Dyeing of polyester and wool with solvent-assisted color extract from ratanjot

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A series of homologous alcoholic solvents and their mixtures has been used for the extraction of coloring matter from ratanjot (\textit{Onosma echoides}) powder. The extracted coloring matter is then used for dyeing of wool and polyester fabrics. The dyebaths are prepared based on aqueous, solvent and solvent assisted dyeing mediums. It is found that as compared to a single solvent, a mixture of solvents results in higher extraction of colorants from ratanjot. Also, the depth of shade reduces with increasing hydrophobicity of the dyeing medium using the same extraction medium. While the fastness to washing (change in color) is found to be good to excellent (3-5) on polyester, it is rather low (1-3) on wool. This can be attributed to the hydrophobic nature of colorants extracted from ratanjot, which resemble disperse dyes and have poor wash fastness on wool but show good wash fastness on polyester.

\textbf{Keywords:} \textit{Onosma echoides}, Polyester, Ratanjot, Solvent-assisted dyeing, Solvent extraction, Wool

\section{Introduction}

Synthetic dyes are used in a wide range of applications in various fields like food, cosmetics and textiles. They have the advantage of ease of dyeing, shade reproducibility and overall cost factor. However, their non-biodegradable nature, toxicity and dependency on non-renewable petroleum resources cause need to know other alternatives. One such alternative ‘natural colorants’, on the other hand, is ecofriendly, safe to body contact, obtained from renewable sources and their production involves a minimum possibility of chemical reaction. These colorants do not cause health hazards; instead some of them are used in healthcare, examples being ratanjot and turmeric. There are certain limitations in use of natural dyes however, such as poor color yield, lower stability, complexity of dyeing process, lower fastness and reproducibility of shades\textsuperscript{1}.

Ratanjot (\textit{Onosma echoides}) is a red dye obtained from the roots of various \textit{Boraginaceous} plant species. It has traditionally been used for coloring of food and oils. It is also used to cure eye diseases, bronchitis, abdominal pains,\textsuperscript{1} etc. It is a historical natural dye and also holds immense importance in the field of pharmaceutical, cosmetics and food colorants.

The bark of ratanjot roots contains several naphthoquinone pigments, which give a violet red colour. Alkanin and Shikonin along with their derivatives are considered to be main coloring components present in ratanjot bark\textsuperscript{2}. Alkanin forms a dark red amorphous powder with beetle green iridescence. As alkanin is naphthoquinone based, it is expected to behave as disperse dye\textsuperscript{2}. This dye is applied\textsuperscript{1} at pH 4-5. As the main dye component is hydrophobic, it is best extracted using organic solvents. The main coloring components being hydrophobic in nature, can be extracted with supercritical carbon dioxide and other solvents\textsuperscript{3}.

Alkanin present in ratanjot exhibits high affinity for polyester. Dyeing corresponds to the partition mechanism of polyester dyeing with disperse dye\textsuperscript{2}. Ratanjot shows good light fastness and excellent wash fastness properties on polyester. Very little work has been done on the dyeing of textiles with ratanjot dye in the past. Bairagi and Gulrajani\textsuperscript{2} studied dyeing of polyester by shikonin extracted from ratanjot. Extracted dye exhibited high affinity towards hydrophobic fibres.

Gulrajani et al.\textsuperscript{2} carried out dyeing of ratanjot dye on nylon and polyester. It was observed that polyester has lower rate of dyeing than nylon and that the saturation dye uptake of polyester was much less than that of nylon. This was attributed to highly compact structure of polyester compared to that of nylon. Due to this reason, diffusion of dye in polyester was less than in nylon.

Adsorption isotherms for both fibres were found to be linear which indicated that mechanism of dyeing for both the fibres corresponds to partition mechanism of dyeing. Ratanjot showed good light fastness
properties on nylon and polyester and it was attributed to the fact that the naphthoquinone based chromophore is relatively stable to photo fading and the dye may be present in an aggregated form inside the fibre. Also the wash fastness results of Ratanjot on nylon and polyester were reported to be excellent.

In order to accelerate rate of uptake of disperse dyes on the substrate, various organic solvents can be employed as dyebath additives. The ability of the individual dyes to migrate during the process is significantly greater in the solvent system. Solvent-assisted dyeing also gives greater coverage of dye-affinity variations (barriness) compared to totally aqueous systems. On the flip side, solvent lowers the partition coefficient between the dye in fibre and dye in medium due to which dye becomes more soluble in medium and less dye is transferred to the fibre. The light fastness may also reduce as a result of retention of the solvent by the fibre.

In view of the above, the current study is undertaken to carry out solvent dyeing of polyester and wool using ratanjot extract and to analyze the effect of extraction and dyeing media on dyeing behavior.

2 Materials and Methods

Polyester fabric (126 ends/inch, 94 picks/inch, 85 gsm, supplied by JCT, Phagwara, India) and wool fabric (50 ends/inch, 56 picks/inch, 85 gsm, supplied by Madan Textiles, India) were used for the study.

The chemicals sodium hydrosulphite, sodium hydroxide, acetic acid (all from Thomas Baker), methanol, hexane (Merck), butanol (Qualigen) and standard soap (SDC, UK), all of AR grade were used. Distilled water was used for all dilutions and dyeings.

Glycerin bath beaker dyeing machine (HTHP, RBE Electronics) was used for dyeing. The machine consisted of a beaker carriage, which rotated in the glycerin bath at about 24 rpm through a suitable motor and gearbox. The direction of rotation changed after every 5 min.

Bark of the ratanjot roots were dried and ground finely into powder form. Sufficient quantity of this powder was weighed and mixed with extraction medium to give 1% w/v solution. For example, 1 g of dried ratanjot powder was mixed in 100 mL of extraction medium. The mixture was kept for 24 h for extraction at 27±2°C. Then this mixture was filtered using bleached cotton fabric and dye extract was used for dyeing. For the sake of convention, this extract was considered to be a stock dye fabric and dye extract was used for dyeing. For the sake of convention, this extract was considered to be a stock dye solution having a concentration of 1%. Homologous solvents with different polarities, i.e. methanol and butanol and more hydrophobic ones like hexane were used for dye extraction. The following aspects were considered for determining the extraction and dyeing media:

(i) Preliminary experiments revealed that there were many coloring components present in the dye and the overall color of the extract depended on the solvent used for extraction. Hence, different solvents were used to extract multiple coloring components. For example, reddish component was extracted in hexane and purplish component in butanol and methanol.

(ii) Solvent dyeing gives better results in terms of higher diffusion coefficient and better leveling results in poor buildup. Hence, solvent was used as a component in the dyeing medium along with water to increase the buildup.

(iii) Whenever solvent and water were not miscible, leveling is poor. Hence, only those combinations were used for dyeing where total miscibility of solvent components was present.

Therefore, following combinations of solvents were used as dyeing media:

1. Methanol and water (miscible)
2. Butanol, water and methanol (in specific concentrations)

and following combinations were not used:

(a) Butanol and water (not miscible)
(b) Hexane and water (not miscible)

Based on above considerations, the extraction and dyeing medium used for dyeing wool and polyester with ratanjot were decided and are given in Table 1.

<table>
<thead>
<tr>
<th>Code</th>
<th>Substrate</th>
<th>Medium of extraction</th>
<th>Medium of dyeing</th>
<th>pH</th>
<th>Temp., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>Polyester</td>
<td>Methanol</td>
<td>Water</td>
<td>4-5</td>
<td>130</td>
</tr>
<tr>
<td>P2</td>
<td>Polyester</td>
<td>Methanol</td>
<td>Methanol</td>
<td>4-5</td>
<td>130</td>
</tr>
<tr>
<td>P3</td>
<td>Polyester</td>
<td>Methanol</td>
<td>Butanol</td>
<td>4-5</td>
<td>130</td>
</tr>
<tr>
<td>P4</td>
<td>Polyester</td>
<td>Butanol, Methanol, Water</td>
<td>Methanol (20 mL) + water (60 mL)</td>
<td>4-5</td>
<td>130</td>
</tr>
<tr>
<td>P5</td>
<td>Polyester</td>
<td>Butanol</td>
<td>Methanol (20 mL) + water (60 mL)</td>
<td>4-5</td>
<td>130</td>
</tr>
<tr>
<td>P6</td>
<td>Polyester</td>
<td>Butanol</td>
<td>Methanol (20 mL) + water (60 mL)</td>
<td>Neutral</td>
<td>130</td>
</tr>
<tr>
<td>P7</td>
<td>Polyester</td>
<td>Hexane</td>
<td>Methanol</td>
<td>Neutral</td>
<td>130</td>
</tr>
<tr>
<td>W1</td>
<td>Wool</td>
<td>Methanol</td>
<td>Water</td>
<td>4-5</td>
<td>Boil</td>
</tr>
<tr>
<td>W2</td>
<td>Wool</td>
<td>Methanol</td>
<td>Water</td>
<td>Neutral</td>
<td>Boil</td>
</tr>
<tr>
<td>W3</td>
<td>Wool</td>
<td>Butanol, Methanol, Water</td>
<td>Methanol (20mL) + water (60 mL)</td>
<td>4-5</td>
<td>Boil</td>
</tr>
</tbody>
</table>
Fabric samples weighing 2 g were taken in each case and then dye and other additives were added. An MLR of 1:40 was used. Acetic acid of 2% strength was used to maintain pH at 4-5. The dyeing was carried out as per the dyeing profiles shown in Fig. 1. After completion of dyeing, samples were rinsed thoroughly in cold water. In each case 10 mL of dye extract was used to give a shade of 5% owf approximately, using the following relationship:

\[
\text{Amount of stock solution required (mL)} = \frac{w \times p}{c}
\]

where \(w\) is the sample weight; \(p\), the dye concentration (% owf); and \(c\), the stock solution concentration (1%).

In case of dyed polyester samples, reduction clearing was carried out to remove the surface dye. Dyed polyester samples were reduction cleared with 2 g/L sodium hydrosulphite and 2 g/L sodium hydroxide for 15 min at 60°C. Finally, wash fastness testing of all samples was carried out using ISO Test No. 2 on a launderometer (R B Electronics, Mumbai).

The buildup characteristics (rate of change of colour value or \(K/S\) of dyed substrate with change in dye conc.) were determined using dyebath concentration ranging from 0.5% owf to 15% owf. The corresponding amount of dye extracts used is 1, 2, 5, 10, 20 and 30 mL for dye concentrations of 0.5, 1, 2.5, 5, 10 and 15% owf respectively. Spectraflash 600 colorimeter (Datacolor International) was used for the measurement of colorimetric data of dyed samples.

### 3 Results and Discussion

#### 3.1 Colorimetric Data

Colorimetric and wash fastness data of polyester and wool dyed with ratanjot are shown in the Table 2. The depth of shade is maintained at 5% (owf) dye concentration. P1, P2 and P3 are for dyeings with dye extracted in the same medium i.e. methanol but dyed in different mediums and hence they are compared with each other. From the table it is evident that P1 has maximum dye uptake followed by P3 and then P2. This can be judged from corresponding \(l^*\), \(c^*\) and \(K/S\) values. P1 also has more red component (\(a^*\) value) followed by P3 and P2. Also the blue component (\(b^*\) values) in P1 is more than the rest of the two. P2 has small amount of yellow component (\(b^*\) values). In P1, water is used for dyeing and in P3 and P2 methanol and butanol are used respectively. The hydrophobicity of the solvents increases in the order: water < methanol < butanol. As the extraction medium is same in P1, P2 and P3, it can be assumed that the amount and type of colorant are same in all the dyebaths. However, the medium of dyeing is different in three cases. This has reflected in the dyeing, the most hydrophilic (water) giving the darkest and the most hydrophobic (butanol) giving the lightest depth of shade.

Sample P4 which was dyed with dye extracted from a mixture of butanol, methanol and water shows higher color content (\(l^*\), \(c^*\) and \(K/S\) values). Blue component in P4 is more than that in P1 but red component is less (\(a^*\) and \(b^*\) values).

Now comparison of P5 and P6 (both dyed with dye extracted in butanol) indicates that P5 is darker in shade as compared to P6 as evident from \(l^*\) and \(K/S\) values. The difference in shade can be attributed to the difference in dyeing \(pH\), as P5 is dyed at acidic \(pH\) and P6 at neutral. Red component is found to be higher in P5 and blue component is higher in P6 as indicated by \(a^*\) and \(b^*\) values. P7, dyed with dye extracted in hexane, has low color content (as indicated by the high value of \(l^*\) and low values of \(c^*\) and \(K/S\)).

On comparing wool samples W1 and W2 (both dyed in methanol extracted dye), it is quite clear that W1 is darker than W2 (\(l^*\) and \(K/S\) values). This can be attributed to difference in the dyeing \(pH\). It is proposed that the dye components responsible for color are sensitive to neutral \(pH\), hence producing poor color value at higher \(pH\) as compared to that at acidic \(pH\). Additionally, if the extract contains some

![Fig. 1 — Dyeing cycle used for (a) polyester (b) wool](image-url)
anionic colored components, they are likely to be absorbed to a greater extent at acidic pH than at neutral pH. Protonation of wool at acidic pH results in higher exhaustion of anionic color components due to electrostatic attraction between wool protein and anionic color. Red component in W2 is higher (a* values) as compared to that in W1. W2 is yellowish and W1 has light blue component (b* values). W3 (dyed with dye extracted in mixture of butanol, methanol and water) has more yellow and small amount of red component as evident from a* and b* values.

3.2 Buildup Characteristics

Buildup characteristics of ratanjot on polyester are shown in Fig. 2. For dyes with poor buildup properties, color value increases. It is evident from the figure that in case of polyester, dye buildup increases with increase in concentration of dye to a certain point after which it starts decreasing. The decrease in dye uptake after a certain point can be explained as follows. For dyeing, the dye extract in a solvent (not a pure dye powder) is being used. As the concentration of dye in dyebath increases, the amount of solvent in the dyebath also increases. With increase in solvent fraction in dyebath, the solubility of the dye in dyeing medium increases, lowering the partition coefficient in favor of dyebath. It can be observed that in P1 (extracted in methanol, aqueous dyeing medium), dye buildup is the highest, whereas it is the poorest in case of P2. This can be attributed to the fact that in case of P1 the dyebath used is hydrophilic which has less solubility for dye and hence more dye is transferred to the fibre and less is retained in dyebath. In case of P3 and P2, methanol and butanol are used respectively in dyeing medium. For P2, the dyebath has the highest hydrophobicity and hence the dye uptake is the poorest, as most of the dye tends to remain in dye bath.

Buildup characteristics of ratanjot on wool are shown in Fig. 3. It can be observed that W3 has the best buildup, W2 (methanol extracted dye, pH 7) has the poorest buildup and W1 (methanol extracted dye, pH 4-5) has intermediate buildup. This may be due to the extraction of other components (may be in lower percentage) also which are not extracted in methanol alone. These components may have high affinity for wool, which could have resulted in high buildup in case of W3. W2 has the lowest buildup which may be due to the decomposition of dye (acting as disperse dye) at nearly neutral conditions. The other possibility is that the dye extract may have certain water soluble anionic coloring components, which may be exhausted better in acidic medium.

3.3 Wash Fastness Properties

The wash fastness of wool and polyester dyed with ratanjot extracted from solvent media is given in Table 2. The wash fastness of dyed polyester is good to excellent. This is to be expected since ratanjot extracts behave as disperse dyes which show excellent wash fastness on polyester. However, wash fastness on wool is poorer than on polyester. The reason for poor wash fastness lies with the fact that the ratanjot extract components act as disperse dyes, which can form only weak hydrophobic interactions with wool fibre.
4 Conclusion

Solvent and solvent-assisted dyeing of polyester and wool using ratanjot-extracted dye gives good results in terms of color and leveling. However, dye uptake is higher when water is also used as dyeing medium. Ratanjot extracted dye has more than one coloring components, which can be extracted in different solvents. This is evident in different shades of dyeings obtained with change in solvent for extraction medium. Good results are produced in terms of wash fastness on dyed polyester. Even darker shades are produced on wool but with poor wash fastness.

<table>
<thead>
<tr>
<th>Code</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>c*</th>
<th>h</th>
<th>K/S</th>
<th>Colour</th>
<th>Wash fastness (Change in colour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>43.4</td>
<td>8.9</td>
<td>-9.05</td>
<td>12.69</td>
<td>314.5</td>
<td>1.68</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>P2</td>
<td>84.9</td>
<td>1.01</td>
<td>0.39</td>
<td>1.08</td>
<td>21.13</td>
<td>0.09</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>P3</td>
<td>76.6</td>
<td>2.26</td>
<td>-0.94</td>
<td>2.45</td>
<td>337.41</td>
<td>0.22</td>
<td></td>
<td>4-5</td>
</tr>
<tr>
<td>P4</td>
<td>56.7</td>
<td>6.49</td>
<td>-10.01</td>
<td>11.93</td>
<td>302.96</td>
<td>0.64</td>
<td></td>
<td>3-4</td>
</tr>
<tr>
<td>P5</td>
<td>59.2</td>
<td>5.25</td>
<td>-9.31</td>
<td>10.69</td>
<td>299.42</td>
<td>0.56</td>
<td></td>
<td>3-4</td>
</tr>
<tr>
<td>P6</td>
<td>59.8</td>
<td>2.71</td>
<td>-13.01</td>
<td>13.29</td>
<td>281.75</td>
<td>0.41</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>P7</td>
<td>71.7</td>
<td>2.98</td>
<td>-6.14</td>
<td>6.83</td>
<td>295.83</td>
<td>0.23</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>W1</td>
<td>35.7</td>
<td>6.26</td>
<td>-0.09</td>
<td>6.26</td>
<td>359.19</td>
<td>1.94</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>W2</td>
<td>36.5</td>
<td>7.79</td>
<td>2.32</td>
<td>8.13</td>
<td>16.6</td>
<td>1.79</td>
<td></td>
<td>2-3</td>
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<tr>
<td>W3</td>
<td>48.0</td>
<td>0.73</td>
<td>2.02</td>
<td>2.15</td>
<td>70.06</td>
<td>2.95</td>
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References