



Extraction of natural color component from the bark of Belleric myrobalan (*Terminalia bellerica*): Kinetic and adsorption studies

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ABSTRACT

Baicalein, a trihydroxy flavone from the bark of *Terminalia bellerica* was identified as a natural colorant. The potential of the natural color component on silk yarn was tested. Its properties of color fastness with regard to light, washing and crocking were investigated and found to be satisfactory. Thermodynamic parameters were evaluated. The positive value of enthalpy of dyeing suggests the endothermic nature of dyeing and the negative entropy implies that the dye molecules are orderly arranged on silk. The positive value of free energy confirms the affinity between the dye molecules and the protein content of silk. Further, adsorption studies were carried out to determine the best fit isotherm model for the present dyeing system. The Langmuir isotherm model fitted the experimental data very well with a relatively high regression coefficient compared to the Freundlich and Tempkin-Pyzhev isotherm models. In conclusion, the *Terminalia bellerica* bark can be used as a potential source of natural dye for silk.

1. Introduction

Synthetic dyes that are extensively used in the processes of dyeing are known to release a large amount of residual dyes. Many of these dyes are toxic, even carcinogenic, and hence pose a considerable hazard to aquatic as well as human life. In view of this, replacing synthetic dyes with natural colorants could be considered a better alternative since natural colorants are eco-friendly and also exhibit better biodegradability [1]. A majority of the natural dyes are derived from various parts of trees [2-4]. *Terminalia bellerica* (*T. bellerica*), commonly known as belleric myrobalan, is an important deciduous, medicinal tree belonging to the family of Combretaceae. The fruit and heartwood of *T. bellerica* are known to possess antimicrobial properties [5-6] and are commonly used as traditional medicine for several ailments such as fever, cough, diarrhea, skin diseases and oral thrush [7-8].

In India, the *T. bellerica* tree is also of great importance as a source of timber [9]. As a part of our on-going research [10] on the identification of color components from tree sources, we extracted and identified a color component from the bark of the *T. bellerica* tree.

In this study, a silk fabric was dyed using the extracted natural dye and the dyeing process was carried out through adsorption-kinetics. The kinetic and adsorption aspects of dyeing process are very significant in understanding the adsorption process of the natural colorant [11-12].

2. Experimental

2.1. Materials

The fresh bark of *T. bellerica* was collected from the western parts of Karnataka (Shimoga district), India. The bark was washed with tap water and dried under ambient conditions. The dried bark was cut into small pieces and ground to a fine powder. An open bath beaker dyeing machine equipped with a programmable control of temperature and time was used to carry out this study. Raw silk yarn of 40 denier was used. All solvents, reagents and chemicals used were of Analar grade.

2.2. Methods

2.2.1. Isolation

For extraction of the color component from *T. bellerica* bark, the powder (1000 g) was subjected to boiling with distilled water at 90 °C for 3 h in a beaker. The extract was collected and distilled water was added repeatedly till the color in the extract became negligible. The total extract was then concentrated under reduced pressure to obtain a solid mass. The solid mass was subjected to extraction with 80:20 v/v ethyl alcohol:water mixture, and filtered. The filtrate was evaporated under reduced pressure to get a concentrated mass. Approximately 20 g of dye concentrate obtained was chromatographically separated in an open column of silica gel (60-120 mesh) in benzene and eluted with benzene, ethyl acetate and methanol in increasing ratios of polarity. The elution with benzene:ethyl acetate (1:10) resulted in a major pale yellow colored fraction. After evaporation of the solvent from the fraction, an amorphous powder was obtained.

2.2.2. Spectral techniques

The Infra-red spectrum (IR) was recorded on a Perkin-Elmer 258 spectrophotometer using KBr pellets. The absorbance of the dye solution was measured using Shimadzu 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.

2.2.3. Determination of absorbance and color strength measurements

Dye solutions containing 1-5 % were prepared and known amounts were taken in the dye bath by maintaining the material to liquor (M:L) ratio at 1:20. The absorbance of the dye solution was recorded before and after the dyeing process with UV-Vis spectrophotometer. The amount of dye uptake was calculated using the equation:

$$\% \text{ Dye absorbance} = \frac{\text{Absorbance before dyeing} - \text{Absorbance after dyeing}}{\text{Absorbance before dyeing}} \times 100 \quad (1)$$

The color strength (K/S values) of the dyed samples was evaluated from the light reflectance technique using Kubelka-Munk equation [13]:

$$K/S = (1-R)^2/2R \quad (2)$$

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

2.2.4. Methods of mordanting

The pre-mordanting and post-mordanting methods were employed at 70 °C for 30 min using 2, 4 and 6 % solutions of tannic acid and alum ($\text{Al}_2(\text{NH}_4)_2(\text{SO}_4)_4 \cdot 12\text{H}_2\text{O}$), as mordants separately. The silk was then washed repeatedly with water and dried.

2.2.5. Dyeing experiments

The silk yarn was dyed at pH 4 in a bath containing 4% dye keeping the M:L ratio of 1:20. The dyeing process was started initially at 40 °C and the temperature was then gradually raised to 90 °C within 20 min and the process was continued for 45 min. After this time, the silk was taken out, rinsed in tap water and soaped at 60 °C for 10 min. Then it was again thoroughly washed with water and dried. For post-mordanting, samples were soaped after mordanting.

2.2.6. Measurement of colorimetric data

Colorimetric data of the dyeing process were derived using a spectrophotometer interfaced to a PC. These data were recorded with the specular component of the light excluded and the UV component included, using illuminant D₆₅ and 10° standard observer.

2.2.7. Measurement of fastness properties

Color fastness tests to light, washing and crocking were carried out. The color fastness of the dyed silk to washing was tested by ISO 105-C10:2006 method. The color fastness to crocking was assessed using AATCC Test Method 8-1996 by a crock meter. Color fastness to light was evaluated as per AATCC Test Method 16-2004 option 5.

3. Results and Discussion

3.1. Spectral characterization of color component

IR spectrum (in cm^{-1}) shows peaks at 3410 (O-H), 2972 (C-H), 1654 (C=O) and 1618 (C=C). ^{13}C NMR spectrum in DMSO-d₆ shows a peaks at δ 182 (C-4), 163 (C-7), 152 (C-2), 150 (C-5), 145 (C-9), 130 (C-4'), 128 (C-32'), 128 (C-5'), 125 (C-1'), 103 (C-22'), 103 (C-6'), 93 (C-8). ^1H NMR spectrum in DMSO-d₆ shows peaks at δ 12.5 (s, 1H, H-5), 10.8 (s, 1H, H-6), 9.64 (s, 1H, H-7), 7.51 (s, 2H, H-3', 5'), 6.8 (s, 1H, H-3), 6.3 (d, 1H, H-8). Mass spectrum (m/z) in positive mode shows a peak at 271 amu ($\text{M}+\text{H}^+$), indicating that the color compound has a molecular weight of 270 amu, which is a characteristic of Baicalein ($\text{C}_{15}\text{H}_{10}\text{O}_5$) [14-16] (Figure 1).

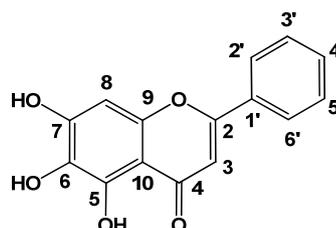


Figure 1. 5,6,7-trihydroxy-2-phenyl-4H-chromen-4-one.

3.2. Effect of concentration of dye on absorption and color strength on dyeing

The absorbance and color strength values (K/S) increased with an increase in the concentration of the dye in the concentration range of 1 to 5%. Table 1 reveals that the dye uptake percentage and K/S values reached a maximum at 4 % dye concentration (Figure 2) and hence this dye concentration was fixed as optimal for the process of dyeing.

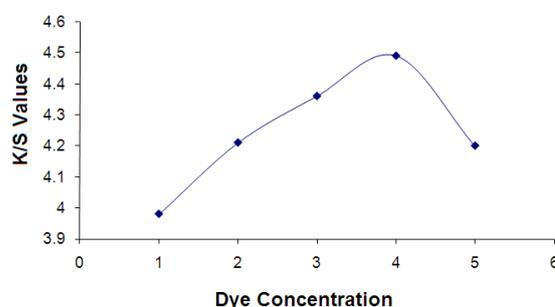


Figure 2. A plot of K/S values versus concentration.

Table 1. Values of absorbance and K/S of different dye concentrations.

Dye (%)	Absorbance		Dye uptake (%)	K/S
	Before dyeing	After dyeing		
1	0.30	0.21	30.0	3.98
2	0.61	0.40	34.4	4.21
3	0.93	0.60	35.0	4.36
4	1.24	0.80	35.5	4.49
5	1.51	0.99	34.4	4.20

3.3. Effect of mordanting on dyeing

Tables 2 and 3 show that the values of K/S and properties of fastness increased more with mordanting compared to unmordanting. The pre-mordanting technique was found to be better as it improved K/S values and fastness properties compared to the post-mordanting technique. It was also observed that K/S values increased with the increase in concentration of alum in the case of pre-mordanting. This indicates that alum is a better mordant compared to tannic acid as it shows better color values and fastness properties.

Table 2. Values of color strength (K/S) and color co-ordinates of dyed samples.

Method	Mordants	K/S	L*	a*	b*	C	h
Pre	Nil	4.49	70.7	8.60	10.7	13.8	50.1
	Alum (2%)	4.66	71.0	5.13	10.8	12.0	63.6
	Alum (4%)	4.83	70.3	5.25	11.6	12.6	64.7
	Alum (6%)	4.87	69.6	5.63	11.8	13.1	63.3
	Tannic acid (2%)	4.60	72.2	8.65	10.1	13.3	48.5
	Tannic acid (4%)	4.62	72.3	8.73	10.0	13.3	47.5
	Tannic acid (6%)	4.84	69.7	9.47	11.6	15.0	50.0
Post	Alum (2%)	4.57	69.1	6.63	11.7	13.4	59.2
	Alum (4%)	4.63	69.5	6.72	12.0	13.5	59.4
	Alum (6%)	4.89	69.9	6.75	11.9	13.6	59.2
	Tannic acid (2%)	4.51	71.3	9.62	11.8	15.1	49.4
	Tannic acid (4%)	4.53	70.2	9.81	12.5	15.8	50.6

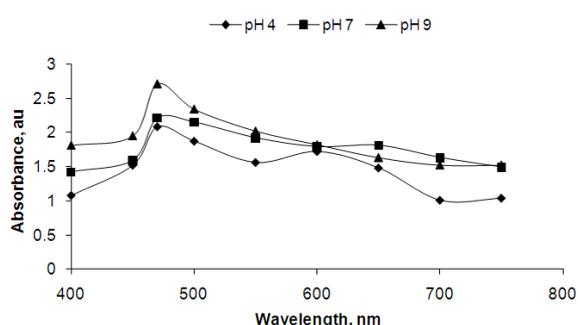
Table 3. Fastness ratings of dyed silk samples.

Method	Mordant	Light fastness	Crocking fastness	Wash fastness	
				Wet	Dry
Pre	Nil	2	4	4-5	4
	Alum (2%)	2-3	4-5	4-5	4-5
	Alum (4%)	2-3	4-5	5	4-5
	Alum (6%)	3	5	5	5
	Tannic acid (2%)	2-3	4-5	4-5	4-5
	Tannic acid (4%)	2-3	4-5	4-5	4-5
	Tannic acid (6%)	2-3	4-5	5	4-5
Post	Alum (2%)	2	4	4-5	4
	Alum (4%)	2	4-5	4-5	4-5
	Alum (6%)	2-3	4-5	4-5	4-5
	Tannic acid (2%)	2-3	4	4-5	4-5
	Tannic acid (4%)	2-3	4	4-5	4-5
	Tannic acid (6%)	2-3	4-5	4-5	4-5

The color co-ordinates observed were positive and lie in the yellow-red quadrant of the color space diagram. The color co-ordinates, color strength values and the fastness properties of the dyed samples determined that the extract is a good source of natural dye for silk.

3.4. Effect of pH on dye extract

The visible spectrum of the dye extract at different pH (4, 7 and 9) is shown in Figure 3, which reveals that the λ_{\max} of the dye extract did not change with varying pH. The absorbance of the dye extract increased with increase in pH, which may be due to the high solubility of phenolic groups in the alkaline pH.

**Figure 3.** Visible spectra of the dye extract at pH 4, 7 and 9.

3.5. Kinetic studies

In order to understand the rate of dye uptake by silk, kinetic studies were carried out using un-mordanted silk with aqueous solution of the extract. Extract solution was prepared by dissolving 0.5 g dm⁻³ of extract in an acetate buffer of pH 4. The dyeing process was carried out with ML ratio of 1:20 at 50 °C. Known volume (5 mL each) of the dyeing solution was pipetted into a cuvette at regular intervals of time (5 min) and absorbance measurements were made at its λ_{\max} of 470 nm (Figure 3). The absorbance readings at t = 0 and t = t are D₀ and D_t. First-order rate constants (k' , s⁻¹) for adsorption were evaluated by log (D₀/D_t) vs. time plots. The experiment was

repeated at 60, 70, 80, and 90 °C and the rate of adsorption was calculated at each temperature. From the linear Arrhenius plot of log k' vs. 1/T (R² = 0.9973), values of activation parameters such as the energy of activation (E_a), enthalpy of activation (ΔH^\ddagger), entropy of activation (ΔS^\ddagger) and free energy of activation (ΔG^\ddagger) were computed (Table 4). The positive value of the standard free energy change indicates that the affinity between the dye molecule and the silk fiber is very strong. The positive enthalpy of activation signifies that the dyeing process is endothermic in nature. The large negative entropy of activation perhaps indicates more orderly distribution of the color component of dye on silk during adsorption.

Table 4. Values of thermodynamic parameters for the dyeing process.

Temperature (°C)	$k' \times 10^4 \text{ s}^{-1}$
50	0.64
60	1.25
70	2.38
80	4.61
90	9.23
E _a (kJ mol ⁻¹)	57.4
ΔH^\ddagger (kJ mol ⁻¹)	54.3
ΔG^\ddagger (kJ mol ⁻¹)	108
ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	-157
Log A	5.10

3.6. Adsorption isotherm studies

The distribution of adsorption molecules between the liquid phase and the solid phase at equilibrium can be explained by adsorption isotherm. The amount of dye adsorbed (q_e mg/g) at equilibrium was calculated by the following mass balance equation [17]:

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

where, V is the volume of solution used in the adsorption experiment, C_i and C_e are the initial and equilibrium concentrations of the dye (mg dm⁻³) respectively, and m is the mass of the silk (g).

Langmuir, Freundlich and Tempkin-pyzhev adsorption isotherm models were examined to describe the adsorption

equilibrium. Langmuir model [18] assumes a homogeneous monolayer adsorption and the linearized Langmuir model is given by the following equation:

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

where C_e is the concentration of the adsorbent (mg/dm^3) at equilibrium; q_e is the amount of dye adsorbed at equilibrium (mg/g); Q_0 is a constant which signifies the adsorption capacity (mg/g); and b is the Langmuir constant related to the adsorption energy (dm^3/mg).

The plot of $1/C_e$ vs. $1/q_e$ gives a straight line with a linear regression coefficient of 0.9793 (Figure 4). From the intercept and slope of such a plot, values of constants Q_0 and b were evaluated as 66.6 mg/g and 3.16 dm^3/mg , respectively.

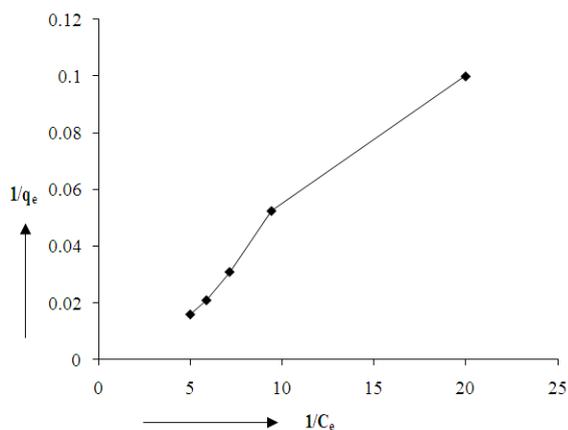


Figure 4. Langmuir isotherm plot for dyeing silk at 80 °C with pH 4.

Further, the important characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor for equilibrium parameter, R_L [19-20] which is expressed as:

$$R_L = \frac{1}{(1 + bC_e)} \quad (5)$$

The value of R_L indicates the type of isotherm to be either irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). In the present study, the value of R_L was 0.75, indicating the Langmuir adsorption isotherm to be a favorable adsorption isotherm.

The Freundlich model assumes a heterogeneous multilayer adsorption surface with sites that have different energies of adsorption which are not equally available. The Freundlich model [21] is:

$$\log q_e = \log K_f + \frac{\log C_e}{n} \quad (6)$$

where q_e is the amount of dye at equilibrium (mg/g); C_e is the dye concentration in the solution (mg/dm^3) at equilibrium; and K_f and n are Freundlich constants incorporating all factors affecting the adsorption process. In general, as the value of K_f increases the adsorption capacity of the adsorbent for the given adsorbate also increases. $1/n$ is the heterogeneity factor, if n is close to 1, the surface heterogeneity could be assumed to be less significant and as n approaches 10, the impact of surface heterogeneity becomes more significant [22]. A plot of $\log q_e$ vs. $\log C_e$ was linear with a regression coefficient of 0.9682 (Figure 5). The values of K_f and $1/n$, were evaluated from such a plot and found to be 5.01 and 1.32, respectively. Further, the value

of $1/n$ is close to unity, suggesting that the adsorption of dye molecules on silk is homogeneous.

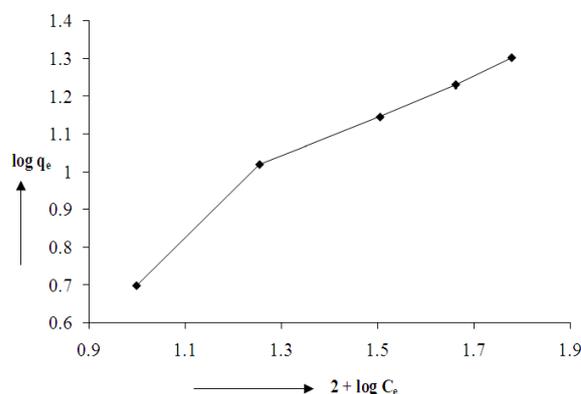


Figure 5. Freundlich isotherm plot for dyeing silk at 80 °C with pH 4.

The Tempkin and Pyzhev [23] isotherm model was also considered to fit the present experimental data. The Tempkin isotherm can be expressed in its linear form as:

$$q_e = B \ln A + B \ln C_e \quad (7)$$

where B and A are the Tempkin constants and can be determined by a plot of q_e vs. $\ln C_e$. The constant B is related to heat of adsorption and A is the equilibrium binding constant. A plot of q_e vs. $\log C_e$ is curvilinear in nature with a very low regression value of 0.8970 (Figure 6) and hence this model does not fit well with the present system.

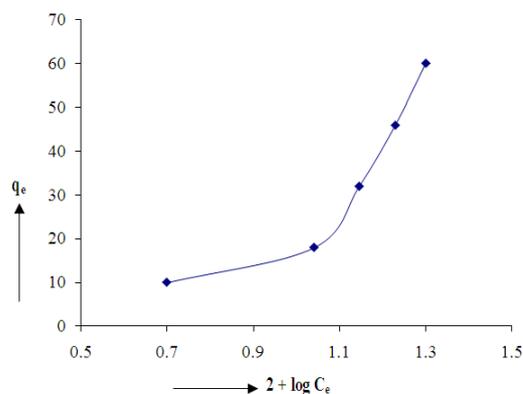


Figure 6. Tempkin-Pyzhev isotherm plot for dyeing silk at 80 °C with pH 4.

The linear regression coefficient was frequently used to decide the most fitted isotherm in the adsorption process. In the present case, the Langmuir model was found to fit better than the other two models with a relatively high regression coefficient ($R^2 = 0.9793$; Figure 4). This indicates that the homogeneous monolayer possibly formed with the interaction between hydroxyl groups of colorant and the amino groups of silk protein. Further, the value of $1/n$ (1.32) in Freundlich isotherm model also supports the homogeneous adsorption of dye molecules on silk.

4. Conclusion

Baicalein, 5,6,7-trihydroxy flavone was found to be a major color component from the bark of *T. bellerica*. The color fastness properties of baicalein on silk in pre-mordanting were found to be appreciable compared to post-mordanting. Thermodynamic parameters were computed by studying the dyeing-kinetics at different temperatures. The enthalpy of

dyeing was found to be positive, suggesting the endothermic nature of dyeing. The negative value of entropy indicates that the dye molecules were arranged in order on silk. The positive change in free energy shows the affinity between the dye molecules and the protein content of silk. Further, the adsorption isotherm studies were carried out on three isotherms. The Langmuir isotherm was found to be the best fit isotherm with relatively high regression value compared to Freundlich and Tempkin and Pyzhev isotherm models. The adsorption data indicates the formation of homogeneous monolayer possibly with the interaction between hydroxyl groups of Baicalein and the amino groups of silk protein. It can be concluded that *T. bellerica* bark can be used as a source of natural dye for textile dyeing. This kind of research provokes natural dyes in dyeing application.

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