# STUDIES ON KINETIC AND THERMODYNAMIC PARAMETERS OF NATURAL DYE EXTRACTED FROM *PUNICA GRANATUM* ON PROTEIN FIBRES

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**Abstract:** *Punica granatum* has been used as a dye for colouration of wool and silk fibres in absence and presence of inorganic salts or mordants. Colouration of those protein fibres with such colourant from an acidic dye bath (pH ~ 4.0) produces appreciable colour yield. Treatment of wool and silk with aluminium sulphate and ferrous sulphate at $70^0$C temperature for 45 minutes prior to dyeing produce significant improvements in the property profiles of dyed substrates. Such pretreatments specially imparted higher order of depth of shade, fastness to light of the dyed substrates and colour retention on washing than those of the respective dyed substrates having not been subjected to such pretreatments with the above inorganic salts. Methanol extract of *Punica granatum* has been used for determination of kinetic and thermodynamic parameters on wool and silk fibres. Diffusion co-efficient, time of half dyeing ($t_{1/2}$), adsorption isotherm, standard affinity and heat of dyeing has been calculated to assess kinetic and thermodynamic parameters. Measurement of kinetic parameter of dyeing indicates that wool has a lower rate of dyeing as compared to that of silk for application of *Punica granatum*. Studies on measurement of adsorption isotherm indicate that this dye has been adsorbed on protein fibres chiefly following Langmuir adsorption mechanism.

***Key words:*** Adsorption isotherm, Kinetic parameters, Punica granatum, Silk, Wool

## 1. Introduction

Pomegranate is the name given to a sweet juicy fruit obtained from the cultivated species *Punica granatum* and *Punica protopunica*. *Punica granatum* is cultivated in tropical and subtropical parts, whereas *Punica protopunica* is found in the Socotra Island [1]. Pomegranate is appreciated for its cool refreshing juice with sweet acidic taste and also for its medicinal properties. The rind of such fruit is the source of natural tannin and is red to brown in colour. Such fruit rind contains about 25% of an ellagi-tannin-flavogallol as the colouring component [2], the structure of which is given in figure 1.

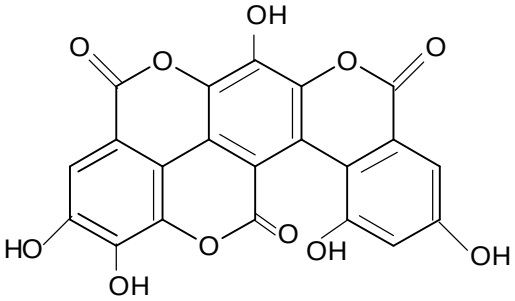


***Figure 1:*** *Flavogallol: Colouring component of Punica granatum*

The application of dye obtained from *Punica granatum* fruit rind on wool and silk in the presence and absence of environment-friendly mordanting agents has been studied [3] and the

dyeing of those fibres with this colourant is found to be effectively accomplished at pH ~ 4.0. Pre- and post-mordanting employing ferrous sulphate and aluminium sulphate improve the colour uptake, light fastness and colour retention on repeated washing [3]. Since the preliminary studies show encouraging results, hence an attempt has been made to conduct kinetic and thermodynamic studies of this colourant on wool and silk fibre to understand the theoretical aspect of dyeing.

## 2. Materials and Methods

### Materials

Silk and wool fibres with average diameters of $12.4 \times 10^{-4}$ cm and $7.2 \times 10^{-4}$ cm respectively were used for studies of kinetic and thermodynamic parameters. *Punica granatum* dye, obtained from M/s ALPS Industries Ltd. India, was used after purifying it by dissolving in methanol, followed by filtration and recrystallisation. All the chemicals used in the study were either of analytical reagent grade and/or of laboratory reagent grade.

## 3. Methods

### Degumming and bleaching of silk

In order to remove sericine, the silk fibre was degummed at $90^0$C for 1 h in an aqueous solution containing olive oil soap (6g/l) and sodium carbonate (2g/l) at a fibre-to-liquor ratio of 1:20 (w/v). Bleaching of the degummed silk fibre was performed at $85^0$C for 30 min using a solution containing hydrogen peroxide (0.9%), non-silicate stabilizer (0.15%) and sodium carbonate (0.1%). Degummed and bleached fibre was washed thereafter at $70^0$C for 10 min, cold washed and finally dried.

### Scouring, bleaching and pre-oxidation of wool fibre

Scouring and bleaching of wool fibre was performed as per the standard procedures [4]. Some portions of those fibre was oxidised by treatment with sodium hypochlorite solution at room temperature for 40 minutes [4].

### Estimation of percentage exhaustion

The exhaustion (dye uptake) of *Punica granatum* from its aqueous solution to wool and silk fibres during application was estimated from the difference of initial concentration of dye solution taken from the dye bath at the start of dyeing and final concentration of dye solution in the dye bath (including that of wash liquor) after exhaustion. The difference was expressed as percentage of initial concentration in each case. The concentration of colouring component in the test solution was obtained from the absorbance value of the latter with the help of a calibration curve previously constructed in a U2000, UV-visible absorbance spectrophotometer, HITACHI, Japan.

**Measurement of kinetic parameters**

**Time of half dyeing ($t_{½}$)**

The rate of dyeing of wool and silk fibres when dyed with *Punica granatum* was calculated and expressed as time of half dyeing ($t_{½}$). Time of half dyeing ($t_{½}$) was calculated from the plot of amount of dye exhausted in the fibre expressed as g/kg at different intervals of time during dyeing ranging from 15 minutes to 24 hours. The exhaustion of dye in the fibre (dye uptake) was estimated in each case colorimetrically as described in earlier section. For study of kinetic parameter, pH of the dye bath was maintained at 4.2 ± 0.2 using 0.2M sodium acetate and 0.2M acetic acid buffer system and the dyeing was carried out at a fibre-to-liquor ratio of 1:1000 in a thermostatically controlled open bath beaker dyeing machine duly equipped with appropriate shaking device.

**Estimation of diffusion coefficient**

Estimation of diffusion coefficient was done in accordance with the appropriate formula obtained by Hill [5] as given below:

$$\frac{C_t}{C\alpha} = 1 - 0.692\left[\exp\left(\frac{\cdot 5.785Dt}{r^2}\right) + 0.190\exp\left(\frac{\cdot 30.5Dt}{r^2}\right) + 0.0775\exp\left(\frac{\cdot 74.9Dt}{r^2}\right)...\right]$$

Where, $C_t$ and $C_\alpha$ are the concentrations of dye in the fibre in g/kg at time‘t’ and at dyeing equilibrium respectively, ‘r’ is the radius of fibre and ‘D’ is diffusion coefficient.

**Estimation of thermodynamic parameters**

**Adsorption isotherm**

The plots of adsorption isotherm for the dye-fibre systems was obtained by determining the concentrations of dye in the fibre and that in the residual dye bath when equilibrium was obtained for dyeing of fibres with different initial concentrations of dye solutions at fibre-to-liquor ratio of 1:200 at a constant temperature of $60^0$C and $90^0$C for 24 hours following a standard procedure [5] in a thermostatically controlled open bath beaker dyeing machine duly equipped with appropriate shaking device. Concentrations of dye in the fibre after 24 hours were determined from the difference in concentration of dye in the respective dye bath after 24 hours of dyeing and that at the start of dyeing for applications of *Punica granatum*.

**Standard affinity**

Standard affinity $(-\Delta\mu)_T$ of *Punica granatum* for wool and silk fibres at two specific dyeing temperatures ($60^0$C and $90^0$C) was calculated from the following equation [6] as given below:

$$\frac{1}{[\mathrm{D}]_f} = \frac{1}{K[S]_f[D]_S} + \frac{1}{[S]_f}$$

$(-\Delta\mu)_T$ = Standard affinity at temperature T.
$[D]_f$ = concentration of dye in fibre (g/kg) when equilibrium is attained at dyeing temperature T.

$[D]_s$ = concentration of dye in residual dye bath (g/l) when equilibrium is attained at dyeing temperature T.

### Heat of dyeing

Heat of dyeing for *Punica granatum* on wool and silk fibres were calculated using a standard formula as given below [5].

$$\Delta H = \frac{\left[T_2 \Delta\mu_1 - T_1 \Delta\mu_2\right]}{\left[T_2 - T_1\right]}$$

Where, $T_1$ and $T_2$ are the dyeing temperatures and $\Delta\mu_1$ and $\Delta\mu_2$ are the standard affinity of *Punica granatum* at temperature $T_1$ and $T_2$ obtained using the formula detailed earlier.

## 4. Results and Discussions

### Measurement of kinetic parameters

### Rate of dyeing

Plots of dye uptake with dyeing time for application of *Punica granatum* on silk and wool fibres is shown in figure 2 and the results of time of half dyeing ($t_{1/2}$) for application of this colourant on those protein fibres are reported in table 1.

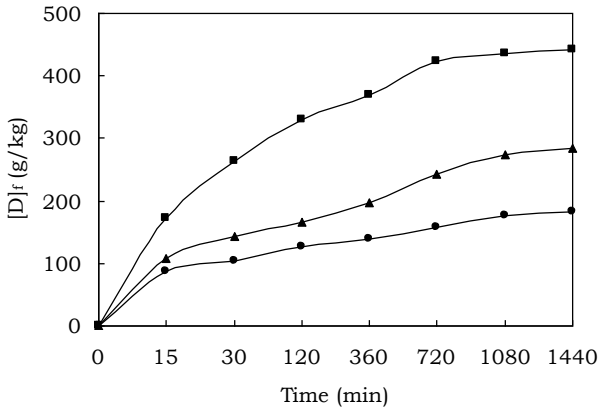


***Figure 2:*** *Plots of dye uptake with respect to time for (■) pre-oxidised wool, (▲) wool and (●) silk dyed with Punica granatum*

From table-1 it is observed that wool dyed at $90^0$C appeared to have more time of such half dyeing ($t_{1/2}$) than silk dyed at the same temperature. The above fact indicates that wool had a lower rate of dyeing as compared to that of silk. In case of wool, rate of dyeing mainly depends on the condition of the surface of the fibre than on its area [7]. Presence of a continuous hydrophobic epicuticle layer on the surface of the wool fibre affects the penetration of dye in such fibre adversely [7, 8]. Table 1 also shows time of half dyeing ($t_{1/2}$) for pre-oxidised wool fibre. Prior chlorination and subsequent sodium bisulphite treatment done for pre-oxidised wool fibre reduced the time of half dyeing ($t_{1/2}$) for application of *Punica granatum* in consequent to

oxidative attack and subsequent removal of oxidised epicuticle by sodium bisulphite treatment from the wool fibre.

**Diffusion coefficient**

The diffusion coefficient for application of *Punica granatum* on silk and wool fibres was calculated following Hill's equation [5] from the data obtained for $C_t$ and $C_\alpha$ and is given in table 1. Table 1 show that the diffusion coefficients of *Punica granatum* was higher for silk than that for wool fibre. Diffusion coefficient signifies the ease of penetration of the dye into the fibre when other factors are kept constant. Presence of epicuticle in wool fibre resists and retards the process of penetration of dye into such fibre as evidenced from the data of diffusion coefficient obtained for this colourant on pre-oxidised wool fibre (Table 1). For pre-oxidised wool, prior chlorination and subsequent bisulphite treatment caused substantial damage to the epicuticle and as a consequence penetration of water soluble *Punica granatum* colourant was facilitated.

***Table 1:*** *Kinetic parameters and diffusion coefficient of Punica granatum for silk and wool*

| Kinetic parameters | Silk | Wool | Pre-oxidised wool |
|---|---|---|---|
| $C_t / C_\alpha$ * | 0.56 | 0.50 | 0.60 |
| Time of half dyeing $t_{1/2}$ (min) | 15.0 | 30.0 | 23.0 |
| Diffusion Coefficient ($\times 10^{-11}$ ,$cm^2/s$) | 1.67 | 0.40 | 0.66 |

* $C_t$ and $C_\infty$ are the concentrations of dye in fibre expressed in g/kg after 30 minutes (t = 30 minutes) of dyeing and when equilibrium is reached ($\infty \sim$ 1440 minutes i.e. 24 hours).

**Thermodynamic parameters**

**Adsorption isotherm**

Quantitative estimation of dye in fibre $[D]_f$ and that in dye bath $[D]_s$ after dyeing of wool and silk fibres with *Punica granatum* till the dyeing equilibrium is attained for different levels of application dose of the colourant accomplished at two different dyeing temperatures ($60^0$C and $90^0$C) was done and the results obtained were plotted as adsorption isotherm and are given in figure 3 and 4 respectively. Such plots shows that *Punica granatum* is commonly adsorbed into both the protein fibres following Nernst adsorption mechanism up to different specified dose levels of such dye, after which adsorption of the dye into the protein fibres distinctly followed Langmuir adsorption mechanism. On overall assessment of the adsorption isotherm shown in figure 3 and 4, it appears that Langmuir adsorption mechanism is predominant for this dye-fibre system. In view of the structure of the dye (Figure 1), it is likely that the dye-fibre attraction depends chiefly on (i) ionic attraction arises out of the electron rich carbonyl groups of flavogallol and electron deficient – $NH_3^+$ groups of protein fibres (charge transfer force) and also on (ii) hydrophobic interactions between the hydrophobic portions of the dye and that of the protein fibres attached chemically to the amide groups. Owing to the above facts, adsorption of the dye should be considered as the resultant effect of (i) idealized electrostatic attraction of the

dye operative predominantly for the protonated protein fibres under acidic pH and of (ii) the idealized hydrophobic attraction operative between such dye and protein fibres. The adsorption isotherms drawn from the observed data for application of *Punica granatum* on silk and wool fibres indicate that, the nature of adsorption of the dye is similar to adsorption of typical acid class of dyes on protein fibres from aqueous medium [6]. However, in view of presence of oxygen atom in the structures of *Punica granatum*, the contribution of hydrogen bonds in the event of adsorption of the dye into protein fibres can not also be precluded.

## Standard affinity

In view of the fact that Langmuir adsorption mechanism is followed for adsorption of *Punica granatum*, the standard affinity was calculated following an equation suitable for Langmuir adsorption mechanism [6] and the results are expressed in table 2. Results show that the standard affinity for the above dye for wool is more than that for the silk fibre at the two dyeing temperatures studied ($60^0$C and $90^0$C). More affinity of the above dye for the wool than that for silk is the consequence of presence of (i) more number of amino groups in wool fibre than that in silk [9] and (ii) more amorphous region in the morphological structure of wool fibre than that in the silk fibre [7], which makes the positive site of the substrate more available and accessible for the negatively charged dye. Increase in dyeing temperature from $60^0$C to $90^0$C resulted in a common increase in the value of standard affinity during application of *Punica granatum* on both the above protein fibres. Increase in kinetic energy of the system, reduction in viscosity [10] and increase of swelling of the substrate fibre [5, 7] with consequent increased accessibility are the facts responsible for increased affinity of the dye for the wool and silk substrates.

***Table 2:*** *Calculated values of the standard affinity and heat of dyeing for Punica granatum on wool and silk*

| Standard affinity (KJ mol $^{-1}$) | | | | Heat of dyeing (KJ mol $^{-1}$) | |
|---|---|---|---|---|---|
| Wool | | Silk | | Wool | Silk |
| $60^0$C | $90^0$C | $60^0$C | $90^0$C | | |
| 14.56 | 18.91 | 13.23 | 17.63 | 33.72 | 35.61 |

## Heat of dyeing

Heat of dyeing was calculated using the relationship described in the Materials and Methods section for this dye – fibre system and the results are also given in table 2. From the data in table 2, it appears that the dye – fibre system considered in this study have positive value of heat of dyeing. Such positive value indicates that the adsorption of the above dye on both wool and silk fibres is an endothermic process.

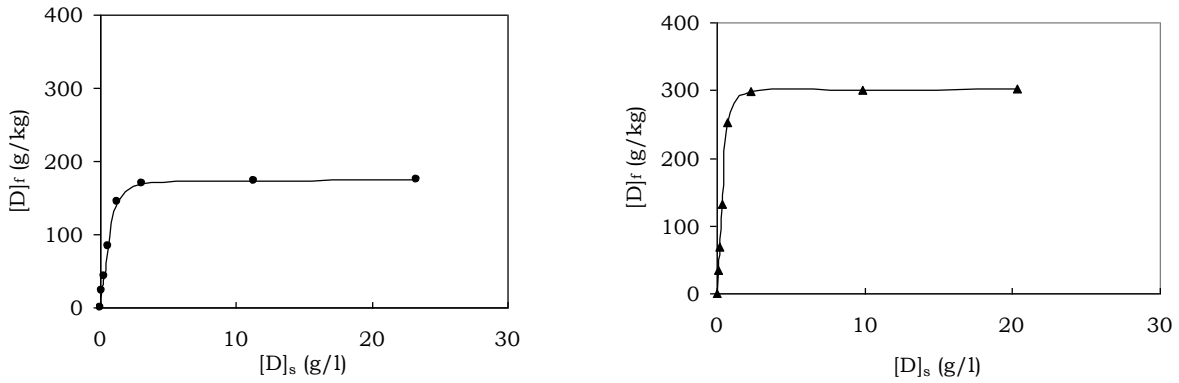


***Figure 3:*** *Adsorption isotherm for dyeing of wool with Punica granatum at (●) 60$^0$C and (▲) 90$^0$C*

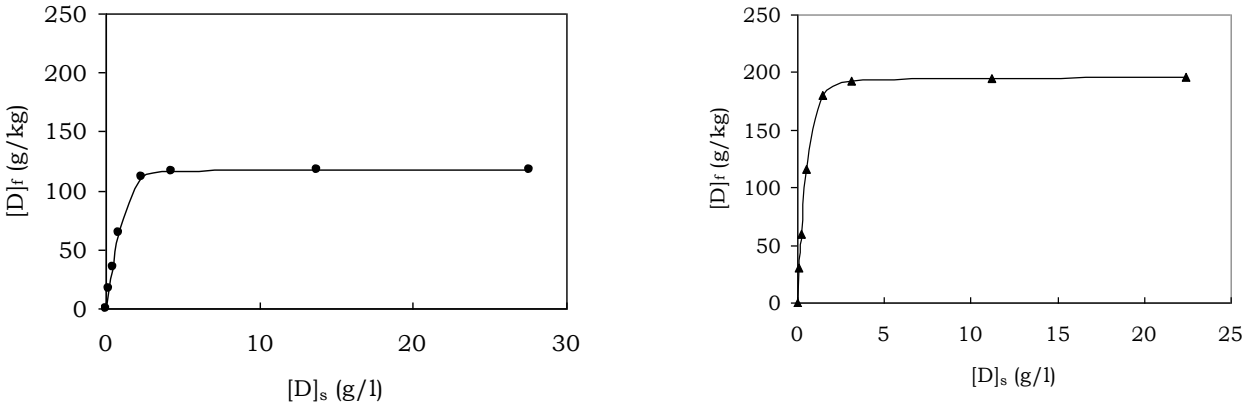


***Figure 4:*** *Adsorption isotherm for dyeing of silk with Punica granatum at (●) 60$^0$C and (▲) 90$^0$C*

## 5. Conclusion

The colouring component obtained from Punica granatum has an affinity for both wool and silk fibres. Measurement of kinetic parameter of dyeing indicates that, wool has a lower rate of dyeing as compared to that of silk for application of *Punica granatum*. Estimation of diffusion coefficients for dyeing of wool and silk with colourant obtained from *Punica granatum* indicates that, the quantity of the colourant diffuses through unit surface area of the substrates in unit time under unit concentration gradient was more in silk, than that in wool. Studies on measurement of adsorption isotherm indicate that, *Punica granatum* dye is adsorbed on protein fibres (wool and silk) chiefly following Langmuir adsorption mechanism. Affinity of the dye obtained from *Punica granatum* for the wool fibre is found to be more than that for the silk fibre. Estimation of heat of dyeing shows that the process of adsorption of the above natural dyes on protein fibres is endothermic in nature.

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