Colour matching on wool using natural and synthetic dyes

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Wool fabric samples were dyed using natural dyes and mordants singly and in their binary mixtures. Computer colour matching system was used to evaluate these dyeings and generate matching dyeing recipes for synthetic trichromatic acid dyes which are ecofriendly. After dyeing with acid dyes, the natural dyed and acid dyed samples were evaluated for colour differences and it has been observed that in almost all cases, good matchings are observed for the natural dyed wool samples. This indicates that selective classes of synthetic dyes, which exhaust to higher levels and have proven non-toxicity, could be used with due concern to ecology and economy.

Keywords: Acid dyes, Computer colour matching, Dyeing, Natural dyes, Wool

1 Introduction

Colouration of textiles can be achieved by using either natural or synthetic dyes, both of which have their inherent advantages and disadvantages associated. Natural dyes have been existing in plants, trees, insects, minerals, sea animals, etc. since ages. Prior to the invention of the first synthetic dye in 1856, all the colouring matters were extracted from the natural sources and these are broadly classified according to their origin as vegetable origin, animal origin and mineral origin.

Natural dyes are mainly mordant dyes, although some vat dyes, a few solvent dyes, some pigments and some direct and acid dyes are also known. Mostly, these natural dyes are the mixture of two or more colouring matters. Mordants fix the natural colourants onto the fibre, which is essential for achieving good fastness properties for the dyed material. Metallic mordants, tannin and tannic acid and oil mordants are the common mordant types.

The interest in the natural dyes drastically reduced since more and more synthetic dyes were invented. In recent years, however, the concern for the clean environment has created a deep interest in natural dyes. The attempt to replace the synthetic dyes by natural dyes is not often based on the scientific facts but clouded with other considerations about the toxicity of synthetic dyes during their production and recent awareness about natural products being ecofriendly. However, the natural dyes have several limitations, like poor fastness properties, absence of standardized application methods, non-availability in the commercial standard form due to variable production and extraction methods and conditions, non-reproducibility of shades, heavy metal pollution caused by metallic mordants, etc. Moreover, the yield of natural dyes is so small that it is very difficult to obtain adequate supplies to meet today's requirement of dyestuff consumption and their harvesting would have tremendous adverse impact on the environment. Also, the entire process of application of natural dyes needs optimization from the point of view of economy and ecology.

The synthetic dyes are found cheaper to use, mainly due to simplified process of their application, ease in getting them in standard forms, greater variety of shades, brilliancy and improved colour fastness. Their disadvantage is that they create pollution during manufacture by virtue of the use of toxic petroleum chemicals. During dyeing also, they may pose problems in the form of effluent, as these dyes require a lot of acids, alkalis, salts and other auxiliaries and many times show incomplete exhaustion as well. However, it may be wrong to classify all synthetic dyestuffs as being harmful to the environment, simply because of problems associated with some dyes. Some natural dyes also possess structures similar to synthetic dyes and, therefore, their properties are alike.

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The performance of a particular dye vis-a-vis a particular fibre is evaluated by the shade and tone of dyeing and fastness properties of the dyed materials. To obtain reproducible results during colouration, critical assessment is essential. Visual colour assessment has several limitations due to its subjective nature. It is notoriously unreliable and the performance of a colourist may get influenced by a number of parameters, including psychological, medical and environmental factors.

Nowadays, most of the dye house colouration is controlled by the computer colour matching (CCM) technique, which not only saves manpower, energy and time but also increases the accuracy of matched dyeings. CCM finds applications in a number of areas in textile processing industry such as colour formulations, match predictions, design selections, viscosity control, cost reduction, inventory control, etc. Such a system also helps the textile colourist to analyze a colour and to evaluate the compatibility of dye mixtures by measuring various colour parameters related to it.

In the present work, wool fabric samples were dyed using natural dyes and mordants singly and in their binary mixtures. CCM system was then used as a tool to evaluate these dyeings and then generate the matching dyeing recipes for synthetic trichromatic acid dyes, which are ecofriendly. After dyeing with acid dyes, the natural dyed and acid dyed samples were evaluated for colour differences. Thus, an attempt has been made to indicate that it is still worth to continue with the conventional practice of dyeing with synthetic dyes with due concern to ecology and economy than to use natural dyes for achieving same colour on the textiles.

2 Materials and Methods

2.1 Materials

2.1.1 Substrate

Scoured and bleached wool fabric, supplied by Raymond Woollen Mill, Thane, was used for dyeing.

2.1.2 Dyes

The natural dyes used were Turmeric, Manjistha, Lac and Henna available in powder form. These were used as 1% extracts in water singly as well as in their binary mixtures. The synthetic dyes used belonged to acid class, supplied by Clariant (India) Ltd, and the selection was based on the concept of trichromatic combination having primary hues. These were Sandolan Blue EBRNI, Sandolan Fast Yellow 4GLI and Sandolan Red RSNI.

2.1.3 Mordants

The mordants used for dyeing with natural dyes were as follows:

- **M1**—potassium dichromate
- **M2**—copper sulphate
- **M3**—stannous chloride
- **M4**—alum (potash alum)
- **M5**—ferrous sulphate
- **M6**—tannic acid

2.2 Method

2.2.1 Mordanting of Wool

For pre-mordanting of wool fabric material, the concentration of all the mordants used was 10% (owf), except for stannous chloride (M3) which was used as 5% (owf).

The wool fabric was introduced in a solution containing the required amount of mordant with a liquor ratio of 40 at room temperature. The temperature was raised to boil and the mordanting was carried out for 45 min. The fabric was then taken out, dried and subjected to dyeing with natural dye. Binary mordant mixtures in 1:1 proportion were also used in a similar way for pre-mordanting of the fabric.

2.2.2 Dyeing with Natural Dyes

Substance containing natural dye was mixed with the required amount of water and boiled for 1 h. The contents were then cooled to room temperature and filtered. The filtrate (1% extract) was used as a dye solution for dyeing.

Dye bath with a liquor ratio of 40 was prepared with 1% extract of the natural dye solution. Mordanted fabric samples were put into the dye bath at room temperature. The temperature was raised to boil and dyeing was continued further for 45 min. After dyeing, cold wash was given followed by soaping with 2 g/l of a non-ionic detergent at boil for 15 min. Finally, the samples were washed thoroughly and dried. Dyeings were similarly carried out using equiproportional binary mixtures of the natural dyes.

2.2.3 Evaluation of Dyed Samples

The natural dyed samples were evaluated with the CCM system Spectraflash SF300 [Data Color International, USA] in terms of CIELab colour coordinates \(L^*, a^*, b^*\) with illuminants \(D_{65}\), A and CWF and with 10° observer. In addition, the colour strength of dyed sample was evaluated in terms of \(K/S\) through quality control program of the CCM system. The results with the more common illuminant \(D_{65}\) only are reported in this paper.
2.2.4 Recipe Prediction by CCM
The above natural dyed fabrics were attempted to
match by dyeing with synthetic acid dyes. For this,
the natural dyed samples were subjected to evaluation
on CCM for recipe prediction using acid dyes for
wool.

Colour matching software for ‘Formulation’ or
‘Recipe Prediction’ works by creating colour data
bank of the dyestuffs to be used for this purpose. This
was created by preparing calibration dyeings of
individual acid dyes. Ecofriendly acid dyes for wool
dyeing were used in near primary (yellow, red and
blue) colours on the basis of their commercial
availability. Each dye was accurately dyed on a wool
fabric sample for different shades (0.1, 0.25, 0.5, 1.0,
1.5, 2.0 and 3.0%) and then evaluated on CCM to
create the data bank. The system then computed the
possible combinations of these colourants and their
amounts to produce matches with each of the natural
dyed wool samples. The best possible recipe based on
metamerism was selected in each case. With these
predicted recipe formulations using acid dyes, the
wool fabric was dyed and evaluated again using CCM
for possible colour differences with the natural dyed
fabric.

2.2.5 Dyeing of Wool Fabric with Acid Dyes
Dye bath was prepared with the required amounts
of acid dye solution as per the recipe given by CCM,
4% acetic acid and 10% Glauber’s salt. Dyeing was
started at 50°C and the temperature was raised to
80°C in 15 min. Dyeing was further carried out for 10
min. Sulphuric acid (2%) was then added into the dye
bath and the dyeing continued further for 30 min. The
sample was removed, washed with cold water and
then soaked with 2 g/l non-ionic detergent (Auxipon
NP) at boil for 15 min. Finally, the sample was
washed thoroughly and dried.

2.2.6 Evaluation of Wash Fastness
Composite samples of 10 cm × 4 cm were stitched
for the dyed fabrics using wool and cotton fabrics on
either side of the sample. These samples were
subjected to a treatment with 5 g/l soap solution at
50±2°C for 45 min. Samples were then removed and
dried. Grey scale ratings were assigned to the tested
samples.

2.2.7 Evaluation of Light Fastness
The light fastness of the natural and synthetic dyed
samples was tested on Suntest CPS (Heraeus-B150,
Germany) after partially exposing the samples to the
xenon arc lamp for 12 h and graded for the colour
change with the ratings.

3 Results and Discussion
The results on colour coordinates of dyed samples
are given in Table 1. It is observed that all the dyeings
have their colour coordinates positive with respect to
lightness $L^*$, red-green $a^*$, yellow-blue $b^*$ and,
therefore, all of them lie in the yellow-red quadrant of
the colour space diagram. The plots for different
natural dyed samples and their respective matchings
with the synthetic acid dyes have been given
collectively for the sake of comparison in Figs 1-3.
The maximum lightness is observed for the sample
no. 1 (Turmeric dyed on wool premordanted with M4)
which has somewhat brighter appearance as compared
to all other samples and the colour obtained is reddish
yellow. The lowest lightness is observed for the
sample no. 5 (Manjistha dyed on wool premordanted
with a mixture M1+M6).
The selected ecofriendly acid dyes based on the
trichromatic combination concept were used to create
the data bank in the CCM system. This was followed
by predicting the recipes using these acid dyes to
match with the samples dyed with natural dyes,
through match prediction software of CCM. The
amounts of these acid dyes (% owg) have been given
in Table 2. Using these amounts, the dyeings of wool
fabric samples were carried out and then subjected to
CCM system for evaluation of the colour differences
with the respective natural dyed samples.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Natural dye</th>
<th>Mordant</th>
<th>$L^*$</th>
<th>$a^*$</th>
<th>$b^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Turmeric</td>
<td>M4</td>
<td>66.53</td>
<td>13.29</td>
<td>80.56</td>
</tr>
<tr>
<td>2</td>
<td>Turmeric</td>
<td>M1+M6</td>
<td>41.88</td>
<td>11.04</td>
<td>39.89</td>
</tr>
<tr>
<td>3</td>
<td>Turmeric</td>
<td>M5+M6</td>
<td>41.30</td>
<td>1.57</td>
<td>28.20</td>
</tr>
<tr>
<td>4</td>
<td>Manjistha</td>
<td>M1+M2</td>
<td>41.14</td>
<td>11.81</td>
<td>22.86</td>
</tr>
<tr>
<td>5</td>
<td>Manjistha</td>
<td>M1+M6</td>
<td>25.68</td>
<td>15.25</td>
<td>9.89</td>
</tr>
<tr>
<td>6</td>
<td>Manjistha</td>
<td>M3+M4</td>
<td>39.88</td>
<td>39.66</td>
<td>29.48</td>
</tr>
<tr>
<td>7</td>
<td>Manjistha</td>
<td>M5+M6</td>
<td>29.42</td>
<td>9.47</td>
<td>8.26</td>
</tr>
<tr>
<td>8</td>
<td>Henna</td>
<td>M1+M6</td>
<td>45.22</td>
<td>13.17</td>
<td>24.05</td>
</tr>
<tr>
<td>9</td>
<td>Henna</td>
<td>M1+M2</td>
<td>38.80</td>
<td>5.02</td>
<td>24.86</td>
</tr>
<tr>
<td>10</td>
<td>Henna</td>
<td>M1+M6</td>
<td>36.95</td>
<td>9.21</td>
<td>26.43</td>
</tr>
<tr>
<td>11</td>
<td>Henna</td>
<td>M2+M5</td>
<td>27.29</td>
<td>5.45</td>
<td>13.11</td>
</tr>
<tr>
<td>12</td>
<td>Lac</td>
<td>M1+M3</td>
<td>51.47</td>
<td>8.10</td>
<td>13.76</td>
</tr>
<tr>
<td>13</td>
<td>Lac</td>
<td>M5+M6</td>
<td>37.20</td>
<td>5.05</td>
<td>2.97</td>
</tr>
<tr>
<td>14</td>
<td>Turmeric</td>
<td>Manjistha</td>
<td>49.31</td>
<td>19.52</td>
<td>32.80</td>
</tr>
<tr>
<td>15</td>
<td>Turmeric</td>
<td>M6</td>
<td>46.16</td>
<td>10.02</td>
<td>38.71</td>
</tr>
<tr>
<td>16</td>
<td>Henna</td>
<td>Turmeric</td>
<td>56.78</td>
<td>6.06</td>
<td>37.89</td>
</tr>
<tr>
<td>17</td>
<td>Lac</td>
<td>Turmeric</td>
<td>42.20</td>
<td>22.83</td>
<td>14.65</td>
</tr>
</tbody>
</table>
The data on colour difference characteristics between natural dyed and synthetic acid dyed wool samples (Table 3) indicate that the values of $DL^*$.

$Da^*$ and $Db^*$ are well within the tolerance limits. Only for sample no. 2 (Turmeric dyed on wool premordanted with M1+M6), the $Db^*$ value is 6.24, indicating more yellowness for the sample dyed with synthetic acid dyes. As far as the colour difference $DE^*$ values are concerned, it is observed that for sample no. 15 (wool premordanted with M6 and dyed with a mixture of Turmeric and Henna) the $DE^*$ is as high as 8.66, indicating considerable tonal variations between the matched samples. Thus, most of the samples showed good matchings as far as the colour differences are concerned.
The data on colour strength and the light and wash fastness of dyeings are given in Table 4. It is observed that all the samples dyed with the synthetic acid dyes show very good matching with respective natural dyed wool in terms of the depth of colour represented by \( K/S \) values. The wool samples dyed with Lac alone or with Lac in combination with Manjistha show lower colour strengths. The light fastness for the natural dyed unmordanted wool sample is very poor. Considerable improvement is observed for the dyeings on premordanted wool. In comparison, all the synthetic acid dyed samples show good light fastness. Also, the wash fastness of all the synthetic acid dyed samples is better than that of the natural dyed samples.

From Figs 1-3, it may be seen that out of the seventeen different dyeings reported, about \( \frac{2}{3} \) of them show very good matching as regards the tone of dyeing, while the remaining show some tonal differences, although theoretically well within limits.

The natural dyed substrates were coloured with satisfactory wash fastness only when premordanting was carried out. The dye exhaustion as well as exhaustion of mordants was not very high, leaving much of their amounts unused in the bath. Although the natural dyes are very much biodegradable, the use of metallic mordants, except the natural mordant tannic acid, causes highly objectionable heavy metal pollution. This pollution is equally dangerous as the toxicity of synthetic dyes, since the heavy metals are not at all biodegradable and also accumulate in the food-chain, leading to severe ill effects on living organisms.

The synthetic dyes selected for matching were from acid class of dyes. The dye baths of these synthetic dyes used for matching the natural dyed samples were completely exhausted, leaving no dye in the bath. In case of the deeper shades also, it was observed that extremely small amounts of these dyes were left in the dye bath, thereby contributing insignificantly to the pollution load of the effluent.

It may, therefore, be concluded, that it is not always necessary to go for use of natural dyes, which encounter many difficulties during dyeing of textile substrate, only from the point of view of control over toxicity and pollution load. Selective classes of synthetic dyes, which exhaust to higher levels and

### Table 3—Colour difference of synthetic acid dyed and natural dyed wool

<table>
<thead>
<tr>
<th>Dyed sample</th>
<th>DE</th>
<th>DL</th>
<th>Da</th>
<th>Db</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turmeric (M4)</td>
<td>0.78</td>
<td>-0.16</td>
<td>0.70</td>
<td>0.30</td>
</tr>
<tr>
<td>Turmeric (M1+M6)</td>
<td>6.33</td>
<td>0.85</td>
<td>0.64</td>
<td>6.24</td>
</tr>
<tr>
<td>Turmeric (M5+M6)</td>
<td>3.35</td>
<td>1.22</td>
<td>-2.46</td>
<td>1.92</td>
</tr>
<tr>
<td>Manjistha (M1+M2)</td>
<td>3.12</td>
<td>2.19</td>
<td>-1.67</td>
<td>1.47</td>
</tr>
<tr>
<td>Manjistha (M1+M6)</td>
<td>3.57</td>
<td>-2.14</td>
<td>0.10</td>
<td>2.85</td>
</tr>
<tr>
<td>Manjistha (M3+M4)</td>
<td>4.59</td>
<td>-2.22</td>
<td>-2.99</td>
<td>-2.69</td>
</tr>
<tr>
<td>Manjistha (M5+M6)</td>
<td>1.57</td>
<td>1.29</td>
<td>0.76</td>
<td>0.46</td>
</tr>
<tr>
<td>Henna</td>
<td>4.21</td>
<td>4.20</td>
<td>-0.05</td>
<td>-0.19</td>
</tr>
<tr>
<td>Henna (M1+M2)</td>
<td>4.16</td>
<td>0.19</td>
<td>1.67</td>
<td>3.80</td>
</tr>
<tr>
<td>Henna (M1+M6)</td>
<td>3.15</td>
<td>2.07</td>
<td>-1.59</td>
<td>1.76</td>
</tr>
<tr>
<td>Henna (M2+M5)</td>
<td>1.52</td>
<td>-0.78</td>
<td>-0.37</td>
<td>-1.25</td>
</tr>
<tr>
<td>Lac (M1+M3)</td>
<td>3.08</td>
<td>-2.01</td>
<td>1.38</td>
<td>1.88</td>
</tr>
<tr>
<td>Lac (M5+M6)</td>
<td>2.91</td>
<td>2.28</td>
<td>-1.62</td>
<td>0.79</td>
</tr>
<tr>
<td>Turmeric + Manjistha</td>
<td>1.36</td>
<td>1.00</td>
<td>0.37</td>
<td>0.84</td>
</tr>
<tr>
<td>Turmeric + Henna (M6)</td>
<td>8.66</td>
<td>6.74</td>
<td>-1.20</td>
<td>5.31</td>
</tr>
<tr>
<td>Turmeric + Lac</td>
<td>3.34</td>
<td>-1.75</td>
<td>2.15</td>
<td>1.87</td>
</tr>
<tr>
<td>Manjistha + Lac (M6)</td>
<td>1.23</td>
<td>-0.41</td>
<td>0.32</td>
<td>1.11</td>
</tr>
</tbody>
</table>

### Table 4—Colour strength and fastness properties of natural and synthetic dyed wool

<table>
<thead>
<tr>
<th>Dyed sample</th>
<th>Natural</th>
<th>Synthetic</th>
<th>Light fastness</th>
<th>Wash fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td>K/S</td>
<td></td>
<td></td>
<td>Natural</td>
<td>Synthetic</td>
</tr>
<tr>
<td>Turmeric (M4)</td>
<td>23.51</td>
<td>25.36</td>
<td>2</td>
<td>5-6</td>
</tr>
<tr>
<td>Turmeric (M1+M6)</td>
<td>21.83</td>
<td>22.64</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Turmeric (M5+M6)</td>
<td>15.36</td>
<td>15.40</td>
<td>4</td>
<td>5-6</td>
</tr>
<tr>
<td>Manjistha (M1+M2)</td>
<td>9.29</td>
<td>9.53</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Manjistha (M1+M6)</td>
<td>18.32</td>
<td>18.6</td>
<td>3-4</td>
<td>6-7</td>
</tr>
<tr>
<td>Manjistha (M3+M4)</td>
<td>13.32</td>
<td>13.77</td>
<td>4</td>
<td>6-7</td>
</tr>
<tr>
<td>Manjistha (M5+M6)</td>
<td>11.67</td>
<td>12.67</td>
<td>4-5</td>
<td>6-7</td>
</tr>
<tr>
<td>Henna</td>
<td>10.48</td>
<td>10.59</td>
<td>3</td>
<td>6-7</td>
</tr>
<tr>
<td>Henna (M1+M2)</td>
<td>16.56</td>
<td>17.01</td>
<td>3-4</td>
<td>5-6</td>
</tr>
<tr>
<td>Henna (M1+M6)</td>
<td>20.12</td>
<td>20.44</td>
<td>3-4</td>
<td>5-6</td>
</tr>
<tr>
<td>Henna (M2+M5)</td>
<td>21.33</td>
<td>21.70</td>
<td>4</td>
<td>5-6</td>
</tr>
<tr>
<td>Lac (M1+M3)</td>
<td>4.50</td>
<td>6.88</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Lac (M5+M6)</td>
<td>5.55</td>
<td>5.96</td>
<td>3-4</td>
<td>5-6</td>
</tr>
<tr>
<td>Turmeric + Manjistha</td>
<td>9.98</td>
<td>10.17</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>Turmeric + Henna (M6)</td>
<td>14.69</td>
<td>14.76</td>
<td>2-3</td>
<td>6</td>
</tr>
<tr>
<td>Turmeric + Lac</td>
<td>8.22</td>
<td>8.89</td>
<td>2</td>
<td>5-6</td>
</tr>
<tr>
<td>Manjistha + Lac (M6)</td>
<td>6.35</td>
<td>6.96</td>
<td>4</td>
<td>6-7</td>
</tr>
</tbody>
</table>
have proven non-toxicity, can be used instead with better and brilliant shades and fastness properties. CCM as a tool for matching the shades has been found to be extremely useful, since for almost all the dyeings studied, the predicted recipes gave very good matchings.

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5 Gulrajani M L & Gupta D, Natural Dyes and Their Application to Textiles (Indian Institute of Technology, New Delhi ), 1992, 46.