STUDIES OF KINETICS AND THERMODYNAMIC PARAMETERS OF CASHMERE DYEING WITH BIO-PREPARATION OF URTICA CANNABINA L

Tserendulam S.*, Ganchimeg Yu., Nadmid G. and Soyol-Undrakh Kh.

1 Research and Development Institute of Light Industry, Mongolian University of Science and Technology, Ulaanbaatar, Mongolia
2 Chemical Engineering Department, School of Applied Sciences, Mongolian University of Science and Technology, Ulaanbaatar, Mongolia

Abstract: In this study, dyeing Mongolian cashmere with bio-preparation extracted from Urtica cannabina L. was investigated. Dyeing experiments were carried out under varying pH, temperature and contact time. The results have been used to investigate the kinetic and thermodynamic parameters of dyeing cashmere. This process is pH dependent and it has been found that the most suitable condition is pH 4.5. Increase in adsorption capacity with increase in temperature indicates that the dyeing process is endothermic. Thermodynamic parameters like standard affinity (Δµ), standard enthalpy (ΔH) and standard entropy (ΔS) were evaluated.

Keywords: Cashmere; dyeing; natural dye; adsorption; nettle;

INTRODUCTION

Cashmere is a natural fibre taken from the cashmere down. It is one of the most luxurious and rare fibres. Cashmere yarn is renowned for being light, airy, delicate, glossy and its warmth. Thanks to these properties, cashmere is used as a raw material for luxury woven or knit products. Around 30.0% of the world cashmere is produced in Mongolia. As of 2015, 43.2% of the total livestock of Mongolia were cashmere goats. The Mongolian goat breed is often reddish, red, grey, black, dark brown, and white [1-3].

The process of producing a cashmere apparel includes a number of steps starting with fibre preparation to garment processing. Among the many production steps, dyeing is essential in order to produce cashmere garments, especially with natural dyeing for “Eco-organic product” [4].

International awareness about environment,
ecology and pollution control led to an upsurge in the use of natural dyes in the middle of the 20th century.

During the last few decades, increasing attention has been given by researchers all over the world towards various aspects of natural dye applications [5, 6].

Flora- and animal-based natural dyes/biopreparations are believed to be eco-friendly, safe and a viable substitute to synthetic colorants because of their non-toxic, non-carcinogenic and biodegradable nature [7, 8]. Moreover, natural dyes neither cause pollution nor waste water problems.

Natural dyes can give suitable and elegant colours through to the brightest colour to the fibers, yarns and fabrics. The major part of natural dyes are anthraquinone, anthocyanin and flavonoid dyes, or polyphenolic compounds most of which have yellow, red and brown shades (Bechtold and Mussak., 2009) [9].

Urtica.Cannabina L. is commonly known as a nettle which grows almost everywhere in Mongolia. The herb grows from 1.5-3.0 m in height. The herb is the chief source of Mongolian nettle and finds application in folk medicine and food. In spring, when the plant is young it has a rich content of vitamin C, which can be used as a raw material for hair shampoo and conditioner and can also be used for colouration of textile materials.

Major active constituents of Urtica. Cannabina.L are protein chlorophylls a, b, c and quercetin, luteolin, tannic and gallic acids, free amino acids, vitamins A, C, D, E, F, K, P and B-Complexes as well as thiamin, riboflavin, niacin and these plants also high a content of such metals as selenium, zinc, iron and magnesium.

Most of the natural yellows are derivatives of hydroxyl and methoxy substituted flavones and isoflavones. Flavonoids add brilliant colours to wool and silk, the structure of which is given in Figure 1.

The objectives of this work are: (1) to determine optimum condition of dyeing; (2) to estimate thermodynamic and kinetic parameters of the process; and, (3) to determine a suitable model describing the isotherms.

MATERIALS AND METHODS

Natural light grey dehaired cashmere (fineness 16.32 mkm, average length 38.6 mm) by the Gobi company of Mongolia was scoured with an aqueous nonionic surfactant solution at a temperature of 45°C for 20 minutes, then it was throughly rinsed with cold water and air dried at room temperature.
Plant, dye bio-preparation

Fresh natural *Urtica cannabina* L. leaves and stems were collected from the experimental garden of the Botanical Institute of Mongolia. The leaves were dried in a dark room under room temperature (20-25°C). After that, dried leaves were crushed into fine powder. This powder was used in all succeeding experiments to extract bio-preparation *Urtica cannabina* L. for dyeing. Dyeing bio-preparation solutions by water were prepared for 60 minutes, at a temperature of 80°C with the M:L ratio at 1:30 [12].

Dyeing Process

The dyeing of cashmere fibre was carried out at pH 4.5. Laboratory grade acetic acid (CH₃COOH) was used for adjusting the pH of the dyeing bath. The dyeing process of cashmere fibres was carried out at pH 4.5 condition using a bath containing extracted *Urtica cannabina* L. bio-preparation solution at a ratio of 1:50 for cashmere fiber and dyeing bio-preparation. The dyed cashmere fiber were washed with water and dried at room temperature. After which the surface analysis of the cashmere was carried out on undyed and dyed cashmere samples.

Thermodynamic studies

The thermodynamic parameters of the process, such as standard affinity, Δµ₀ (kJ/mol), standard entropy, ΔS₀ (J/mol·K) and standard enthalpy, ΔH₀ (kJ/mole) were calculated by using the following equation [1, 2, 3]:

\[-\Delta\mu_0 = RT\ln\left(\frac{D_f^{eq}}{D_f}\right)\]

\[K_e = \frac{C_{ad}}{C_e} = \frac{V}{m}\]

\[\ln K_e = \frac{\Delta H_0}{RT} + \frac{\Delta S_0}{R}\]

where, \(K_e\) is the equilibrium constant, \(C_{ad}\) is the adsorbed dye concentration (mg/l), \(C_e\) is the equilibrium dye concentration, \(V\) is the volume (l) and \(m\) is the mass of the cashmere fiber (g); \(R\) is the gas constant (8.314 J mol⁻¹ K⁻¹); \(T\) is the absolute temperature (in Kelvin).

The variations of ΔH₀ and ΔS₀ were calculated from the slopes and intercepts of the plot of lnKₑ versus 1/T are linear, respectively.

Kinetics of dyeing

Kinetic studies were carried out for the time periods ranging from 30 minutes to 100 minutes, using a bath containing extracted *Urtica cannabina* L bio-preparation solution at 1:50 M:L ratio. Kinetics of dyeing was studied by fitting first-order and second order reactions to experimental data. The pseudo first-order model is given in the following equation [4]:

\[\log(q_t - q_e) = \log q_e - \frac{k_1 t}{2.303}\]

The linear form of pseudo second order rate equation is given as follows [5]:

\[\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{k_2 q_e}\]

where, \(k_1\) (min⁻¹), \(k_2\) (g/mg min) are rate constants of pseudo-first order, pseudo-second order rate equation, \(q_t\) and \(q_e\) the amounts of dye into cashmere fibre at time \(t\) and equilibrium, respectively (mg/g);

The amounts of dye uptake by cashmere fiber were calculated using the following equation [6, 7]:

\[q_t = \frac{(C_0 - C_t)V}{m}\]

\[q_e = \frac{(C_0 - C_e)V}{m}\]

where, \(q_t\) and \(q_e\) are the amounts of dye in the cashmere fiber at time \(t\) and equilibrium, respectively (mg/g); \(C_0\), \(C_t\) and \(C_e\) are the initial, time \(t\) and equilibrium concentration of dye in the solution (mg/l); \(V\) is the volume of dye bio-preparation solution (L); \(m\) is the mass of cashmere fiber (g) and \(t\) is the sorption period (min).
**Isotherm model**

Langmuir and Freundlich isotherm model is commonly used to reflect the performance of adsorbents in adsorption processes.

Langmuir model assumes monolayer adsorption given by [8]:

\[
\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0}
\]  

(8)

Freundlich isotherm model assumes multilayer adsorption given by [9]:

\[
\ln q_e = \ln K_f + b \ln C_e
\]  

(9)

where, \( Q^0 (\text{mg/g}) \) is the maximum adsorption capacity, \( b \) is the Langmuir constant and \( K_f (l/g) \) and \( n \) are Freundlich constants [13-18].

**RESULTS AND DISCUSSION**

**Effect of dye bath pH on exhaustion of bio-preparation on cashmere fibre**

To investigate the effect of bio preparation pH on dyeing cashmere, the pH was varied 4.5 to 6.5. The experimental results are presented in Fig. 2.

![Figure 2. Effect of dye bath pH on dye exhaustion on cashmere fiber (initial concentration 630 mg/l, temperature 353K, t=60 min)](image)

But dye exhaustion decreased from 46.03% to 31.75% when the dyeing pH range conditions was 4.5, 5.5, 6.5. Hence, pH 5.0 was taken for further experimental work.
Effects of dyeing temperature and time periods on exhaustion of bio-preparation on cashmere fibre

The effect of temperature on dyeing cashmere is investigated at pH 5.0 condition. The temperature was varied from 333K to 363K, time was varied from 30 min to 100 min, while the initial concentration of bio-preparation was 630 mg/l.

Figure 3. Effects of dyeing temperature and time period on exhaustion of bio-preparation on cashmere fibre (initial concentration 630 mg/l, pH=5.0, ML 1:50)

Figure 4. Undyed cashmere picture by the SEM
In figure 3, dye exhaustion is increased by raising the temperature. The maximum value of dye exhaustion is reached at about 42.85% at 353K, 60 min. And the dyeing temperature at 363K, dyed at 40 min is 38.1%, and at 50 min it is 42.86%. But the observed dyed cashmere fibers were felted because the fiber cuticle was damaged when temperature was higher.

The cashmere fibre were dyed at 80°C and 90°C and with a duration of 50 and 60 minutes respectively, so as to study the dyeing time and temperature dependences in changing the surface morphology of the wool fibre under the influence of dyeing conditions. After dyeing, the surface morphology of the wool fibre was studied using a scanning electron microscope (Figures 4 and 5).

Figure 4 shows the SEM picture of undyed cashmere fibre in which the escarpments are prominent and well defined. The undyed cashmere fibre surface may be described as a smooth fibre surface.

Figures 5(a) and (b) are the SEM pictures of cashmere fibres dyed at 80°C for 60 minutes and at 90°C for 50 minutes respectively. The appearance of those fibres were quite similar to the untreated fibre. There was no visible change or damage on the scale structure when dyed at 80°C for 60 minutes, but the fibre cuticle’s scale dyed at a temperature of 90°C for 50 minutes was slightly lifted and was
observed to be broken.

The dye exhaustion of cashmere fibre dyed at 353K for different time periods has been carried out. The time of dyeing is calculated as 60 min. It has been observed that as the time of dyeing increases from 30 min after which equilibrium is achieved. A similar trend was reported for the kinetics and thermodynamics of dye extracted from *Arnebia Nobilis Rech.f.* on wool [19] and dyeing kinetics of wool yarn with *Rubia Tinctorium L.* [20].

Therefore, 353K and 60 minutes were chosen as suitable temperature and time for cashmere dyeing with bio-preparation.

**Thermodynamic and kinetic parameters**

Experimental results of the effects of temperature and time were used to calculate thermodynamic and kinetic parameters.

Thermodynamic parameters such as change in standard affinity (Δµ⁰), standard enthalpy (ΔH⁰) and standard entropy (ΔS⁰) were evaluated by the equation (1, 2, 3). ΔH⁰ and ΔS⁰ were calculated from the slope and intercept of the Vant Hoff’s plot of lnKc verses 1/T as shown in Fig. 6.

The thermodynamic parameters are given in Table 1.

![Figure 6. Vant-Hoff’s plot at concentration of 630 mg/l](image)

**Table 1. Thermodynamic parameters for cashmere dyeing with Urtica cannabina. L**

<table>
<thead>
<tr>
<th>Temperature, (K)</th>
<th>Bio preparation concentration, mg/l</th>
<th>Δµ⁰, (kJ/mol)</th>
<th>ΔH⁰, (kJ/mol)</th>
<th>ΔS⁰, (kJ/mol·K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>373</td>
<td>630</td>
<td>-13.25</td>
<td>63.5</td>
<td>151.4</td>
</tr>
<tr>
<td>343</td>
<td></td>
<td>-11.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>353</td>
<td></td>
<td>-9.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>363</td>
<td></td>
<td>-8.75</td>
<td></td>
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</tbody>
</table>

From Table 1, positive values of ΔH⁰ indicate that the dyeing of cashmere with *Urticacannabina L.* is an endothermic process.

The negative values of Δµ⁰ have been increasing slowly with a rise in temperature.

The increasing of the dyeing temperature will lead to higher dye affinity up to a certain temperature limit, above which the dye uptake
will gradually reduce. This suggests that the adsorption process is spontaneous in nature and spontaneity decrease with the increase in temperature.

In other words, practically there is a decrease in dye affinity and there are little or almost no significant changes in dye affinity with increase of dyeing temperature. Similar results were reported earlier in similar studies [21-24].

The kinetic parameters have been given in Table 2. The $k_1$ and $q_e$ have been calculated from the slope and intercept of plots of log ($q_e$-$q_t$) versus $t$ according to pseudo-first-order model (Fig. 7) and versus $t$ according to pseudo-second-order model (Fig. 8) $q_e$ and $k_2$ from the slope and intercept have been calculated.

From Table 2, the correlation coefficient values for the pseudo-second-order rate equation 0.985 was found to be higher than the pseudo-first-order rate equation of 0.942.

![Figure 7. Pseudo-first-order plots for dyed cashmere](image1)

![Figure 8. Pseudo-second-order plots for dyed cashmere](image2)
In addition, the value of the absorption capacity calculated by the pseudo-second-order is in close proximity to the experimental value.

**Table 2. Kinetic parameters for cashmere dyeing with Urtica cannabina L.**

<table>
<thead>
<tr>
<th></th>
<th>( k_1 ) (min(^{-1}))</th>
<th>( q_e ) (mg·g(^{-1}))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order</td>
<td>56.9 x10(^{-2})</td>
<td>16.57</td>
<td>0.94</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>11.92x10(^{-4})</td>
<td>14.82</td>
<td>0.982</td>
</tr>
<tr>
<td>Experimental value</td>
<td></td>
<td>15.07</td>
<td></td>
</tr>
</tbody>
</table>

This indicates that cashmere dyeing process can be explained with pseudo-second-order equation. These data suggest that the mechanism of adsorption of pseudo-second-order is predominant and that the overall rate adsorption of *Urtica cannabina* L. dye’s bio preparation is more likely to be controlled by the chemisorption process [25].

In fact, this was already anticipated due to the chemical attraction earlier discussed and it was also reported by Tserendulam and Das et al [26, 27].

**Dyeing isotherm**

The isotherms of cashmere dyeing are presented in Figure 9.

![Figure 9. Nonlinear adsorption isotherm of Langmuir, Freundlich model and experimental values](image)

Cashmere dyeing is better adjusted to the Freundlich model according to the experimental data. The Freundlich model assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and are not equal. It predicts the formation of multi-layers (Freundlich, 1906). Possibly, the monolayer occurs with the interaction between the hydroxyl groups of the dye and the amino groups of the protein fibres [25]. The multi-layer is formed through the chemisorption of other radicals that interact.
with the dye.

Therefore, the Freundlich model that emphasizes the importance of both phenomena comes naturally as the model that may represent the equilibrium data of the dyeing bio-preparation extracted from *Urtica cannabina* L. in the cashmere. Parameters for the dyeing isotherm for cashmere dyeing are shown in Table 3.

**Table 3. The theoretical parameters of isotherms for cashmere dyeing**

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Isotherm constants</th>
<th>Corbent: cashmere</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$Q_0$, mg/g</td>
<td>66.66</td>
</tr>
<tr>
<td></td>
<td>$b$</td>
<td>0.0028</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_f$, l/g</td>
<td>3.68</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>1.26</td>
</tr>
</tbody>
</table>

Equilibrium data were fitted to the Freundlich model, which is in total agreement with the isotherm shape for dyeing cashmere.

**CONCLUSIONS**

With the increase in dyeing time, the dye uptake increases on cashmere up to 50 min of dyeing time and then gradually slows down and the dyeing process becomes stable. The best result of dyeing the cashmere was achieved using a temperature of 80°C, pH 5.0, 60 minutes and initial dye concentration of extracted by water with an ML ratio of 1:30. Also the best result of bio-preparation extracting was achieved using a temperature of 80°C, 80 minutes and ML ratio 1:30 by water of *Urtica cannabina* L. according to our experimental data [12, 28].

The thermodynamics parameters of cashmere dyeing are endothermic and spontaneous. Therefore, there will be an increase in dye absorption with an increase in temperature of dyeing after which the dyeing process slows down and dye adsorption at a certain temperature where equilibrium of dyeing is achieved. The kinetics of dyeing can be fitted by pseudo-second-order model as a correlation coefficients and values of the absorption capacity. The pseudo-second-order model may successfully represent the kinetic experimental data for cashmere dyeing. According to the kinetic and equilibrium results, it was concluded that chemisorption is quite important in cashmere dyeing. The equilibrium data for cashmere fibre can be represented by the Freundlich model.

Considering that the dyeing process has a great contribution of chemisorption which promoted good colour fastness to laundering, it can be concluded that dyeing with *Urtica cannabina* L. has huge advantages as the textile waste water is much more biodegradable than the textile waste water generated with synthetic dyes.
REFERENCES


