets of dyeing (Set I & Set II).

ii. Non-Conventional CDI based Method

An alternative method of assessing compatibility of binary pairs of dyes is also proposed. After the application of different proportions of binary pairs of dyes on the same fabric, the magnitudes of the respective ΔE, AC, ΔH and MI values, irrespective of their sign and direction, may be utilized to obtain colour difference index (CDI) using the following proposed empirical relationship [9]:

\[
\text{Colour Difference Index (CDI)} = \frac{\Delta E \times \Delta H}{\Delta C \times \text{MI}}
\]

Proposed relative compatibility rating (RCR) or compatibility grading system may be represented in Table 2 as per earlier reference of study [9].

<table>
<thead>
<tr>
<th>Compatibility grade</th>
<th>RCR</th>
<th>Highest values of differences between maximum CDI values and individual CDI values*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent</td>
<td>5</td>
<td>&gt;0 but ≤0.05</td>
</tr>
<tr>
<td>Very Good</td>
<td>4-5</td>
<td>&gt;0.05 but ≤0.10</td>
</tr>
<tr>
<td>Good</td>
<td>4</td>
<td>&gt;0.10 but ≤0.20</td>
</tr>
<tr>
<td>Moderate</td>
<td>3-4</td>
<td>&gt;0.20 but ≤0.30</td>
</tr>
<tr>
<td>Average</td>
<td>3</td>
<td>&gt;0.30 but ≤0.40</td>
</tr>
<tr>
<td>Fair</td>
<td>2-3</td>
<td>&gt;0.50 but ≤1.00</td>
</tr>
<tr>
<td>Poor</td>
<td>2</td>
<td>&gt;1.00 but ≤5.00</td>
</tr>
<tr>
<td>Very Poor</td>
<td>1-2</td>
<td>&gt;5.00 but ≤10.00</td>
</tr>
<tr>
<td>Worst</td>
<td>1</td>
<td>&gt;10.00 but ≤15.00</td>
</tr>
<tr>
<td>Non-compatible</td>
<td>0</td>
<td>&gt;15.00</td>
</tr>
</tbody>
</table>

*For dyeing using different proportions of mixtures of selective pair of dyes on the same fabric under the comparable dyeing conditions.

3. Results and Discussion

The study deals with the following three major objectives for the coloration of bleached cotton khadi fabrics with selected binary pairs of natural dyes, viz, colour strength and related parameters, colour fastness of dyed cotton khadi fabrics and compatibility of selected binary pairs of dyes.

It has been reported earlier that the pre-mordanting using 15% myrobalan followed by 15% potash aluminium sulphate is the most suitable system for dyeing bleached cotton khadi fabric with Manjistha wood dye. Hence, the same system of pre-mordanting of cotton khadi fabric has been used for this study.

Table 3 shows the K/S values at a common wavelength (420 nm) for pre-mordanted cotton khadi fabrics dyed with selected binary pairs of dyes in different proportions (75:25, 50:50 and 25:75) and also for individual natural dyes taken without any mixture (i.e 100:1 and 0:100) for each combination. Data are also given for total colour differences (ΔE), changes in hue (ΔH), change in chroma (ΔC), metamerism index (MI) and brightness index (BI). The data for total colour difference show the minimum ΔE values for the combination M5 (Mj: CT) irrespective of the proportions of the mixture of each selected pair of dyes.

<table>
<thead>
<tr>
<th>Dye Combination</th>
<th>K/S</th>
<th>ΔE</th>
<th>ΔC</th>
<th>ΔH</th>
<th>MI</th>
<th>BI</th>
<th>CDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>For (100:0) proportion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1 (Madder:Anar)</td>
<td>2.96</td>
<td>1.21</td>
<td>0.72</td>
<td>0.55</td>
<td>0.23</td>
<td>16.38</td>
<td>3.99</td>
</tr>
<tr>
<td>M2 (Madder:Babool)</td>
<td>2.96</td>
<td>1.21</td>
<td>0.72</td>
<td>0.55</td>
<td>0.23</td>
<td>16.38</td>
<td>3.99</td>
</tr>
<tr>
<td>M3 (Madder:RSW)</td>
<td>2.96</td>
<td>1.21</td>
<td>0.72</td>
<td>0.55</td>
<td>0.23</td>
<td>16.38</td>
<td>3.99</td>
</tr>
<tr>
<td>M4 (Madder:Tesu)</td>
<td>2.96</td>
<td>1.21</td>
<td>0.72</td>
<td>0.55</td>
<td>0.23</td>
<td>16.38</td>
<td>3.99</td>
</tr>
<tr>
<td>M5 (Madder:Catechu)</td>
<td>2.96</td>
<td>1.21</td>
<td>0.72</td>
<td>0.55</td>
<td>0.23</td>
<td>16.38</td>
<td>3.99</td>
</tr>
<tr>
<td>For (75:25) proportion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1 (Madder:Anar)</td>
<td>7.46</td>
<td>1.96</td>
<td>0.53</td>
<td>0.90</td>
<td>0.38</td>
<td>9.06</td>
<td>8.46</td>
</tr>
<tr>
<td>M2 (Madder:Babool)</td>
<td>2.76</td>
<td>0.90</td>
<td>0.36</td>
<td>0.57</td>
<td>0.13</td>
<td>16.27</td>
<td>10.96</td>
</tr>
<tr>
<td>M3 (Madder:RSW)</td>
<td>3.08</td>
<td>2.20</td>
<td>0.73</td>
<td>1.06</td>
<td>0.44</td>
<td>15.73</td>
<td>7.28</td>
</tr>
<tr>
<td>M4 (Madder:Tesu)</td>
<td>3.31</td>
<td>1.87</td>
<td>0.79</td>
<td>0.97</td>
<td>0.39</td>
<td>14.88</td>
<td>5.87</td>
</tr>
<tr>
<td>M5 (Madder:Catechu)</td>
<td>5.19</td>
<td>0.74</td>
<td>0.27</td>
<td>0.25</td>
<td>0.12</td>
<td>9.43</td>
<td>6.16</td>
</tr>
<tr>
<td>For (50:50) proportion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1 (Madder:Anar)</td>
<td>11.37</td>
<td>1.14</td>
<td>0.60</td>
<td>0.41</td>
<td>0.20</td>
<td>8.52</td>
<td>3.82</td>
</tr>
<tr>
<td>M2 (Madder:Babool)</td>
<td>2.97</td>
<td>2.1</td>
<td>0.51</td>
<td>0.82</td>
<td>0.32</td>
<td>15.32</td>
<td>10.75</td>
</tr>
<tr>
<td>M3 (Madder:RSW)</td>
<td>3.57</td>
<td>2.25</td>
<td>1.25</td>
<td>1.47</td>
<td>0.53</td>
<td>14.01</td>
<td>5.00</td>
</tr>
<tr>
<td>M4 (Madder:Tesu)</td>
<td>4.18</td>
<td>1.18</td>
<td>0.51</td>
<td>0.61</td>
<td>0.21</td>
<td>12.23</td>
<td>6.72</td>
</tr>
</tbody>
</table>
For 100:0 proportion of mixture of manjistha (madder) and other natural dyes in combination, all results are same as other dye taken is zero, and hence contribution of individual other natural dye does not exists due to their full absence.

While, for 0:100 proportion of mixture of manjistha (madder) and other natural dyes in combination, all results are different as, madder or manjistha is absent here and other natural dye does not exist and hence contribution of individual other natural dye very much influences and exists due to their proportionate contribution of individual other natural dyes except madder dye.

Irrespective of negative or positive signs, the increasing orders of magnitude for the ∆C and ∆H values for these binary pairs of dyes (50:50) are found to increase in the following order: MJ:PR˂MJ:CT˂MJ:TF˂MJ:RSW.<MJ:BL

The values for change in hue angle (ΔH) are found to be negative for all the combinations M1, M2, M3, M4 and M5.

Comparison of the negative values for change in chroma (ΔC) shows that the changes in chroma values for the combination M5 (MJ:CT) are always lower or minimum, while a maximum change in the same is observed for M3 (MJ:RSW) for all the dye proportions studied.

The values for change in hue angle (ΔH) are found to be negative for all the combinations M1, M2, M3, M4 and M5.

Irrespective of negative or positive signs, the increasing orders of magnitude for the ∆C and ∆H values for each binary pair’s dyes in equal proportion (50:50) are:


The minimum MI values are observed for the combination M5 (MJ: CT) for all the three proportions of dyes mixture. Irrespective of the proportions of pair of dyes, the order of increasing MI is as follows:


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 increase in the following order:


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


### 3.2. Colour Fastness

Table 4 shows the colour fastness data for selected binary pairs of dyes applied in different proportions (75:25, 50:50 and 25:75) to pre-mordanted cotton khadi fabrics.

<table>
<thead>
<tr>
<th>Dye Combination</th>
<th>K/S</th>
<th>ΔE</th>
<th>ΔC</th>
<th>ΔH</th>
<th>MI</th>
<th>BI</th>
<th>CDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>For (25:75) proportion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1 (Madder:Anar)</td>
<td>13.24</td>
<td>1.44</td>
<td>0.30</td>
<td>0.38</td>
<td>0.16</td>
<td>8.48</td>
<td>11.39</td>
</tr>
<tr>
<td>M2 (Madder:Babool)</td>
<td>3.29</td>
<td>1.73</td>
<td>0.44</td>
<td>1.24</td>
<td>0.42</td>
<td>19.57</td>
<td>11.88</td>
</tr>
<tr>
<td>M3 (Madder:RSW)</td>
<td>3.09</td>
<td>1.98</td>
<td>0.53</td>
<td>1.05</td>
<td>0.40</td>
<td>16.69</td>
<td>9.90</td>
</tr>
<tr>
<td>M4 (Madder:Tesu)</td>
<td>4.78</td>
<td>0.87</td>
<td>0.57</td>
<td>0.26</td>
<td>0.13</td>
<td>10.97</td>
<td>2.97</td>
</tr>
<tr>
<td>M5 (Madder:Catechu)</td>
<td>5.40</td>
<td>0.69</td>
<td>0.34</td>
<td>0.24</td>
<td>0.13</td>
<td>9.39</td>
<td>3.75</td>
</tr>
<tr>
<td>For (0:100) proportion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1 (Madder:Anar)</td>
<td>13.71</td>
<td>1.12</td>
<td>0.56</td>
<td>0.29</td>
<td>0.14</td>
<td>8.76</td>
<td>4.10</td>
</tr>
<tr>
<td>M2 (Madder:Babool)</td>
<td>2.81</td>
<td>1.16</td>
<td>0.29</td>
<td>0.54</td>
<td>0.22</td>
<td>19.91</td>
<td>9.54</td>
</tr>
<tr>
<td>M3 (Madder:RSW)</td>
<td>3.00</td>
<td>1.76</td>
<td>1.01</td>
<td>0.40</td>
<td>0.30</td>
<td>17.05</td>
<td>2.32</td>
</tr>
<tr>
<td>M4 (Madder:Tesu)</td>
<td>5.34</td>
<td>0.99</td>
<td>0.39</td>
<td>0.20</td>
<td>0.11</td>
<td>9.92</td>
<td>4.60</td>
</tr>
<tr>
<td>M5 (Madder:Catechu)</td>
<td>6.46</td>
<td>0.80</td>
<td>0.43</td>
<td>0.33</td>
<td>0.20</td>
<td>7.85</td>
<td>3.06</td>
</tr>
</tbody>
</table>

Table 4. Color fastness data for pre-mordanted [15% Harada + Potash Alum (75:25)] cotton fabrics dyed with selected binary pairs of natural dyes in different proportion.
The binary pair M5 (MJ:CT) and M1 (MJ:PR) shows better fastness to washing without after treatment and the fastness to washing for both LOD and ST is one unit lower and may be improved to a measurable extent by the use of any one of the cationic fixing agents. For MJ: BL, Fastness of the binary pair M4 (MJ:TF) is, however totally unsatisfactory with or without fixing agents. For MJ: BL, Fastness of the binary pair M4 (MJ:BL) shows better fastness followed by M2 (MJ:BL) and M3 (MJ:RSW). However, M5 (MJ:CT) shows unsatisfactory results of light fastness.

In all cases, the fastness to dry and wet rubbing is between 4-5 and 4 except for the binary combination M5 (MJ:CT) and hence need no special treatment for its further improvement. Good rub fastness in all these cases indicate 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 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 pair M5 (MJ:CT) and M1 (MJ:PR) shows better fastness followed by M2 (MJ:BL) and M3 (MJ:RSW). However, M5 (MJ:CT) shows satisfactory results of perspiration fastness while binary pair M4 (MJ:TF) shows unsatisfactory results of perspiration fastness.

It is observed that wherever there is Tesu (Buteamonomospermafrondosa) the colour fastness to wash and light are inferior and hence, with increase in proportion of Tesu, colour fastness grade are drastically reduced. This may be due to less anchoring of Tesu on cotton for less number of hydroxyl/ phenoxy groups in this dye structure of Tesu. As colour component, while other dyes like, Manjistha, Babool, Catechu & Red Sandal wood, all of them had some tannin content in it besides large number of phenoxy/ hydroxyl group and hence the affinity and anchoring power in the said dye-fibre-mordant system is much higher for the above said Manjistha, Babool, Catechu & Red Sandal wood dyes than that for Tesu.

### 3.3. Compatibility Tests

Binary pairs of dyes vary considerably in their response to dyeing processes. A given pair dyes may exhibit compatibility under one set of dyeing conditions but prove to 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 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 ∆C vs ∆L or K/S vs ∆L for two sets of progressive depth of shade [3-6, 17] 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 some form of quantitative term expressed as relative compatibility rating for the various pairs that will help the dyer by providing options for selecting dyes to match a target shade. Therefore, an easy method of determining relative compatibility rating between any pair of natural dyes has been proposed by postulating a new colour difference index as mentioned in section 2.1.6.

The closer 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 & proposed) have 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.
Figure 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 and a’; M2-b and b’; M3-c and c’; M4-d and d’; M5-e and e’].

In case of binary pair M1 (MJ:PR), plots of K/S vs ΔL show that the curves for Sets 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 widely spaced and do not approach one another. In the proposed RCR system, the pairs of dyes exhibit grade 2-3 (Fair) relative compatibility rating (Table 5), showing predominantly closer similarity with the behaviour in the K/S vs ΔL plots.

In case of binary pair M2 (MJ: BL), the two curves for Sets I and II do show similar build-up behaviour in both the
plots (b and b'). This is indicative of ‘Poor’ compatibility for this binary pair of dyes. In the RCR system, this binary pair also exhibits Grade 2 (Poor) relative compatibility rating (Table 5). Thus, the conventional and the proposed methods show very similar results.

In case of binary pair M3 (MJ:RSW), the plots K/S vs ∆L show that the two curves for sets I and II run similarly with only slight separation, indicating fair degree of compatibility showing rating of 2-3 (Fair) (Table 5). In case of binary pair M4 (MJ: TF), the plots K/S vs ∆L show that the two curves for sets I and II show slight deviation, indicating a fair degree of compatibility. In the corresponding plots ∆C vs ∆L, 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 2-3 (Fair) relative compatibility rating (Table 5).

In case of binary pair M5 (MJ: CT), the plots K/S vs ∆L show that the two curves for sets I and II initially overlap and then deviated, indicating worst degree of compatibility. Thus these two dyes are totally incompatible with one another when applied as a binary pair by any method. In the proposed RCR method, this binary pairs of dyes exhibits Grade 0 (Non-compatible) relative compatibility rating (Table 5).

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

<table>
<thead>
<tr>
<th>Dye Concentration</th>
<th>CDI max</th>
<th>CDI min</th>
<th>CDI max - CDI min</th>
<th>RCR</th>
<th>Compatibility Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1 (Madder:Anar)</td>
<td>2.96</td>
<td>2.96</td>
<td>0.00</td>
<td>1-2</td>
<td>Very Poor</td>
</tr>
<tr>
<td>M2 (Madder:Babool)</td>
<td>2.96</td>
<td>10.96</td>
<td>7.00</td>
<td>2</td>
<td>Poor</td>
</tr>
<tr>
<td>M3 (Madder:RSW)</td>
<td>2.96</td>
<td>2.96</td>
<td>0.00</td>
<td>2</td>
<td>Poor</td>
</tr>
<tr>
<td>M4 (Madder:Teju)</td>
<td>2.96</td>
<td>2.96</td>
<td>0.00</td>
<td>2</td>
<td>Poor</td>
</tr>
<tr>
<td>M5 (Madder:Catechu)</td>
<td>2.96</td>
<td>2.96</td>
<td>0.00</td>
<td>2</td>
<td>Poor</td>
</tr>
</tbody>
</table>

### 4. Conclusions

i. A variety of browner shades are thus possible to obtain on cotton using binary mixture of madder/manjistha with Catechu, Pomegranate Rind, Babul bark, Red sandal wood, etc after suitable mordanting and dyeing, both under un-optimized condition.

ii. The binary pair M5 (MJ: CT) and M1 (MJ: PR) shows better fastness to washing without after treatment. Binary pair M2 (MJ: BL) binary mixture of dyes with 75:25 and 25:75 ratio; the fastness to washing is satisfactory and may be improved to a measurable extent by the use of any one of the cationic fixing agents. Fastness of the binary pair M4 (MJ: TF) is, however totally unsatisfactory with or without after treatment, except in the case of M3 (MJ: RSW) which shows better fastness compared to M4, irrespective of the proportions of binary pair of dyes.

iii. The data for fastness to light indicate that the binary pair M5 (MJ: CT), M2 (MJ:BL) and M1 (MJ:PR) shows better fastness to light followed by M3 (MJ:RSW) and the binary pair M4 (MJ:TF) shows unsatisfactory results of light fastness, due to possible higher uv-absorption character of those dyes, causing early fading under exposure to uv light.

iv. In all cases, the fastness to dry and wet rubbing is between 4-5 and 4 except for the binary combination M5 (MJ:CT) and hence need no special treatment for its further improvement.

v. The data for fastness to perspiration indicate that the binary pair M1 (MJ: PR) shows better fastness followed by M2 (MJ: BL) and M3 (MJ: RSW). However, M5 (MJ: CT) shows satisfactory results of perspiration fastness while binary pair M4 (MJ: TF) shows unsatisfactory results of perspiration fastness.

vi. The result 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 ∆L and ∆C vs ∆L plots. According to the newer RCR system, the order of relative degree of compatibility of selected pairs of dyes is: MJ:BL >> MJ:TF >> MJ:RSW >> MJ:CT >> MJ:PR

Thus, this proposed method of the relative compatibility rating system may be useful to identify compatible binary pairs of natural dyes for dyeing cotton khadi fabric with binary mixture of natural dyes in various proportions, providing the dyer an option for selecting correct and compatible mixture of natural dyes to match a target compound shade.

Industrial Importance: The present study offers an easy and simple colorimetric method of relative numerical rating of compatibility to identify and select proper compatible natural dyes to get different compound shades with improved wash and light fastness for cotton khadi fabric products.

### Acknowledgements

The authors are thankful to Dr. P. B. Kale, Director, Mahatma Gandhi Institute for Rural Industrialization (MGIRI), Wardha, India for encouragement and all administrative support to carry out the major part of R&D work at MGIRI. Authors also submit their sincere thanks to the Ministry of Micro, Small & Medium Enterprises (Govt. of India) for sanctioning this R&D project on Standardization of process of dyeing Cotton Khadi with natural dyes.
References


