Kinetic and adsorption studies of Indian siris (Albizia lebbeck) natural dye on silk

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Spectral techniques have been used to identify and characterize the color constituent of the bark of Albizia lebbeck. The dyeing potential and color fastness properties of the extract have been evaluated on silk yarn. Pre-mordanting of the dye is found to be better than post-mordanting, particularly with alum which gives higher color strength values. The color co-ordinates of dyed samples lie in the yellow-red quadrant of color space diagram. The kinetic and adsorption studies on the dye uptake by silk yarn have also been carried out. The positive standard affinity indicates a spontaneous adsorption. During the dyeing process the enthalpy change is positive, indicating an endothermic process with large negative entropy change. This implies an uniform ordered distribution of dye on silk. The adsorption of the dye fits in to the Langmuir model of isotherm having high regression coefficient. These findings indicate that the color extract of the bark of Albizia lebbeck serves as a potential natural dye for silk fabrics.

Keywords: Adsorption Albizia lebbeck, Silk, Kinetic study

1 Introduction

Manufacturing of synthetic dyes largely depends on petrochemical sources and some of these used in dyeing industries are toxic, resulting in environmental pollution. Natural dyes derived from plant sources on the other hand are non-toxic, ecofriendly and biodegradable. These dyes from natural sources if judiciously used do not pose effluent problems. For these reasons, the research investigation carried out throughout the world has steadily increased to identify, isolate and extract natural colorants and use them for dyeing textile fibres. Our interest in the identification of the dye from plant sources has shown that a species, namely Albizia lebbeck (Indian siris) belonging to the family Fabaceae, and found in India, Bangladesh and Sri Lanka, contains a color component which can be exploited in dyeing silk fibre. Large quantities of bark of this tree generated in the timber industry hitherto are discarded. The bark is shown to contain antiprotozoal, hypoglycemic and anticancer properties. The use of the bark of A. lebbeck as a potential source of dye is interesting and hence, the present work was undertaken to identify, extract, and isolate the major coloring component of the bark and study the kinetics of adsorption of the dye on silk. The colour values and fastness properties of the dye have also been investigated.

2 Materials and Methods

2.1 Materials

The bark of A. lebbeck collected from timbering industry in Bangalore, India was washed, dried and ground well to a finely powdered form. Raw silk yarn of 40 denier was scoured prior to use by treatment with an aqueous solution of 2 g dm⁻³ non-ionic detergent and 1 g dm⁻³ sodium carbonate at 85 °C for 1 h. The scoured yarn was rinsed well with tap water and dried in air. Open bath beaker type dyeing machine equipped with programmable temperature control was used to carry out dyeing studies. All chemicals used were of AR grade.

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2.2 Methods

2.2.1 Extraction of Color Component

Air dried powdered sample (450 g) of A. lebbeck bark was subjected to soxhlet extraction using 80:20 methanol: water solvent. The procedure was repeated till the complete extraction. The methanol was then removed using rotary evaporator under reduced pressure at 50 °C to obtain an aqueous extract. The aqueous extract was partitioned between chloroform and ethyl acetate. The ethyl acetate fraction was subjected to column chromatography using silica gel (60-120 mesh) as an adsorbent, and EtOAc:MeOH:H2O (70:25:5) as solvent. The separated two fractions were confirmed by thin layer chromatography. The first fraction was used for further studies.

2.2.2 Absorbance and Color Strength Measurements

Dye solutions (1-5 %) were prepared from the crude methanol extract by maintaining material-to-liquor (M:L) ratio at 1:20. The absorbance of the dye solution was recorded before and after dyeing process with UV-Visible spectrophotometer. The per cent dye uptake was calculated using the following relationship:

\[
\text{% Dye uptake} = \frac{\text{Absorbance before dyeing} - \text{Absorbance after dyeing}}{\text{Absorbance before dyeing}} \times 100
\]

... (1)

The reflectance and the corresponding CIE L*, a*, b* C h data for the dyed samples were measured in a Gretag Macbath Color Eye 7000A spectrophotometer interfaced to a PC under illuminant D65, using a 10° standard observer with including UV component and excluding specular component. Colour strength (K/S) was calculated from the reflectance values using the following Kubelka-Munk equation:

\[
K / S = \frac{(1-R)^2}{2R}
\]

... (2)

where R is the reflectance; K, the absorption coefficient; and S, the light scattering coefficient.

2.2.3 Mordanting Technique

Pre-mordanting and post-mordanting techniques were carried out at 70 °C for 30 min using 2, 4 and 6 % solutions of tannic acid and alum [Al2(NH3)3(SO4)2×12H2O] as mordants separately at 1:20 M:L ratio. The silk was then rinsed and dried.

2.2.4 Dyeing Experiment

The silk yarn was dyed at pH 4 in a bath containing 5% of the Methanol: water extract (1:20). The dyeing process was started initially at 40 °C and the temperature was then gradually raised to 85 °C within 20 min and maintained constant up to 45 min. After dyeing, fabrics were taken out, rinsed in tap water, soaped at 60 °C for 15 min, again rinsed thoroughly with tap water and dried. For post-mordant samples, soaping was done after mordanting.

2.2.5 Fastness Properties

Dyed samples were subjected to wash fastness test as per ISO 105-C10-A(1):2006 method and crock fastness was assessed using a crockmeter as per AATCC test method 8-1996. Fastness to light was evaluated as per AATCC test method 16-2004 option 5 with 20 AFU exposure.

2.2.6 Spectral Analysis

IR spectral investigation of the compound was done on a Perkin-Elmer 298 grating IR Spectrophotometer. The UV/Visible absorption spectrum was recorded on a Shimadzu UV 1700 UV/Visible spectrophotometer. The NMR spectrum of the sample was recorded on Spect 400 NMR spectrophotometer. The mass spectral analysis was done using an Esquire-3000 plus spectrophotometer.

3 Results and Discussion

3.1 Spectral Studies of Isolated Color Compound

Mass spectrum (m/z) in positive mode shows peaks at 611 amu (M+1)+, 465 amu (M-Rha)+ and 303 amu (M-Rha-Glu)+. These fragments are characteristic of aglycone residues after loss of their rhamnosyl and rhamnoglucosyl moieties respectively. The IR spectrum shows hydroxyl (3390 cm⁻¹), ester (1705, 1220 cm⁻¹), conjugated carbonyl (1656 cm⁻¹) and aromatic (1602, 1502 cm⁻¹) absorption bands.

\[^1\text{H}-\text{NMR}\] (chemical shift δ in ppm, coupling constant J in Hz, DMSO-d₆) spectrum shows peaks at 12.6 (1H, s, C5-OH), 10.8 (1H, s, C7-OH), 9.65 (1H, s, C4'-OH), 9.15 (1H, s, C3'-OH), 7.54 (1H, d, J = 2.2, C6'-H), 7.51 (1H, s, C2'-H), 6.81 (1H, d, J = 16.8, C5'-H), 6.39 (1H, d, J = 2.0, C8-H), 6.19 (1H, s, J = 4.36, C6-H), 5.34 (1H, d, J = 7.44, C1G-H), 5.26 (1H, d, J = 3.84), 5.09 (1H, d, J = 3.44), 5.05 (1H, d, J = 5.76), 4.51 (1H, d, J = 5.24), 4.37 (1H, d, J = 1.2), 4.32 (1H, d, J = 4.08), 3.82 (1H, d, J = 10.8, C2G-H) and 0.98 (3H, d, J = 6.16, CH₃-R).
\(^{13}\)C-NMR (chemical shift \(\delta\) in ppm, DMSO-\(d_6\)) spectrum shows peaks at 177.3 (C-4), 163.9 (C-7), 161.5 (C-5), 156.5 (C-2), 156.3 (C-9), 148.3 (C-3', 144.6 (C-4'), 133.2 (C-3), 121.5 (C-6'), 121.1 (C-1'), 116.2 (C-2'), 115.1 (C-5'), 103.9 (C-10), 101.1 (C-1-R), 100.6 (C1-G), 98.5 (C-6), 93.4 (C-8), 76.4 (C5-G), 75.8 (C3-G), 74.0 (C2-G), 71.8 (C4-R), 70.5 (C2-R), 70.3 (C3-R), 69.9 (C4-G), 68.1 (C5-R), 66.9 (C6-G) and 17.6 (C6-R).

Above spectral analyses results confirm the structure of rutin (Fig. 1), a flavonoid glycoside \(^{14-17}\) having a color index number of 75730.

### 3.2 Effect of Dye Concentration and Color Strength on Dyeing

Within the range of dye concentration studied (1-5%), the maximum uptake was observed at 5% of the dye concentration (Table 1). Further, \(K/S\) values also increase with the increase in dye concentration (Table 1), indicating deeper shades observed at higher concentrations. The maximum dye concentration of 5% was therefore taken for the further dyeing process.

### 3.3 Effect of Mordanting on Dyeing

\(K/S\) values of the samples dyed with mordanting are found to be higher compared to that observed without mordanting. Pre-mordanting using alum is found to be better. Table 2 shows the \(K/S\) values and fastness properties of pre-mordanted, post-mordanted and un-mordanted samples. Alum mordanted samples result in deeper shades and fastness ratings with reference to tannic acid in both the cases. Table 2 also gives the color co-ordinates which are all positive and hence the dyed samples lie in yellow-red quadrant of the color space diagram. The color values and the fastness properties obtained suggest that the bark can be effective as a new source of natural dye on silk.

### 3.4 Effect of \(pH\) on Dye Extract

The visible spectra of the dye extract of \(A.\ lebbeck\) bark were measured at \(pH\) 4, 7 and 9. The spectra (Fig. 2) show the same \(\lambda_{max}\) of 552 nm at different \(pH\) studied. However, the absorbance value of the dye increases with the increase in \(pH\), which may be attributed to increased solubility of phenolic groups at alkaline \(pH\).

### Table 2—Absorbance of different dye concentrations of \(A.\ lebbeck\) bark extract

<table>
<thead>
<tr>
<th>Dye conc.</th>
<th>Absorbance</th>
<th>Dye uptake</th>
<th>(K/S) value</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>Before dyeing</td>
<td>After dyeing</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.26</td>
<td>0.18</td>
<td>30.7</td>
</tr>
<tr>
<td>2</td>
<td>0.41</td>
<td>0.28</td>
<td>31.7</td>
</tr>
<tr>
<td>3</td>
<td>0.59</td>
<td>0.39</td>
<td>33.8</td>
</tr>
<tr>
<td>4</td>
<td>0.73</td>
<td>0.46</td>
<td>36.9</td>
</tr>
<tr>
<td>5</td>
<td>0.92</td>
<td>0.52</td>
<td>39.1</td>
</tr>
</tbody>
</table>

### Table 2—Color co-ordinates, color strengths and fastness properties of silk samples dyed with color component of \(A.\ lebbeck\)

<table>
<thead>
<tr>
<th>Method</th>
<th>Mordant</th>
<th>(K/S)</th>
<th>(L^*)</th>
<th>(a^*)</th>
<th>(b^*)</th>
<th>(C)</th>
<th>(h)</th>
<th>Light fastness</th>
<th>Crocking fastness</th>
<th>Wash fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-mordanting</td>
<td>Alum</td>
<td>4.10</td>
<td>72.0</td>
<td>5.23</td>
<td>10.9</td>
<td>12.1</td>
<td>64.6</td>
<td>2-3</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.24</td>
<td>71.3</td>
<td>5.35</td>
<td>11.5</td>
<td>12.7</td>
<td>65.1</td>
<td>2-3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.27</td>
<td>70.6</td>
<td>5.73</td>
<td>11.9</td>
<td>13.2</td>
<td>64.3</td>
<td>3</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td></td>
<td>Tannic acid</td>
<td>3.99</td>
<td>73.2</td>
<td>8.75</td>
<td>10.2</td>
<td>13.4</td>
<td>48.9</td>
<td>2-3</td>
<td>3-4</td>
<td>4-5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.05</td>
<td>73.3</td>
<td>8.83</td>
<td>10.1</td>
<td>13.4</td>
<td>49.5</td>
<td>2-3</td>
<td>4</td>
<td>4</td>
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<tr>
<td></td>
<td></td>
<td>4.27</td>
<td>70.7</td>
<td>9.57</td>
<td>11.7</td>
<td>15.1</td>
<td>51.0</td>
<td>2-3</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td>Post-mordanting</td>
<td>Alum</td>
<td>4.02</td>
<td>70.1</td>
<td>6.73</td>
<td>11.8</td>
<td>13.5</td>
<td>60.2</td>
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<td>4</td>
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<td></td>
<td></td>
<td>4.07</td>
<td>70.5</td>
<td>6.82</td>
<td>12.0</td>
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<td>60.4</td>
<td>2</td>
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<td></td>
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<td>3.79</td>
<td>70.9</td>
<td>6.85</td>
<td>11.9</td>
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<td>2-3</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td></td>
<td>Tannic acid</td>
<td>3.94</td>
<td>72.1</td>
<td>9.72</td>
<td>11.8</td>
<td>15.2</td>
<td>50.4</td>
<td>2</td>
<td>3-4</td>
<td>4-5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.18</td>
<td>71.2</td>
<td>9.91</td>
<td>12.5</td>
<td>15.9</td>
<td>51.6</td>
<td>2</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.04</td>
<td>71.2</td>
<td>10.1</td>
<td>13.0</td>
<td>16.4</td>
<td>52.1</td>
<td>2-3</td>
<td>4-5</td>
<td>4-5</td>
</tr>
</tbody>
</table>
3.5 Kinetic Studies

In order to understand the rate of dye uptake by silk, kinetic studies were carried out with the dye extract using unmordanted silk. The dyeing process was carried out with 1:20 M:L ratio at 50 °C with 0.50 g dm$^{-3}$ dye solution in acetate buffer (pH 4). The absorbance at $\lambda_{max}$ of 552 nm of the dye was measured (Fig. 2). Considering the absorbance $D_o$ at $t = 0$ and $D_t$ at $t = t$, a plot of log ($D_t/D_o$) versus time ($t$) yields the rate of adsorption ($k_t$). The experiment was repeated at 60, 70 and 80 °C. The rate of dye uptake increases with the increase in temperature. From the Arrhenius plot of log $k_t$ versus $1/T$ ($r = 0.9993$), the energy of activation ($E_a$) value is found to be 63.7 kJ mol$^{-1}$.

The associated thermodynamic parameters such as $\Delta H^e$, $\Delta S^e$, $\Delta G^e$ and log A are given in Table 3. The positive value of the standard affinity ($\Delta G^e$) reveals that the spontaneous adsorption of color components occurs on silk yarn. The enthalpy of dyeing ($\Delta H^e$) being positive confirms an endothermic adsorption. The large negative entropy ($\Delta S^e$) perhaps indicates more orderly distribution of the color component of the dye during adsorption on silk yarn.

3.6 Adsorption Isotherm Studies

The adsorption studies on the dye uptake by silk yarn have been carried out at 80 °C and pH 4. The equilibrium concentration of the dye adsorbed on silk ($q_e$) has been calculated $^{18}$ using the following equation:

$$q_e = V (C_i - C_e) / m \quad \ldots (3)$$

where $V$ is the volume of dye solution; $C_i$ and $C_e$, the initial and equilibrium concentrations of the dye (mg/dm$^3$) respectively; and $m$, the mass of silk yarn (g).

The Langmuir adsorption isotherm $^{19}$ has been applied to many sorption processes of monolayer adsorption. This model assumes that the intermolecular forces decrease rapidly with distance and the adsorption occurs at specific homogeneous sites on the adsorbent. Langmuir equation also assumes structurally homogeneous adsorbent having similar sorption sites, which are energetically identical. Theoretically, a saturation value is reached for adsorption. The saturated sorption capacity can be given as shown below:

$$C_e = \frac{1}{Q_0} + \frac{C_e}{Q_0} \quad \ldots (4)$$

where $C_e$ is the dye concentration (mg dm$^{-3}$) at equilibrium; $q_e$, the amount of dye at equilibrium per gram of silk (mg/g); $Q_0$, the constant signifying limiting adsorption capacity when the surface is completely covered by dye molecules (mg/g); and $b$ (dm$^3$/mg), the Langmuir constant which depends on the energy of adsorption.

In the present work, a plot of Langmuir isotherm $1/q_e$ versus $1/C_e$ is found to be linear with regression coefficient of 0.9961. From the slope and intercept of such a plot, Langmuir constants $Q_0$ and $b$ are found to be 500 mg/g and 0.34 respectively. The reported $Q_0$ value signifies the amount of dye required to form a complete mono layer at equilibrium.

The Freundlich model of isotherm $^{20}$ assumes a heterogeneous sites having energetically different adsorption sites which are not equally accessible. The Freundlich isotherm can be written as:

$$\log q_e = \log K_f + \frac{\log C_e}{n} \quad \ldots (5)$$

where $q_e$ is the amount of adsorbent at equilibrium (mg/g); $C_e$, the adsorbent concentration in solution (mg dm$^{-3}$) at equilibrium; and $K_f$ & $n$, the constants which include all factors affecting the adsorption.

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*Table 3— Thermodynamic parameters for the dyeing of coloring component of A. lebbeck on silk yarn*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k' \times 10^4$, s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>50°C</td>
<td>1.91</td>
</tr>
<tr>
<td>60°C</td>
<td>3.79</td>
</tr>
<tr>
<td>70°C</td>
<td>7.87</td>
</tr>
<tr>
<td>80°C</td>
<td>14.8</td>
</tr>
<tr>
<td>$E_a$, kJ mol$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>63.7</td>
<td></td>
</tr>
<tr>
<td>$\Delta H^e$, kJ mol$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>60.9</td>
<td></td>
</tr>
<tr>
<td>$\Delta S^e$, kJ mol$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>103</td>
<td></td>
</tr>
<tr>
<td>$\Delta G^e$, kJ mol$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>-125</td>
<td></td>
</tr>
<tr>
<td>log A</td>
<td>6.59</td>
</tr>
</tbody>
</table>

---

*Fig. 2— Visible spectra of A. lebbeck bark extract in aqueous solution at different pH*
process. With the increase in adsorption capacity of the adsorbent the \( K_f \) value increases for the given adsorbate. The heterogeneity factor is \( 1/n \) and if \( n \) is close to unity, the surface heterogeneity is less important but as the value of \( n \) approaches 10, the surface heterogeneity becomes increasingly significant\(^{21}\). In the present work, a plot of \( \log q_e \) versus \( \log C_e \) is also found to be linear (\( r = 0.9921 \)). The slope and intercept of such a plot give values of \( 1/n \) and \( K_f \) which are found to be 0.6 and 2.46 respectively. Further, the value of \( 1/n \) (0.6) which is approaching unity signifies that the adsorption process is homogeneous.

Tempkin and Pyzhev model\(^{22}\) considered the effects of indirect adsorbate-adsorbent interactions on the adsorption isotherms. They observed that the heat of adsorption would decrease linearly with surface coverage due to adsorbate-adsorbent interactions. The Tempkin isotherm is written as shown below:

\[
q_e = B \ln A + B \ln C_e \quad \ldots (6)
\]

where \( B \) and \( A \) are the Tempkin constants and can be determined by a plot of \( q_e \) versus \( \ln C_e \). The constant \( B \) depends on the heat of adsorption and \( A \) is the equilibrium binding constant. In the present work, a plot of \( q_e \) versus \( \log C_e \) is curvilinear in nature (\( r = 0.9590 \)). The results observed does not fit into Tempkin and Pyzhev model because of lower regression coefficient.

The linear regression method was used to determine the best fit isotherm in adsorption process. In the present work, the Langmuir isotherm model is found to be a best fit model with relatively high regression value of 0.9962, wherein amino groups in silk attract the phenolic groups in the color component. Further, the value of \( 1/n \) (0.60) from Freundlich isotherm also supports the monolayer formation.

**4 Conclusions**

The color constituent isolated from bark of *A. lebbeck* is found to be rutin, a flavonoid glycoside moiety. The pre-mordanted dyed samples show better fastness properties and color strength values. The color co-ordinates of dyed samples lie in yellow-red quadrant of color space diagram. The positive standard affinity indicates spontaneous adsorption and the enthalpy of dyeing being positive suggests an endothermic adsorption process. A large negative entropy signifies a more uniformly order distribution of dye with silk material. The results give a best fit Langmuir model for adsorption of the color constituent on silk. The findings of present work indicate that the bark of *A. lebbeck* can be a good source of natural dye for textile industries.

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**References**