Effectiveness of sal, Shorea robusta Gaertn. f. bark dye on mordanted silk

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The effectiveness of sal (Shorea robusta Gaertn. f.) bark dye on silk fabric treated with four different mordants was studied. Four types of mordants, viz. alum, CuSO₄, Al₂(SO₄)₃ and citric acid were used, each at 1, 2 and 3% of weight of fabric (o.w.f.) and with material liquor ratio (MLR) of 1:40. The variations in colour and intensities were analysed with the help of Hunterlab colour scale. It was observed that the maximum change in colour with respect to undyed silk fabrics was for 3% CuSO₄ mordant treated samples with the ∆E* value of 48.52±0.14. However, the values were not significantly different from samples treated with CuSO₄ at 2% level. The change in chroma (∆C*) was also maximum for the 3% CuSO₄ mordant (37.41±0.40). The colour fastness analysis with respect to washing, rubbing and sunlight also indicated that all mordants and concentrations used in the study excepting 1% alum offered adequate fastness characteristics. Unmordanted samples had moderate fastness. In view of the colour fastness with respect to washing, rubbing and exposure to light, the sal dye can be applied with any of the selected mordants at 3% level.

Keywords: Mordanting, Wash fastness, Rubbing fastness, Colour scale, Alum, Copper sulphate, Aluminium sulphate, Citric acid.

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Introduction

Natural dyes offer a wide range of shades and can be obtained from various parts of plants, animals/creatures, sediments, microorganisms, etc. The roots, bark, leaves, flowers, fruits are the different plant parts that can be used for preparation of dyes. Since the advent of widely available and cheaper synthetic dyes in 1856 having moderate to excellent colour fastness properties, the use of natural dyes having poor to moderate wash and light fastness has declined to a great extent. However, recently there has been revival of the interest in the application of natural dyes on natural fibers due to worldwide environmental consciousness¹². India is still a major producer of most natural dyed textiles. Recently, a number of commercial dyers and small textile export houses have started looking at the possibilities of using natural dyes for regular basis dyeing and printing of textiles.

India has rich biodiversity and there are more than 450 plants yielding dyes and pigments. Sal (Shorea robusta Gaertn. f.) is one such plant, the bark of which can be used as a natural dye. The plant is widely available in the natural ecosystem of India and other countries and hence the raw material should not be a problem. The plant has a good potentiality for development of dye³. However, for successful commercial use of natural dyes, the appropriate and standardized dyeing techniques need to be adopted without deteriorating the quality of dyed textiles materials. Therefore, to obtain newer shades with acceptable colour fastness behaviour and reproducible colour yield, appropriate scientific techniques need to be derived from scientific studies on dyeing methods, dyeing process variable, dyeing kinetics and compatibility of selective natural dyes⁴.

Natural dyes are mostly non-substantive and must be applied on textiles by the help of mordants, usually a metallic salt, having an affinity for both the colouring matter and the fibre. Different types and selective mordants or their combination can be applied on the textile fabrics to obtain varying colour or shade, to increase the dye uptake and improve the colour fastness behaviour of any natural dye⁵. Therefore the present study was planned to check the colour intensities of sal bark dye on silk with the help of four mordants at three levels of concentrations and to study the colour fastness, wash fastness and rub fastness so as to standardize the type of mordant and concentration thereof.

Textile materials and garment are susceptible to microbial attack, as these provide large surface area
and absorb moisture required for microbial growth\textsuperscript{5}. Natural fibres have protein (keratin) and cellulose, etc., which provide basic requirements such as moisture, oxygen, nutrients and temperature for bacterial growth and multiplication. This often results in objectionable odour, dermal infection, product deterioration, allergic responses and often related diseases. Fortunately most of the plants used for dye extraction are also classified as medicinal and some of these have recently been shown to exhibit antimicrobial activity\textsuperscript{6}. As the sal plant also has many medicinal properties, the dye obtained from the sal bark might also have some antimicrobial effect, which can prove beneficial for the textile manufacturer and users. Therefore, the sensitivity of the sal bark dye for four different strains of bacteria and two fungi were also studied.

\textbf{Materials and Methods}

\textbf{Extraction of dye}

The barks of sal trees were collected from the natural ecosystem of Daringbadi in Kandhamal district of Odisha in the month of November. The barks were then cleaned and dried under shade till it reached the equilibrium moisture content, which ranged between 9.17 and 11.60 \% (on dry weight basis) in the prevailing climatic conditions. The barks were then chopped into tiny pieces manually and then ground into the form of fine powder (200 mesh). Higher temperature during pulverization process might influence the colour fastness and antimicrobial properties of the dye. Hence, the pulverization was done in a hammer mill so that the temperature of the powder could be restricted to remain below 50\(^\circ\)C.

The powdered dye was taken in water (@ 1:10 w/w basis, i.e.100 g powder in 1 lt water) and was boiled under pressure for 1 h. Boiling caused some loss of water and hence, the final water content was adjusted to make it a 10\% stock solution. The liquid was strained (by filter paper Whatman No. 4) and kept in a refrigerator for further use. Plate 1 shows the different stages of the preparation of dye from the bark. The dye solution was subjected to light of wavelength 300-700 nm using UV visible spectrophotometer (Perkin-Elmer) and the \(\lambda_{\text{max}}\) was found out to be 390 nm.

\textbf{Collection and degumming of silk sample}

It is required to degum the silk before dyeing because the natural gum sericin present in the silk reduces dye absorption as well as the luster of the fibre. Thus, white mulberry silk fabric was taken and degummed in a solution prepared by dissolving 5 gpl (g/lt) neutral soap and 1\% (w/w) sodium carbonate in water with material liquor ratio (MLR) of 1:40. The temperature of the bath was gradually raised from room temperature to 90\(^\circ\)C and the process was continued for one hour. After removing the silk from degumming bath, it was squeezed to remove the excess liquid and thereafter rinsed under running water to remove the residues of detergent and other chemicals. Subsequent drying was carried out under shade.

\textbf{Mordanting}

Four common mordants, viz. alum (K\(_2\)SO\(_4\), Al\(_2\)(SO\(_4\))\(_3\), 24H\(_2\)O), copper sulphate (CuSO\(_4\)), aluminum sulphate (Al\(_2\)(SO\(_4\))\(_3\)) and citric acid (C\(_6\)H\(_8\)O\(_7\)), were used for the study. These mordants (chemicals) basically serve as cross linking agents.

Pre-mordanting of the fabrics have been preferred to post mordanting and simultaneous mordanting because of higher effectiveness\textsuperscript{1}, and hence, the same was adopted in the present study. The quantities of mordants were taken at three levels, viz. 1, 2 and 3\% of the weight of the fabric (o.w.f.). Known quantity of mordant was added to distilled water to get the MLR of 1:40 and was dissolved completely. Degummed silk fabric was put into mordant bath at normal temperature. The temperature was then raised to 90\(^\circ\)C for 30 minutes. The mordant solution was allowed to cool and the sample was dried in the laboratory by normal air circulation\textsuperscript{7}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image}
\caption{Plate 1—Stages in the preparation of dye from sal bark}
\end{figure}
Dyeing silk fabric

Open dye beaker baths with 1:40 MLR were used for dyeing the silk fabric. The temperature and time of soaking were maintained at 90°C and 1 h, respectively. The dyed samples were then spread and cooled naturally up to 50°C. It was followed by washing the test fabrics under running water to remove the unfixed dye particles, un-reacted mordants and any extra deposits from the surface. Then soaping by non-ionic detergent (NID) for 10 minutes was carried out to remove remaining particles and other chemical reagents. The samples were dried in the laboratory at room temperature under forced convection.

Measurement of colour variations and intensity

The colour intensities and variations were analysed with the HunterLab colorimeter with the CIE L*a*b* colour scale. The maximum for L* is 100, which represents a lightness of a perfect reflecting diffuser. The minimum for L* is zero which represents black. Positive ‘a*’ values indicate amounts of red, negative ‘a*’ values indicate amounts of green. Positive ‘b*’ corresponds to yellowness and negative ‘b*’ corresponds to blueness. The average colour values for the samples were recorded and the total colour difference $\Delta E*$ was calculated, which was a single value that takes into account the differences between the L*, a* and b* of the dyed sample and the control sample (undyed silk).

$$\Delta E* = \sqrt{\Delta L^*2 + \Delta a^*2 + \Delta b^*2} \tag{1}$$

The change in chroma value was also calculated as follows:

$$\Delta C* = \sqrt{\Delta a^*2 + \Delta b^*2} \tag{2}$$

Five replications were taken for all individual parameters and the statistical analysis was conducted with SAS 9.3 to find out the individual effects of type of mordant and concentration and the interaction effects.

Colour fastness tests

The colour fastness of dyed samples have been earlier studied by standard test procedures recommended by the Bureau of Indian Standards. The dyed fabric samples were tested for colour fastness for washing, rubbing and exposure to sunlight. Bleeding of colour occurs during laundering if dyes are held loosely by the fibre, i.e. dyes that have not penetrated the fibre sufficiently, or dyes which are held only by forces such as hydrogen bond or Vander Waal’s forces. Similarly the rubbing fastness indicates if some dye molecules are superficially held on the fabric. Such dye molecules need to be removed by appropriate post-treatments.

Standard procedures are available for testing the colour fastness under different conditions. Colour fastness to washing Test -1 (IS 687:1979) determines the effect of washing on the colour fastness of the textiles, and the same was adopted for the study. The reagent used was neutral soap (05 g/L). The test specimen of 10 cm X 4 cm was placed in between the two adjacent, undyed test cloth pieces (cotton and silk) and stitched along all four sides to form a composite specimen. Each composite specimen was placed in the container separately and necessary amount of soap solution was added to give a MLR of 1:50, which was preheated (40±2°C). The composite samples were agitated for 30 min in launderometer (digiWash ST™) with (40±2) rev/min. Then the samples were removed and rinsed in cold water. The stitches were ripped out along the two long sides and one short side. The composite specimen was opened and dried in air at room temperature. The change in colour of the treated test specimen and the degree of staining of the two pieces of adjacent fabrics was evaluated with the help of SDC Grey scale (Make: Paramount, ISO 105 A02 1993 BS EN 20105-A02 1995) and the rating was assigned from 1 (very poor) to 5 (excellent).

Colour fastness to washing Test-2 was done as per IS 3361:1979. The method was same as above except that the temperature maintained was 50±2°C and the time was 45 min. Neutral soap (05 g/L) was used as the reagent.

Colour fastness to sunlight was tested as per IS 686:1985. The test specimen (1cm X 6 cm) was placed along with the standard blue wool patterns, with scores 1 to 8. The score 1 denotes very poor light fastness and 8 is outstanding. One third portion of the test specimen and blue wool standards were covered with the help of opaque card sheet, and exposed to day light by mounting on the exposure rack. The rack kept at an angle of 45° facing south under direct sunlight from 9 am to 4 pm for 4 days. The fastness was assessed by comparing the fading of the specimen with that of blue wool patterns.
Colour fastness to rubbing/crocking was tested as per IS 766:1998, which was based on ISO 105/X-1984. Two test specimen from each fabric sample was used, one each for dry and wet tests. For the dry crocking test, two test specimen were placed on the base of the crock meter (Make: Paramount) so that they rested flat on the abrasive cloth with their long dimension in the direction of rubbing. A dry undyed test cloth (cotton) of size 5 cm X 5 cm was mounted over the end of the finger which projected downward from the weighed sliding arm. A spherical spiral wire clip was used to hold the test cloth in place. The finger was kept to cover the test specimen and it was crocked back and forth 20 times by making 10 complete turns. The undyed test cloth was removed and tested.

For the wet crocking test, the undyed (white colour) test cloth was thoroughly wetted in distilled water and then squeezed. Thereafter it was mounted on the finger. The remaining procedure was same as that of dry crocking test. To assess the colour change and the staining for both the above, SDC grey scale was used.

Antimicrobial activity

The extracted dye solution was put to agar test with four strains of bacteria, viz. Escherichia coli, Streptococcus sp., Staphylococcus luteus and Salmonella sp., and two stains of fungi, viz. Aspergillus niger and Salmonella sp., and two stains of fungi, viz. Staphylococcus aureus, and two stains of fungi, viz. Aspergillus niger and Candida albicans as per Kirby-Bauer disk diffusion susceptibility test. The bacterial isolates, earlier stored in frozen condition, were revived in nutrient agar broth and 24 h fresh culture was used. Muller Hinton Hi Veg™ agar plate was prepared. A sterilized cotton swab was dipped into the bacterial suspension and used to evenly inoculate the entire surface of Muller Hinton agar plate. After the agar surface was dried for about 5 min, the appropriate test discs were placed on it, with sterilized forceps. The plate was immediately incubated at 37°C for 24 h (for bacteria). For fungi the incubation temperature was 28-30°C for 24-48 h. After incubation period, the diameters of the zones of inhibition were measured to nearest mm. Kirby-Bauer test results were interpreted using a table that relates zones diameter to degree of microbial resistance.

It was also considered necessary to know the extent of retention of antimicrobial property on the fabric surface after dyeing with the different dyes. The fabric was shredded into very minute pieces and put in the agar solution. The procedure was repeated as above.

Results and Discussion

Variation in colour and intensity

The different shades obtained on the silk samples after treating them with four different mordants, viz. alum (K2SO4, Al2(SO4)3, 24H2O), copper sulphate (CuSO4), aluminium sulphate (Al2(SO4)3) and citric acid (C6H8O7), at three different concentrations, viz. 1, 2 and 3% o.w.f. and then subsequently coloured with the dye obtained from the sal bark were compared. It was observed that there was extensive variation in the colour depending on the type of mordant and its concentration (Plate 2).

The effect of the mordants and their level of concentrations on the changes in colour (ΔE*), chroma value (ΔC*) and lightness/darkness (ΔL*) obtained for the dyed cloth are shown in Fig. 1. The mean colour parameters of undyed silk were observed to be L*: 88.27±0.84, a*: 2.46±0.14 and b*: -2.19±0.44. The positive values of ΔL* (L*dyed fabric−L*undyed fabric) indicate that the fabric became darker after the treatment.

The statistical analysis of the effects indicated that both treatments and their levels caused significant differences in the colour. Considering the individual effects of type of mordant on the ΔE*, it was observed that the CuSO4 exhibited highest ΔE* values, followed by the Al2(SO4)3, alum and citric acid and the effects were significantly different from each other. Similarly the 3% o.w.f. gave the maximum ΔE* values. The change in chroma values were also affected in a similar manner by the individual effects of mordants and their level of concentrations. CuSO4 gave the maximum darkness among all types of mordants. However, considering the level of concentrations, it was observed that for sal dye, the unmordanted samples imparted the maximum darkness to the final product, and there was no significant difference between the individual effects of 1-3% o.w.f. mordant.

Considering the interaction effects of type of mordant and concentration thereof, the maximum ΔE* value (48.52±0.14) was observed for 3% CuSO4 mordant treated samples. However, the values were not significantly different from samples treated with CuSO4 at 2% o.w.f. The ΔC* values were maximum for the 3% CuSO4 mordant (37.41±0.40), though the ΔC* values offered by 3% Al2(SO4)3 was not significantly different than the above. The observations on the darkness of samples indicate that CuSO4 mordant at 3% o.w.f. gave the maximum darkness (ΔL* value 30.89±0.70), though the effect was not
significantly different from the effects of CuSO₄ mordant at 1 and 2% o.w.f..

Colour fastness test of dyed fabrics

Table 1 gives the effect of washing, rubbing and exposure to sunlight on colour fastness of Sal bark dyed samples. As expected, the mordanted specimen exhibited better colour fastness compared to samples on which no mordant was applied.

*Colour fastness to washing (Test 1):* All the mordants and concentrations excepting 1% alum offered good to excellent (4-5) colour fastness, whereas samples
without mordant and 1% alum treated samples had good colour fastness (4). All specimens including unmordanted samples exhibited excellent colour fastness staining on undyed cotton. Staining on undyed silk fabric also had excellent colour fastness except samples without application of mordant.

**Colour fastness to washing (Test 2)**: The colour change for all specimens varied from good (4) and good to excellent (4-5) except specimens without mordant, which exhibited fair (3) colour fastness. Staining on undyed cotton samples attained excellent colour fastness including unmordanted samples. Staining on undyed silk samples showed excellent colour fastness for all three mordants. The samples dyed with citric acid mordant had good to excellent fastness. Unmordanted samples showed good fastness.

**Colour fastness to crocking**: All the dyed specimens with mordants had excellent (5) and good to excellent (4-5) fastness to both dry and wet crocking except unmordanted samples, which had good (4) colour fastness.

**Colour fastness to sunlight**: The samples dyed with alum, aluminum sulphate and citric acid mordants exhibited fairly good (4) fastness, whereas those dyed with copper sulphate exhibited good (5) fastness when exposed to day light. Unmordanted samples had moderate fastness.

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### Table 1—Colour fastness of silk samples dyed with sal bark

<table>
<thead>
<tr>
<th>Name of Mordant</th>
<th>Mordant concentration (o.w.f.)</th>
<th>Light fastness</th>
<th>Colour fastness to washing (Test 1)</th>
<th>Colour fastness to washing (Test 2)</th>
<th>Rubbing fastness Test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Change in colour</td>
<td>Stain on cotton</td>
<td>Stain on silk</td>
<td>Change in colour</td>
</tr>
<tr>
<td>No mordant</td>
<td></td>
<td>3</td>
<td>4 5</td>
<td>4/5</td>
<td>3 5</td>
</tr>
<tr>
<td>Alum</td>
<td>1%</td>
<td>4</td>
<td>4 5</td>
<td>5 5</td>
<td>4 5</td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>4</td>
<td>4/5</td>
<td>5 5</td>
<td>4 5</td>
</tr>
<tr>
<td></td>
<td>3%</td>
<td>4</td>
<td>4/5</td>
<td>5 5</td>
<td>4/5</td>
</tr>
<tr>
<td>CuSO₄</td>
<td>1%</td>
<td>5</td>
<td>4/5</td>
<td>5 5</td>
<td>4/5</td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>5</td>
<td>4/5</td>
<td>5 5</td>
<td>4/5</td>
</tr>
<tr>
<td></td>
<td>3%</td>
<td>5</td>
<td>4/5</td>
<td>5 5</td>
<td>4/5</td>
</tr>
<tr>
<td>Al₂(SO₄)₃</td>
<td>1%</td>
<td>4</td>
<td>4/5</td>
<td>5 5</td>
<td>4 5</td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>4</td>
<td>4/5</td>
<td>5 5</td>
<td>4 5</td>
</tr>
<tr>
<td></td>
<td>3%</td>
<td>4</td>
<td>4/5</td>
<td>5 5</td>
<td>4 5</td>
</tr>
<tr>
<td>Citric acid</td>
<td>1%</td>
<td>4</td>
<td>4/5</td>
<td>5 5</td>
<td>4 5</td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>4</td>
<td>4/5</td>
<td>5 5</td>
<td>4 5</td>
</tr>
</tbody>
</table>

Scores for washing fastness test: 5-Excellent; 4-Good; 3- Fair; 2-Poor; 1-Very poor. Scores for staining: 1-Much change; 2-Considerable change; 3-Noticeable change; 4-Slight change and 5-Negligible change. Score for light fastness test: 1- Very poor; 2- Poor; 3- Moderate; 4- Fairly good; 5- Good; 6- Very good; 7- Excellent; 8- Outstanding. Parameters for colour fastness to washing (Test 1): Temperature 40±2°C, agitation time 30 min with (40±2) rev/min.

Parameters for colour fastness to washing (Test 2): Temperature 50±2°C, agitation time 45 min with (40±2) rev/min.
with alum, \(\text{Al}_2\text{O}_3\) had good colour fastness. Further, the samples dyed exhibited fairly good fastness, whereas those dyed with \(\text{CuSO}_4\) exhibited good fastness when exposed to day light. Unmordanted samples had moderate fastness. In view of the colour fastness, viz. fastness for washing, rubbing and exposure to light, the sal bark dye should be applied with any of the selected mordants at 3% level. The sal dye has some antimicrobial properties. However, further investigations are required to quantify the effects and to see the durability of the effect.

Acknowledgements
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References

Thus, in view of the above, viz. fastness for washing, rubbing and exposure to light, the Sal dye can be applied with any of the selected mordants at 3% level.

Antimicrobial property
The results of the agar test for the sal dye is given in Table 2. It was observed that the sal dye was sensitive to all the species of bacteria under study, however, the two fungi tested were resistant. Saravanan et al. have also observed restricted sensitivity for different strains of bacteria on the fabric treated with \(\text{Odina wodier}\) L. bark dye. Earlier studies have indicated that the method of extraction also plays important role on the antimicrobial effect and hence the antimicrobial properties of sal dye need further investigation.

<table>
<thead>
<tr>
<th>Type of isolates</th>
<th>Zone size (mm)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bacterial isolates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Escherichia coli</td>
<td>13</td>
<td>S</td>
</tr>
<tr>
<td>Staphylococcus luteus</td>
<td>15</td>
<td>S</td>
</tr>
<tr>
<td>Streptococcus sp.</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Salmonella sp.</td>
<td>16</td>
<td>S</td>
</tr>
<tr>
<td>Fungal isolates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aspergillus nigerican</td>
<td>0</td>
<td>R</td>
</tr>
<tr>
<td>Candida albicans</td>
<td>0</td>
<td>R</td>
</tr>
</tbody>
</table>

S: Sensitive, R: Resistant

Table 2—Antimicrobial profile of bacterial isolates for sal dye

Conclusion
All the mordants and concentrations thereof were found to significantly affect the colour intensity, variations and fastness properties of silk coloured with sal bark dye. The maximum change in colour was observed for 3% \(\text{CuSO}_4\) mordant treated samples. However, the values were not significantly different from samples treated with \(\text{CuSO}_4\) at 2% level. The chroma values were maximum for the 3% \(\text{CuSO}_4\) mordant followed by 3% \(\text{Al}_2(\text{SO}_4)_3\). All the mordants and concentrations excepting 1% alum offered good to excellent colour fastness, whereas samples without mordant and 1% alum treated samples had good colour fastness. Staining on undyed silk fabric also had excellent colour fastness except unmordanted samples. All the dyed specimen with mordants had excellent and good to excellent fastness to both dry and wet crocking except unmordanted samples, which had good colour fastness. Further, the samples dyed with alum, \(\text{Al}_2(\text{SO}_4)_3\) and citric acid mordants...