Physico-chemical study of dyed wool: Part I—Bougainvillaea as wool colourant with mixed mordant

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Received 3 December 1999; revised received and accepted 13 July 2000

The extract of red petaloid bracts of bougainvillaea has been used as wool colourant with mixed mordants and the physico-chemical properties of the dyed samples studied. The petaloid bracts when treated with water at 97.5°C for nearly 20 min yield 7.43% of bougainvillaea (BV) colourant. The optimum conditions for dyeing of wool have been determined as pH 4.5, BV concentration 0.06 g per gram of wool, temperature 97.5°C, and time 45 min. It is observed that the use of lanthanum (III) as first mordant and chromium (VI) as second mordant reduces the quantity of Cr (VI) in the spent dye bath and causes less damage to the wool fibre in comparison to the dyed yarn mordanted with Cr (VI) alone. This binary mixed-mordant dyeing also reduces the environmental pollution caused due to the discharge of toxic chromium ion in the effluent.

Keywords: Bougainvillaea petaloid, Dyeing, Wool

1 Introduction
Very little is reported in the literature regarding the use of bougainvillaea, a natural dyestuff, in dyeing of textiles. The present work deals with the extraction of bougainvillaea (BV) colourant from its red petaloid for the dyeing of wool at the optimum conditions, estimation of chromium contents in the mordanted dyed wool fibre, and physico-chemical studies, viz. colour fastness, U.B solubility and tensile behaviour.

2 Materials and Methods
2.1 Substrate
Two-ply worsted Bharat Merino wool yarn (50 tex) was procured from the Central Sheep & Wool Research Institute, Avikanagar (Rajasthan).

2.2 Extraction of BV
The fresh red petaloid bracts (100 g) were boiled with 500 ml distilled water for about 20 min till the petaloid bract become colourless. The extract was concentrated under reduced pressure on water bath, shaken with 70:30 (v/v) alcohol-water mixture for 1 h and then filtered. The filtrate was evaporated under reduced pressure to collect the dried mass (BV) of 7.43 g. The dried powder thus obtained was stored in amber coloured bottles for about 3 months without any disadvantage.

1.0 g BV per 100 ml of the solution was dissolved in distilled water to prepare the stock solution for dyeing. The reddish purple colour of BV is stable in acid and neutral mediums. Its acidic solution can be stored in amber coloured bottles in refrigerator for about 15 days.

2.3 Spectral Analysis
The spectrum of about 10 ppm aqueous solution of BV was recorded on uv-visible spectrophotometer (Shimadzu, UV-160 A). The following absorption maxima were observed:

(I) \(537 (\epsilon = 0.392), 406 (\epsilon = 1.470)\) and \(352 (\epsilon = 0.991)\)

(II) \(534 (\epsilon = 0.972), 432 (\epsilon = 1.987)\) and \(352 (\epsilon = 0.991)\)

The results show a small variation in first absorption band while the other absorbance band shows a large variation. Hence, the wavelength at 540 nm (Fig. 1) was chosen for analytical studies as it is easily assessable in visible region and on commonly available spectrophotometers.
2.4 Scouring

The wool yarn was scoured as per the BIS method (IS: 1349:1964) and then treated with ethanol in soxhlet apparatus for 3 h at the rate of 6 siphons/h to ensure the removal of residual soap. The yarn was then rinsed with distilled water and dried at room temperature.

2.5 Optimization of Dyeing Conditions

The optimum conditions with respect to pH, BV concentration, temperature and treatment time were determined for dyeing of wool yarn.

2.5.1 pH

The scoured yarn (1.0 g) was soaked for nearly 30 min in acidulated water (5 ml glacial acetic acid per 100 ml of solution, pH 2.5) and then subjected to dyeing for 60 min at 97.5°C in a dye bath containing 2.0 ml BV (stock solution) and 5.0 ml glacial acetic acid plus distilled water solution so as to make total volume to about 100 ml in the dye bath. The absorbance of the dye bath was recorded before and after dyeing of yarn at 540 nm. The amount of BV absorbed was calculated using the following equation:

\[
\% \text{BV absorbed} = \left( \frac{\text{Absorbance after dyeing} - \text{Absorbance before dyeing}}{\text{Absorbance before dyeing}} \right) \times 100
\]  

Eq (1)

The above dyeing procedure was repeated at pH 4.5 (2.0 ml glacial acetic acid per 100 ml) and 6.5 (0.6 ml glacial acetic acid per 100 ml). The results (Fig. 2) indicate that the wool absorbs maximum BV at pH 2.5 but the optimum pH was taken as 4.5 as discussed later.

2.5.2 BV Concentration

The above dyeing procedure was repeated for eight different concentrations of BV such as 0.5, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0 and 12.0 ml separately per 100 ml of solution at pH 2.5, 4.5 and 6.5. The absorbance measurements were made at 540 nm and % BV absorbed by wool was calculated in each case using Eq (1). The results (Fig. 3) show that the optimum concentration of BV corresponding to the maximum absorbance of BV is found to be 0.06 g per gram of wool at pH 4.5.

2.5.3 Treatment Time

Six (6) scoured wool yarn samples (1.0 g each) were treated with 6.0 ml of BV stock solution at pH 2.5, 4.5 and 6.5 and temperature 97.5°C as described earlier. The BV concentration in the spent dye bath was measured at the regular interval of 0, 15, 30, 45, 60, 75 and 90 min. The results (Fig. 4) show that the optimum treatment time for the maximum absorbance of BV is 45 min.

2.5.4 Temperature

Six (6) scoured wool yarn samples (1.0 g each) were treated with 6.0 ml of BV stock solution at pH
2.5 for 45 min at different temperatures viz. 40, 50, 60, 70, 80, 90 and 97.5°C. The absorbance of BV in the spent dye bath was measured before and after the treatment. The experiment was repeated at pH 4.5 and 6.5 under identical conditions. The results (Fig. 5) show that the optimum temperature for maximum absorbance of BV is 97.5°C at approximately one atmospheric pressure which is in agreement with the earlier findings.

2.6 Dyeing and Mordanting

Five (5) samples of scoured wool yarn, weighing 5.0 g each, were soaked in separate dye bath each containing 500 ml of acidulated water (2.0 ml glacial acetic acid per 100 ml of the solution, pH 4.5) for nearly 30 min at 40-50°C. The BV stock solution (30 ml, 0.06 BV per gram of the yarn) was then added to each dye bath. The temperature was raised slowly to boil and the contents were kept for nearly 40 min. At this stage, 5 ml of La (III) solution (0.5 g La$_2$O$_3$ per 100 ml of the solution containing 10 ml conc. HCl) was added to each dye bath and the heating was further continued for nearly 30 min. The dye bath was then cooled to about 70°C and about 2.0 ml glacial acetic acid was added. The contents were mechanically stirred. At this stage, potassium dichromate solution (0.015 g per gram of the yarn) was added to each dye bath. The temperature of the dye bath was again raised slowly to boil and maintained for about 60 min. The loss of water by evaporation was maintained by adding hot acidulated water from time to time. After cooling the contents of the dye bath to room temperature, the dyed yarns were taken out and washed with 2% Na$_2$CO$_3$ solution containing 0.1 ml ultravan JU (detergent) per 100 ml. The yarns were finally rinsed with distilled water and dried at room temperature.

The above procedure was repeated using Cr(VI) or La(III) as a single mordant. The dyed yarn samples were treated with either of the above mordants for 60 min at 97.5°C and pH 4.5.

2.7 Estimation of Chromium

The dyed yarns mordanted with Cr (VI) were cut into small pieces (8-10 cm) and dried in an oven at 110±1°C. A known weight of these pieces (50-60 mg) was digested with 2.0 ml mixture of HNO$_3$, H$_2$SO$_4$ and HClO$_4$ (volume ratio 2.5:0.5:1.0) at 200°C in a pyrex tube so as to obtain clear solution. The contents were then made up to 10 ml by adding double distilled water in a volumetric flask. Chromium was then estimated in this solution by using Perkin-Elmer atomic absorption spectrophotometer (model 2380). The process was repeated for other samples. The results (Table 1) reveal that the dyed yarn treated with La (III) absorbs higher concentration of chromium (VI) as compared to untreated dyed yarn.

2.8 Physico-chemical Studies

2.8.1 Light Fastness

The dyed yarns were assessed for light fastness as per the BIS method (IS: 2454-1967) using Shirley development light fastness tester SDL-237. The Instrument was adjusted at 65±2% relative humidity to expose the specimen and blue wool standard (rating 1-8) for 5 h at one stretch of time and for a total period of 40 h. The results (Table 2) reveal that the colour of the dyed yarn mordanted with Cr (VI), with or without lanthanum (III), can withstand on exposure to light as per the BIS requirement.
Table 1—Estimation of chromium in mordanted wool yarn

<table>
<thead>
<tr>
<th>Yarn</th>
<th>Yarn Weight (mg)</th>
<th>Chromium found in test portion of the yarn (mg)</th>
<th>Chromium in spent dye bath (%)</th>
<th>Average chromium ion in spent dye bath (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dyed &amp; mordanted with Cr(VI)</td>
<td>57.3</td>
<td>0.860</td>
<td>0.533</td>
<td>38.02</td>
</tr>
<tr>
<td></td>
<td>58.9</td>
<td>0.884</td>
<td>0.512</td>
<td>42.08</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>57.5</td>
<td>0.863</td>
<td>0.546</td>
<td>36.73</td>
</tr>
<tr>
<td></td>
<td>59.8</td>
<td>0.897</td>
<td>0.529</td>
<td>41.03</td>
</tr>
<tr>
<td></td>
<td>58.6</td>
<td>0.879</td>
<td>0.533</td>
<td>37.09</td>
</tr>
<tr>
<td>Dyed &amp; mordanted first with La(III) and then with Cr(VI)</td>
<td>58.3</td>
<td>0.881</td>
<td>0.749</td>
<td>14.98</td>
</tr>
<tr>
<td></td>
<td>57.9</td>
<td>0.869</td>
<td>0.749</td>
<td>17.03</td>
</tr>
<tr>
<td></td>
<td>60.2</td>
<td>0.903</td>
<td>0.759</td>
<td>15.95</td>
</tr>
<tr>
<td></td>
<td>59.4</td>
<td>0.891</td>
<td>0.742</td>
<td>16.72</td>
</tr>
<tr>
<td></td>
<td>58.3</td>
<td>0.875</td>
<td>0.706</td>
<td>19.35</td>
</tr>
</tbody>
</table>

(b)=(a×1.5)+100; (d)=[(b-c)+(b'×100)

Table 2—Physico-chemical studies of wool yarn

<table>
<thead>
<tr>
<th>Yarn</th>
<th>pH</th>
<th>Light fastness</th>
<th>Wash fastness</th>
<th>U B solubility (%)</th>
<th>Tex</th>
<th>Tenacity (g/tex)</th>
<th>Extension - at-break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scoured undyed</td>
<td></td>
<td></td>
<td></td>
<td>34.58</td>
<td>56.79</td>
<td>7.25</td>
<td>12.74</td>
</tr>
<tr>
<td>Dyed</td>
<td>2.5</td>
<td>1-2</td>
<td>1-2</td>
<td>26.54</td>
<td>56.83</td>
<td>6.27</td>
<td>15.02</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>1-2</td>
<td>1-2</td>
<td>26.91</td>
<td>57.67</td>
<td>6.48</td>
<td>14.87</td>
</tr>
<tr>
<td></td>
<td>6.5</td>
<td>1-2</td>
<td>1-2</td>
<td>25.49</td>
<td>56.98</td>
<td>6.32</td>
<td>13.36</td>
</tr>
<tr>
<td>Dyed &amp; mordanted with La(III)</td>
<td>4.5</td>
<td>3-4</td>
<td>4-5</td>
<td>24.86</td>
<td>59.08</td>
<td>6.13</td>
<td>14.48</td>
</tr>
<tr>
<td>Dyed &amp; mordanted with Cr(VI)</td>
<td>4.5</td>
<td>4-5</td>
<td>4-5</td>
<td>19.18</td>
<td>58.99</td>
<td>5.64</td>
<td>15.85</td>
</tr>
<tr>
<td>Dyed &amp; mordanted first with La(III) and then with Cr(VI)</td>
<td>4.5</td>
<td>4-5</td>
<td>4-5</td>
<td>23.72</td>
<td>59.16</td>
<td>5.9</td>
<td>15.42</td>
</tr>
</tbody>
</table>

2.8.2 Wash Fastness
The dyed yarns were knitted (10 cm × 4 cm size) and then subjected to washing in laundrometer as per the BIS method (IS: 687-1979). The results (Table 2) reveal that the yarn dyed at pH 2.5 bleed more colours in comparison to those dyed at pH 4.5 and 6.5. The mordanting treatment improves the wash fastness of the dyed yarn.

2.8.3 Urea-metabisulphite (UB) Solubility
The solubility of wool (1.0g) in urea-metabisulphite solution (3.0 g sodium metabisulphite and 50 g urea per 100 ml of solution) was determined for 60 min at 65±2°C as per the BIS method (IS: 3430:1966). The results (Table 2) reveal that the Cr(VI) causes less damage to the wool in a dyed yarn mordanted with La(III) as compared to unmordanted yarn.

2.8.4 Tensile Behaviour
The yarns were subjected to conditioning at 27±2°C and 65±5% R H for 48 h and the tensile testing was carried out on an Instron model TM 1102. The cross-head speed was so adjusted to break the yarn (50 cm length) within 20±2 s. The tex values were estimated for each tested yarn. An average of twenty five (25) measurements was taken for each tex, tenacity (breaking load/tex) and extension-at-break (Table 2). Both the urea-metabisulphite solubility and tensile strength data indicate that the mordanting action of La (III) causes much less damage to the yarn as compared to Cr(VI). The data further indicate that the mordanting action of Cr(VI) on the La (III) mordanted dyed yarn causes less damage to wool as compared to that caused by Cr(VI) alone on the dyed wool fibre.
3 Results and Discussion

The BY colourant extracted from red petaloid bracts of bougainvillea imparts its yellow colour to wool due to the presence of betanin and vulgaxanthin (both have 2,6-pyridine dicarboxylic acid units).

![BY colourant](image)

The wool in its protofibrils contains 2-3 polypeptide chains with different R groups of amino acids. The wool fibre contains equal amount of amino and carboxyl groups which ionise and form a zwitter ion.

At low pH, the hydrogen ions are absorbed by carboxyl groups of wool protein (keratin) (Scheme 1). At high pH, the protein loses H⁺ ion leaving behind ionized groups (Scheme 2).

The wool when put in an acid dye bath gets wetted and swells. The BY molecule migrates from the solution to the surface of the fibre, gets adsorbed on the surface and diffuses through swollen pores into the interior of the fibre. The BY molecule interacts with NH and carboxyl functional groups of keratin (wool protein) forming WD complex, where W and D are the keratin and BY molecules.

![WD complex](image)

On addition of the lanthanum ion (M₁) in dye bath, the ions interact with carboxyl groups of keratin and that of colourant to form WDM₁ complex.

![WDM₁ complex](image)

Scheme 1—Reaction showing the hydrogen ion absorption by the carboxyl groups of wool protein at low pH

![Scheme 1](image)

Scheme 2—Reaction showing the loss of hydrogen ion by the wool protein at high pH

![Scheme 2](image)
Chromium (VI) also interacts in a similar fashion when it is used alone as mordant to form WDM\(_2\) complex, where M\(_2\) is Cr(III). The Cr (III) has coordination number 6.

The chromium (VI), present in the interior of fibre, causes oxidation of colourant and cystine molecule and gets reduced to Cr(III)\(^{6.7}\). The Cr(III) now interacts with La(III)-BV-wool complex to form WDM\(_1\)M\(_2\) mixed complex.

Table 1 shows that the intake of Cr(VI) in dyed yarn mordanted with La(III) is much more than that in dyed yarn mordanted with Cr(VI) alone. This may be due to the fact that the higher coordination number (>6) is more common rather than exception in lanthanides, i.e. more binding sites are available in the dyed yarn treated with La (III) mordant.

The pH of the solution in the interior of the fibre is reported\(^8\) to be about two units higher than the pH of the solution in the dye bath. Thus, the pH of the solution in the interior of the fibre may be about 6 and at this pH, La(III) and Cr(III) are capable of forming hydroxo complexes. These complexes may be polymeric in nature formed through oxy or hydroxy linkages.

\[
\text{[La(H}_2\text{O)}\_n]^{3+} + \text{H}_2\text{O} \rightarrow \text{[La(H}_2\text{O)}\_n\cdot \text{(OH)}^{2+}} + \text{H}_3\text{O}^+ \\
\text{[Cr(H}_2\text{O)}\_n]^{3+} + \text{H}_2\text{O} \rightarrow \text{[Cr(H}_2\text{O)}\_n\cdot \text{(OH)}^{2+}} + \text{H}_2\text{O}^+
\]

The mixed metal chalete WDM\(_1\)M\(_2\) is thus retained into the interior of the fibre and consequently the concentration of chromium is considerably reduced in the spent dye bath.

4 Conclusion

The physico-chemical studies, viz. colour fastness, U B solubility and tensile behaviour, of the dyed yarn mordanted with binary mixed mordant shows that the use of lanthanum (III) as first mordant and chromium (VI) as second mordant reduces the quantity of Cr (VI) in the spent dye bath and causes less damage to the wool fibre in comparison to the dyed yarn mordanted with Cr(VI) alone. The use of lanthanum (III) as binary mixed mordant results in the decrease in environmental pollution caused due to the discharge of toxic chromium ion in the effluent.

Acknowledgement

The authors are thankful to the Head, Department of Chemistry, University of Rajasthan, for providing facilities. One of the authors (JPM) is grateful to the Director, Central Sheep & Wool Research Institute, Avikanagar, for the grant of study leave and for the facilities extended to him.

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