Physico-chemical studies on dyeing of jute and cotton fabrics using jackfruit wood extract: Part II — Dyeing kinetics and thermodynamic studies

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Bleached jute and cotton fabrics have been double pre-mordanted applying 20% myrobolan (harda) as 1st mordant and 20% Al₂(SO₄)₃ or 20% FeSO₄ as 2nd mordant and subsequently dyed with aqueous extract of jackfruit wood under optimized conditions of dyeing. The physico-chemical parameters of dyeing, such as dyeing affinity, rate of dyeing, absorption isotherms and associated thermodynamic parameters like heat of dyeing (ΔH), entropy of dyeing (ΔS) and Gibb’s free energy (ΔG), have been assessed to explain the interaction among different fibre-mordant-dye systems. It is observed that all of these dyeing processes are endothermic, ΔH values being positive. Among different fibre-mordant-dye systems studied, jute fabric double pre-mordanted with harda and FeSO₄ shows a non-linear Langmuir type dye-absorption isotherm, while dye-absorption isotherms of all other fibre-mordant-dye systems are found to be linear following Nernst absorption isotherm, indicating the formation of co-ordinated complex in jute-harda + FeSO₄—dye sample, and hydrogen bonding in all other cases of fibre-mordant-dye systems studied. However, the negative ΔG values of all the systems studied indicate that the potentiality of chemical interaction/reaction of these fibre-mordant-dye systems in some otherwise favorable conditions of dyeing need to be further studied.

Keywords: Cotton, Dyeing kinetics, Jackfruit wood, Jute, Mordanting, Natural dye, Thermodynamic parameters
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1 Introduction

Chemically, jute is composed of cellulose (54-60%), hemicellulose (20-24%) and lignin (12-14%), while cotton contains 92-97 % pure cellulose. Jute fibre contains primary –OH group of cellulose, secondary –OH group of cellulose / hemicellulose, –COOH group of gluco-uronic acid residue and some –CHO group of hemicellulose, besides some –C=C– unsaturation of lignin component. Cotton contains both primary and secondary –OH groups of cellulose. Thus, dyeing kinetics and thermodynamic parameters along with substantivity or affinity and absorption character of any natural dye will differ in jute and cotton for their varying chemical composition and chemical functionality pattern as well as for the differences in their gross and fine structures.

There are variety of natural dyes obtained from different plants, animals and minerals sources having colour components of varying chemical nature. Most of these colour components are either mordantable or non-ionic in nature with or without different substituent chemical groups/ functionality. These dyes can be successfully applied to silk¹,² and wool³,⁴, but exhibit many difficulties when applied on cotton⁵-⁷ and jute⁸. In our earlier communication⁹, the effects of different mordanting systems and dyeing process variables on colour yield and colour fastness behaviour for dyeing bleached jute and cotton fabrics using aqueous extract of jackfruit wood have been reported. There are limited reports available on dyeing kinetics for dyeing of either jute and cotton materials using different natural dyes. Hence, in the present work, an attempt has been made to study the dyeing kinetics and thermodynamic parameters for dyeing of jute and cotton fabrics with aqueous extract of jackfruit wood.

2 Materials and Methods

2.1 Materials

Conventionally bleached jute and cotton fabrics with the following specifications were used:
Laboratory reagents grade of ferrous sulphate and aluminium sulphate, and commercial grade of acetic acid, common salt, sodium carbonate, sodium hydroxide and non-ionic soap obtained from local suppliers were used. Myrobalan (harda) as natural mordant was also used in the study.

Aqueous extract of jackfruit (*Artocarpus heterophyllus* Lam) wood (JFW) was used as the dye liquor. The colour component extracted from the jackfruit wood is morol, a typical flavanol (hydroxyl flavone).9,10

2.2 Methods

2.2.1 Extraction and Purification of Colour Component of Jackfruit Wood

Jackfruit wood was initially chopped into small chips which were then boiled in aqueous solution at 100°C for 30 min, using initial MLR of 1:10 to get an aqueous coloured extract of jackfruit wood under optimized conditions of extraction.9

For chemical characterization of the extracted natural dye and for the study of dyeing kinetics, the concentrated aqueous extract of the jackfruit wood obtained was filtered and the filtrate was evaporated to a semi-dry mass under water bath. This semi-dry mass of the dye was then taken in a soxhlet apparatus under a piece of folded blotting paper for further extraction and purification using 50:50 alcohol-benzene mixture for 10 cycles for 2h at 70°C. The purified alcohol-benzene extract of the colour component obtained was then evaporated in a water bath at 50°C to a complete dry mass. Finally, this dry mass of the colour component was washed with acetone before washing the same with methyl alcohol followed by final drying in air to obtain the dry powder of the pure colour component from jackfruit wood.

2.2.2 Double Pre-mordanting of Jute and Cotton Fabrics with Harda and Metallic Salts

It has been observed earlier9 that the double pre-mordanting using 20% harda as 1st mordant and 20% AL₂(SO₄)₃ or 20% FeSO₄ as 2nd mordant is optimum for both bleached jute and cotton fabrics giving maximum colour yield for jackfruit wood colour. Preparation of known concentration of harda solution is already reported.9 Pre-wetted conventionally H₂O₂ bleached jute and cotton fabrics were seperately treated with 20% (w/w) harda solution in separate bath at 40-50°C and then the temperature of the harda solution was gradually raised to 80°C and the mordanting was continued for 30 min. After this harda mordanting, the fabric samples were dried in air without washing to make it ready for second mordanting.

The jute and cotton fabric samples after initial 1st mordanting with 20% of harda were again mordanted (second) prior to dyeing using either 20% aluminium sulphate or 20% ferrous sulphate at 80°C for 30 min, maintaining the material-to-liquor ratio at 1:20. After the final mordanting, the fabric samples were dried in air without washing to make it ready for subsequent dyeing.

2.2.3 Dyeing of Pre-mordanted Jute and Cotton Fabrics

Bleached and/or double pre-mordanted jute and cotton fabrics were dyed using the purified dye powder of jackfruit wood under optimized dyeing conditions,9 such as concentration of dye, 20%; MLR, 1:20; common salt, 10gpl; pH, 11.0 (with addition of requisite amount of NaOH solution); dyeing temperature, 100°C and dyeing time, 60 min.

After the dyeing is over, the samples were repeatedly washed with hot and cold water and finally dried in air. The dyed samples were subjected to soaping with 2gpl soap solution at 60°C for 15 min, followed by repeated water wash and drying under sun.

2.2.4 Determination of Thermodynamic Parameters for Study of Dyeing Kinetics

2.2.4.1 Determination of Dₛ and Dᶠ

After completion of dyeing, the residual dye bath liquor admixed with all wash out liquor was collected carefully and the volume of the left-liquor was made to 500ml using a specific volumetric flask from which, a known volume of left dye liquor solution was taken out. The absorbance of this liquor solution was checked on a Hitachi U-2000 UV-VIS absorbance spectrophotometer to determine the dye concentration in the left-liquor using the pre-calibrated curve for known concentrations of dye solution with the help of a appropriate software installed in it. From the results of dye concentrations in the left-liquor, the dye in the solution (Dₛ) before and after dyeing for specific time of dyeing or
otherwise and the corresponding amount of dye exhausted to the fibre ($D_f$) were estimated by subtraction method. These results of matched pair of $D_f$ and $D_s$ for different cases were used for calculations of thermodynamic parameters of dyeing, namely dye affinity, rate of dyeing, $\Delta H$, $\Delta S$ and $\Delta G$, and also to plot dyeing adsorption isotherm for the study of dyeing kinetics.

2.2.4.2 Chemical Affinity or Dye Affinity

Chemical affinity or dye affinity ($-\Delta \mu$) was calculated using the following equation\textsuperscript{11}:

$$-\Delta \mu = R T \ln \left\{ \frac{[D]_f}{V[D]_s} \right\}$$

where $R$ is the universal gas constant (kJ); $T$, the temperature of dyeing in Kelvin; $[D]_f$, the dye absorbed by the fibre (g/kg); $[D]_s$, the dye in solution (g/L); and $V$, the volume of internal phase of the fibre (L/kg). The value of $V$ for a particular fibre taken is equal to the moisture regain of that fibre at 100% RH; for jute\textsuperscript{12}, this is 0.36 and for cotton \textsuperscript{13}, this is 0.23.

2.2.4.3 Enthalpy of Dyeing

Heat or enthalpy ($\Delta H$) of dyeing was calculated using the following equation\textsuperscript{11}:

$$DF = \frac{T_2 D\mu_1 - T_1 D\mu_2}{T_2 - T_1}$$

where $T_1$ is the initial dyeing temperature in Kelvin; $T_2$, the final dyeing temperature in Kelvin, $\Delta\mu_1$, the affinity at $T_1$ºK; and $\Delta\mu_2$, the affinity at $T_2$ºK.

2.2.4.4 Entropy of Dyeing and Gibb’s Free Energy

The entropy of dyeing ($\Delta S$) and Gibb’s free energy were calculated using the following equation\textsuperscript{11,14}:

$$-\Delta \mu = \Delta H - T \Delta S = \Delta G$$

where $-\Delta \mu$ is the chemical affinity; $\Delta H$, the heat or enthalpy of dyeing; $T$, the temperature of dyeing in Kelvin; and $\Delta G$, the Gibb’s free energy.

3 Results and Discussion

3.1 Kinetic Study of Dyeing

The effects of different mordanting systems on colour yield and colour fastness behaviour for dyeing of bleached jute and cotton fabrics with aqueous extract of jackfruit wood have already been reported.\textsuperscript{9} Among different single and double pre-mordanting systems studied\textsuperscript{9}, the higher colour yields have been obtained in case of sequential double pre-mordanted bleached jute and cotton fabrics using 20% harda as 1st mordant and either of 20% Al$_2$(SO$_4$)$_3$ or 20% FeSO$_4$ as 2nd mordant than those obtained by different single pre-mordanting systems studied. Hence, in the present study, four selective double pre-mordanting systems have been chosen for further study of dyeing kinetics and associated thermodynamic parameters. These selective double pre-mordaning systems are (i) double pre-mordanting of bleached jute fabric with 20% harda and 20% Al$_2$(SO$_4$)$_3$ applied in sequence (a), (ii) double pre-mordanting of bleached cotton fabric with 20% harda and 20% Al$_2$(SO$_4$)$_3$ applied in sequence (a’), (iii) double pre-mordanting of bleached jute fabric with 20% harda and 20% FeSO$_4$ applied in sequence (b) and (iv) double pre-mordanting of bleached cotton fabric with 20% harda and 20% FeSO$_4$ applied in sequence (b’). Study of thermodynamic parameters and dyeing kinetic has been carried out for these four selective double pre-mordanted jute and cotton samples.

3.1.1 Rate of Dyeing

The dye exhaustion curves indicating rate of dyeing ($D_f$ vs $t_d$) for bleached jute and cotton fabrics dyed with aqueous extract of jackfruit wood using above four double pre-mordanting systems (a, a’, b and b’) are shown in Fig. 1. It is observed that with the increase in dyeing time, the dye uptake ($D_f$) increases steadily upto 90 min and then almost levels off in between 90 min and 120 min. Also, the curves for dye uptake in terms of $K/S$ value vs dyeing time as well as $K/S$ value vs dyeing temperatures support the present observation showing a similar trend exhibiting the

![Fig. 1 — Dye exhaustion curves for different dyeing time](image-url)
maximum surface colour strength ($K/S$ value) at about 80°C and for 90 min of dyeing time for mordant systems (b) and (b'). The dye uptake at different temperatures is dependent on heat of dyeing. Heat of dyeing ($\Delta H$) for each of the present case of dyeing of bleached jute and cotton fabrics with jackfruit wood extract has been found to be positive (Tables 1 and 2), indicating that the dyeing in this case is an endothermic process. So, the gradual raising of the dyeing temperature will lead to higher dye affinity up to a certain temperature limit, above which the dye uptake will gradually reduce or levels off, and less dye will be absorbed above a certain temperature or at equilibrium and practically there is a decrease in dye affinity ($-\Delta \mu$) and rate of dyeing in the range of 90-120°C in each case. In case of double pre-mordanting systems (a) and (a'), the higher dissociation of $\text{Al}_2(\text{SO}_4)_3$ at higher temperature of dyeing or for higher dyeing time expectedly may increase the retardation effects in rate of dyeing. Hence, practically the dyeing rate is found to be measurably lower in each case of pre-mordanting systems (a) and (a') than that in pre-mordanting systems (b) and (b') for jute and cotton respectively.

### 3.1.2 Dye Affinity

The dye chemical affinity ($-\Delta \mu$) values for the colourants (dye) from jackfruit wood extract towards

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<th>Table 1 — Thermodynamic parameters for dyeing of jute and cotton fabrics with jackfruit wood extract for double pre-mordanting using 20% harda and 20% $\text{Al}_2(\text{SO}_4)_3$ applied in sequence</th>
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* $[D]_f$ – Conc. of dye in fibre; $[D]_s$ – Conc. of dye in solution; $-\Delta \mu$ – Chemical affinity; $\Delta H$ – Heat of dyeing or enthalpy and $\Delta S$ – Entropy of dyeing; $T_1=333K(60ºC)$ and $T_2=363 K (90ºC)$.

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<th>Table 2 — Thermodynamic parameters for dyeing of jute and cotton fabrics with jackfruit wood extract for double pre-mordanting using 20% harda and 20% $\text{FeSO}_4$ applied in sequence</th>
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* $[D]_f$ – Conc. of dye in fibre; $[D]_s$ – Conc. of dye in solution; $-\Delta \mu$ – Chemical affinity; $\Delta H$ – Heat of dyeing or enthalpy and $\Delta S$ – Entropy of dyeing; $T_1=333K(60ºC)$ and $T_2=363 K (90ºC)$. 
bleached jute and cotton fabrics double pre-mordanted with different fibre-mordanting systems and subsequently dyed at pH 11.0 following optimized conditions of dyeing at two different dyeing temperatures (60ºC and 90ºC) is shown in Tables 1 and 2. It is observed that there is a low but measurable increase in dye affinity values with the increase in dyeing temperature from 60ºC to 90ºC for both bleached jute and cotton fabrics for all the four fibre-mordant systems studied. However, there is little or almost no significant changes in dye affinity for dyeing either with higher duration or with higher dye concentrations. The measurable increase in dye affinity with the increase in dyeing temperature for differently pre-mordanted cellulosic and ligno-cellulosic fibres can be viewed as an effect of additional input of thermal energy to increase the rate of dyeing in this endothermic dyeing process; $\Delta H$ being positive in each case.

3.1.3 Absorption Isotherm

The absorption isotherms ($D_t$ vs $D_s$) for dyeing at optimum dyeing temperature (90ºC) for bleached jute and cotton fabrics after pre-mordanting with four different fibre-mordanting systems are shown in Fig. 2a,b’. The best fit absorption isotherms in the present cases for fibre-mordanting systems (a, a’ and b’) are found to be linear, indicating the partition mechanism of dyeing being more alike to Nernst absorption isotherm. This type of linear Nernst absorption isotherm is observed generally for dyeing of non-polar disperse dyes to hydrophobic polyester fibre. Such linear dyeing isotherm has also been observed in an earlier study$^{15}$ on dyeing of jute fabric with red sandal wood extract. Arshid et al.$^{16}$ in their study on dyeing of wool with logwood and brazilwood as natural dyes and Gulrajani et al.$^3$ in their study on dyeing of wool and nylon with red sandal wood extract also observed the linear dyeing isotherm. Hence, the mechanism of dye absorption in this case is though found to be like absorption of disperse dyes in polyester but it may be presumed that in the present case, jute and cotton being hygroscopic fibres, the absorption of non-polar dye through hydrophobic interaction is of marginal importance. Hence, the major dye absorption is presumed to occur through hydrogen bonding interaction in these cases. However, the fibre-mordant system (b) shows a non-linear langmuir absorption isotherm$^{11}$, which is more alike to the absorption isotherm of dyeing wool with acid dye, indicating the formation of co-ordinated complex in this case. It may be presumed that the jute fibre having $-\text{COOH}$ group in hemicelluloses might have attracted Fe$^{+}+$ ions from FeSO$_4$ mordant during second mordanting to form Jute-hemicyllo-$\text{COO}^-$…Fe ion complex and this (Jute

![Fig. 2 — Dyeing isotherms for bleached jute and cotton fabrics dyed with jackfruit wood extract at 90ºC.](image-url)
-COO\(^{-}\))\(_2\)…Fe\(^{++}\) mordanted complex perhaps facilitates absorption of more and more non-polar / ionic-mordantable colour component (morol) of jackfruit wood, like wool absorbs acid dyes following the Langmuir absorption isotherm.

3.1.4 Enthalpy of Dyeing

For dyeing of bleached jute and cotton fabrics after double pre-mordanting with four selective fibre-mordanting systems, the heat (enthalpy) of dyeing is found to be positive, showing initial high value which then decreases gradually to a moderate or low values with the increase in dyeing time/ dyeing temperature or dye concentrations. Thus, these dyeing processes may be considered as endothermic and hence, in these cases dye should be adsorbed on increasing the dyeing temperature upto a certain temperature limit (90ºC), above which the dye uptake either reduces or almost levels off after the desorption of dyes occurs above a certain temperature limit. From Table 2, it is observed that between the temperature 60ºC and 90ºC, the \(\Delta H\) value (a measure of strength of forces or bonds of attraction which bind relevant dyes to the fibre\(^{11,17}\)) ranges between 21.71 kJ/mol and 9.30 kJ/mol for fibre-mordanting system (a), between 15.99 kJ/mol and 8.11 kJ/mol for fibre-mordanting system (b), between 19.05 kJ/mol and 7.91 kJ/mol for fibre-mordanting system (a') and between 11.21 kJ/mol and 7.50 kJ/mol for fibre-mordanting system (b'). The \(\Delta H\) values gradually decrease with either increased dye uptake or higher dyeing period. These observed results of \(\Delta H\) values indicate that most probably a week dye-fibre force is formed in both jute and cotton fabrics, as these experimental \(\Delta H\) values almost match with the range of hydrogen bond energy\(^{11,17}\) (8.4-41.9 kJ/mol). Moreover, as the dyeing proceeds using higher concentrations of dye or with higher dyeing time, due to quick saturation of hydrogen bond formation utilizing the –OH groups of dyes and fibres, it blocks the possibility of formation of dye-fibre co-ordinated complex utilising the dye sites and hence, the \(\Delta H\) values gradually decrease with increased dye uptake or higher dyeing time.

Among all the fibre-mordanting systems studied, the absorption isotherm for fibre- mordanting system (b) is found to be different than those of the other fibre-mordanting systems studied. For heat of dyeing, the different fibre-mordanting systems (a) and (b) used in case of jute show always higher \(\Delta H\) value as compared to fibre-mordant systems (a') and (b') used in case of cotton. Jute fibre having –COOH group of hemicellulose can ionize in the solution as jute-hemicellulose-CoO\(^{-}\) ion to attract metal ions of mordants and also the mordantable dyes.

3.1.5 Entropy of Dyeing and Gibb’s Free Energy

Entropy of dyeing is observed to be initially high, which however decreases significantly with the increase in dye concentration or time of dyeing for both selectively double pre-mordanted jute and cotton fabrics. As the change in entropy (\(\Delta S\)) along with the change in enthalpy (\(\Delta H\)) are the main indicators of driving force leading to dye absorption and fixation, it is understood from both the \(\Delta H\) and \(\Delta S\) values (Tables 1 and 2) that there are always a measurable decrease in \(\Delta H\) and \(\Delta S\) values with the increase in dye concentration or higher time of dyeing for all the fibre-mordanting systems studied. This may be due to the decrease in further dye-fibre interactions and fixation occurring mostly through hydrogen bonding for fibre–mordanting systems (a), (a') and (b') and through co-ordinated complex formation for fibre-mordanting system (b), particularly when the dye saturation and equilibrium are established. However, slowing down of rate of dyeing (Fig.1) above 60ºC dyeing temperature with the reduction in slope of dye-exhaustion curves above 60ºC and reduction in dye exhaustion above 90ºC dyeing temperature may be viewed as effect of rapid dye absorption on pre-mordanted jute and cotton fabrics. This may be due to physical absorption in case of fibre-mordanting systems (a), (a') and (b') and by chemical sorption in case of fibre-mordanting system (b) upto 60ºC, achieving the dye saturation quickly within this temperature range and slow dye absorption at 60º-90ºC dyeing temperature. Thereafter almost no physical or chemical absorption of dye molecules occur in the fibre surface or voids without any further chemical interaction or complex formation, showing much reduction in \(\Delta H\) and \(\Delta S\) values due to possible desorption of the dye molecules at higher temperature or for higher dyeing time. However, \(\Delta G\) values\(^{14}\) being negative in all these cases for all the fibre-mordanting systems both at 60ºC and 90ºC indicate that there is still some possibility of chemical reaction/co-ordinated complex formation among the fibre, mordant and the dye molecules in some other favourable conditions of dyeing and this may be true even for the case of fibre-mordanting system (b).
4 Conclusions

4.1 From the study of thermodynamics parameters of dyeing, it is understood that the main mode of attachment of the jackfruit wood colourant to bleached jute and cotton fabrics occurs mainly through hydrogen bonding in case of fibre-mordanting systems (a), (a'), and (b') and through coordinated complex formation in case of fibre-mordanting system (b).

4.2 The absorption isotherms are found to be linear for fibre-mordanting systems (a), (a'), and (b'), while the same is found to be non-linear and Langmuir absorption isotherm type for fibre-mordanting system (b).

4.3 Jute and cotton fabrics pre-mordanted with harda and FeSO₄ always show higher dye uptake and higher rate of dyeing than that obtained for jute and cotton fabrics pre-mordanted with harda and Al₂(SO₄)₃. Between jute and cotton fabrics pre-mordanted with harda and FeSO₄, jute always shows higher dye uptake and higher rate of dyeing than cotton.

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References