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Thermodynamics Study of Lac Dyeing of Silk Yarn Coated with Chitosan

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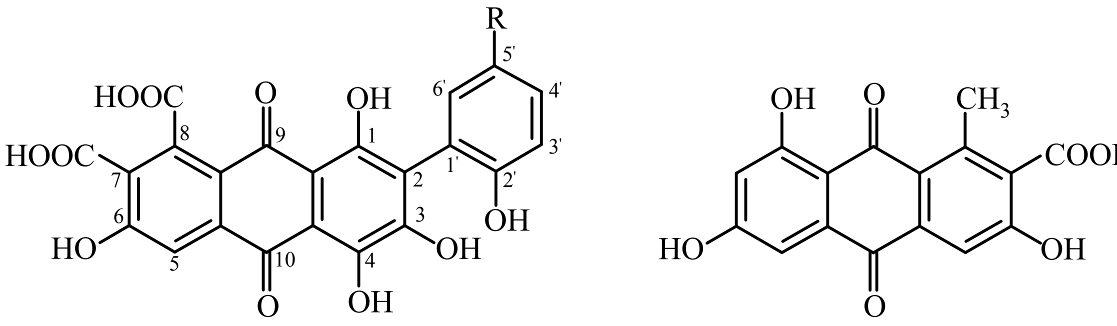
ABSTRACT

A thermodynamic study of lac dyeing of silk pretreated with chitosan at pH 3.0 was investigated in a batch system. It was found that the adsorption of lac dye on silk pretreated with chitosan could be described by the Langmuir isotherm. The results showed that the pretreatment of silk with chitosan provided an enhancement of dye uptake on silk and also decreased the dye desorption from silk yarn compared with the results in the absence of chitosan. The negative value of the enthalpy change (ΔH^{o}) for the adsorption of lac dye on silk pretreated with chitosan indicated that the adsorption process was an exothermic one.

Keywords: Lac dye, thermodynamics, silk, chitosan, laccaic acid, natural dye

INTRODUCTION

Lac dye is a natural red-colored dyestuff extracted from stick lac, which is a secretion of the insect *Coccus laccae* (*Laccifer lacca* Kerr.) [1]. Lac dye, which is the soluble part of stick lac, is composed mainly of 2 major anthraquinone-based components: laccaic acids A and B [2-8]; the minor components, laccaic acids C, D and E, have also been isolated [7-10] (**Figure 1**). In the north and the northeast of Thailand, lac dye is used as a natural red dyestuff for cotton and silk dyeing but the fastness property and consistency in production is still a problem to be solved. Many studies on silk dyeing with lac dye have involved attempts to increase its fastness (e.g. wash fastness) by using different metal salts (e.g. potassium dichromate, tin chloride, stannous chloride, ferrous sulfate and copper sulfate) as mordants [11-13]. Mordants can form complexes with the dye molecules via coordinate bonds. These complexes are insoluble and hence improve the staining ability of a dye as well as increasing its fastness [14]. Unfortunately, wastewater containing these mordants may affect the environment and public health. To avoid these problems, the pretreatment of silk with chitosan, derived from a natural polymer and containing amino groups (**Figure 2**), has been investigated as an alternative to increase the dyeability of a dye to silk. According to Waly and co-workers [15], the pretreatment of silk with chitosan increased the dye uptake and improved the light yellowing resistance compared to the untreated silk. Also, an increase in dyeability of tussah silk fabric after pretreatment with chitosan under acidic conditions was observed compared to the untreated fabric [16,17]. In previous work, the adsorption of lac dye on silk and the kinetics of dyeing at pH 3.0 were investigated [18]. However, the thermodynamics of lac dyeing of silk pretreated with chitosan has not been reported. Therefore, this research work aims to study the thermodynamic properties of lac dyeing of silk pretreated with chitosan. The scientific results from this study may lead to a better alternative for silk dyeing with lac dye by increasing the dye uptake of the silk yarn.



Laccaic acid A R = $CH_2CH_2NHCOCH_3$ MW 537

Laccaic acid B R = CH_2CH_2OH MW 496

Laccaic acid C R = $CH_2CHCOOH$ (NH_2) MW 539

Laccaic acid E R = $CH_2CH_2NH_2$ MW 495

Laccaic acid D MW 314

Figure 1 Chemical structures of the laccaic acids.

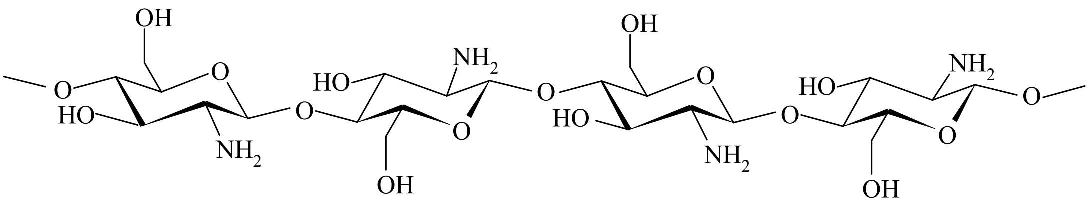


Figure 2 The chemical structure of chitosan.

MATERIALS AND METHODS

Materials and Chemicals

1. Silk Yarn Preparation

The silk yarn used was purchased from villagers in Nakhon Ratchasima, Thailand. To remove the sericin gum, the silk yarn (1 kg) was added to warm water (5 l) with soap flakes (*ca* 100 g), sodium silicate (10 g), sodium carbonate (50 g) and 40 % hydrogen peroxide (100 ml). The mixture was then left for 1 h. The silk was then removed, washed with water, squeezed to remove excess liquor and air dried. Finally, it was treated with 0.5 M HCl (*ca* 3 l) at room temperature for 30 min and then removed and washed with deionized water until the rinsed water was neutral. The silk yarn was then dried at room temperature.

2. Preparation of Lac Dye

Stick lac (500.42 g) from the Rain tree, *Samanea saman* (Jacq.) Merr. (*Pithecolobium saman*, Mimosaceae), in northeast Thailand (Nakhon Ratchasima) was finely powdered (18 mesh) in a grinding mill. The powdered material was extracted with deionized water (1.5 l) at 60 ºC for 1 h. The aqueous solution was filtered and the filtrate concentrated under reduced pressure (rotary evaporator) to give a crude lac dye extract (35.33 g), which was then used without further purification.

3. Silk Pretreatment with Chitosan

Chitosan (medium molecular weight, viscosity 200.000 cps, CAS 9012-76-4, FW 161) was purchased from the Aldrich Chemical Company. A 1 % (w/v) stock solution of chitosan was prepared by dissolving the required amount of chitosan in a 1 % (v/v) aqueous acetic acid solution. The silk yarn (50 g), prepared as noted above, was then immersed directly in a 0.3 % (v/v) aqueous solution of chitosan (2 l) (prepared from the stock solution) at room temperature for 1 h. After this time the yarn was removed and dried at 100 ºC for 30 min and cured at 160 ºC for 10 min. The silk yarn, after pretreatment with chitosan, was rinsed with water at 40 ºC and allowed to air dry in the laboratory.

Concentrations of 0.6, 0.8 and 1.2 % (v/v) aqueous solutions of chitosan were found to give an uneven distribution of lac dye adsorbed on the silk yarn. Therefore, a 0.3 % (v/v) aqueous solution of chitosan was chosen to enhance the dye uptake of the silk sample in this study.

Instruments

A Cary 1E UV-visible spectrophotometer was employed for absorbance measurements using quartz cells of 1 cm path length.

A pH meter (Mettler Delta 320, UK) was used to measure the pH of the lac dye solutions.

A thermostatted shaker bath (Heto-Holten A/S Denmark, Type SBD-50 cold), operated at 150 strokes/min, was used to study the adsorption isotherm of lac dyeing of silk untreated and pretreated with chitosan.

Methods

1. Dye Adsorption and Desorption Studies

The silk yarn with and without pretreatment with chitosan was dyed with an initial dye concentration of 320 mg/l in a thermostatted shaker bath operated at 150 strokes/min. The dyeing conditions were: pH 3.0 and 30 °C. The dye solution (50 ml) in a conical flask (125 ml) was shaken in a thermostatted shaker bath operated at 150 strokes/min. After 30 min, the silk sample (0.50 g), which had been pre-warmed in the thermostatted bath for 30 min, was immersed in the dye solution. The silk samples were then rapidly withdrawn after different immersion times. Dye concentrations were determined at time zero and at subsequent times using a calibration curve of absorbance at λ_{max} 487 nm (Cary 1E UV-visible spectrophotometer) versus the dye concentration of standard lac dye solutions. The amount of dye adsorbed per unit weight of silk sample (q_t) at any time (mg/g silk) was calculated by a mass-balance relationship Eq. (1) as follows:

$$q_t = (C_0 - C_t)\frac{V}{W} \tag{1}$$

where C_0 and C_t are the initial and dye concentrations (mg/l) after dyeing time t respectively, V is the volume of dye solution (l) and W is the weight of silk sample (g) used.

To study the desorption of lac dye from a silk sample at 30 °C, deionized water (50 ml) in a conical flask (125 ml) was shaken in a thermostatted shaker bath operated at 150 strokes/min. After 30 min, the dyed silk sample (0.50 g), which had been pre-warmed in the thermostatted bath at 30 °C for 30 min, was immersed in deionized water. The sample was then rapidly withdrawn after a set time of immersion. The desorbed dye concentration (q_{de}) was determined using a calibration curve of absorbance at λ_{max} 487 nm (Cary 1E UV-visible spectrophotometer) versus the dye concentration of standard lac dye solutions. The amount of the dye desorbed from the silk sample (q_{de}) was calculated and then subtracted from the amount of the dye adsorbed per unit weight of silk sample at equilibrium (q_e).

2. Batch Equilibrium Experiments

Different lac dye concentrations were freshly prepared in deionized water. The pH of each dye solution was adjusted to 3.0 with glacial acetic acid. The experiments were carried out by agitating the silk yarn (0.5 g) with different concentrations of dye solution (50 ml) in a conical flask at 30, 45 and 60 °C for 60 min using a thermostatted shaker bath operated at 150 strokes/min. The amount of dye in the solution was monitored by UV-visible absorption spectroscopy at λ_{max} 487 nm. The initial and equilibrium dye concentrations were determined using a calibration curve of absorbance versus the dye concentration of standard lac dye solutions. Eq. (2) was used to calculate the amount of dye adsorbed per unit weight of silk sample at equilibrium (q_e) (mg/g silk).

$$q_e = (C_0 - C_e)\frac{V}{W} \tag{2}$$

In Eq. (2) C_0 and C_e are the initial and equilibrium dye solution concentrations (mg/l) respectively, V is the volume of the dye solution (l), and W is the weight of silk yarn (g) used.

RESULTS AND DISCUSSION

The Effect of pH on the Adsorption of Lac Dye on Silk Pretreated with Chitosan

The pH of the dye solution is one of the most important parameters controlling the adsorption capacity of the dye onto silk. The effect of pH on the adsorption of lac dye onto silk pretreated with chitosan at 30 °C with an initial dye concentration of 500 mg/l is shown in **Figure 3**, which indicates that the adsorption of lac dye increases with decreasing pH over the pH range of 5.1 - 3.0 and remains constant in the pH range of 3.0 - 2.5.

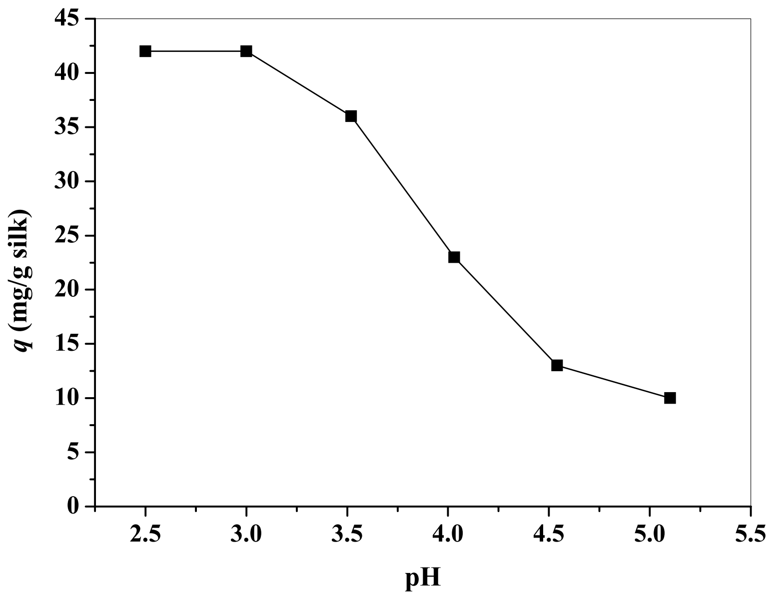


Figure 3 The effect of pH on the adsorption of lac dye onto silk pretreated with chitosan at 30 °C and 1 h contact time.

This is due mainly to an increase in the protonation of the amino ($-NH_2$) groups of chitosan. The protonated amino ($-NH_3^+$) groups of chitosan could interact with the surface of silk via hydrogen bonding and ion-dipole interactions. Laccaic acid A, containing carboxylic acid (–COOH) groups, hydroxyl (–OH) groups and amide (–NHCO–) groups may then bind to the pretreated silk via hydrogen bonding and ionic interactions under acidic conditions. The initial pH of 3.0 was used throughout this study.

Adsorption and Desorption Studies

Under the same conditions, silk pretreated with chitosan showed a higher dye uptake than untreated silk over a time range of 1 - 180 min as shown in **Figure 4**. Desorption of lac dye from silk pretreated with 0.3 % (v/v) aqueous chitosan compared to that from untreated silk was also investigated. The dye bath was replaced with deionized water over a time range of 181 - 360 min. The amounts of the dye desorbed from the silk (q_{de}) in both cases were calculated and then subtracted from that adsorbed per unit weight of silk sample at equilibrium (q_e).

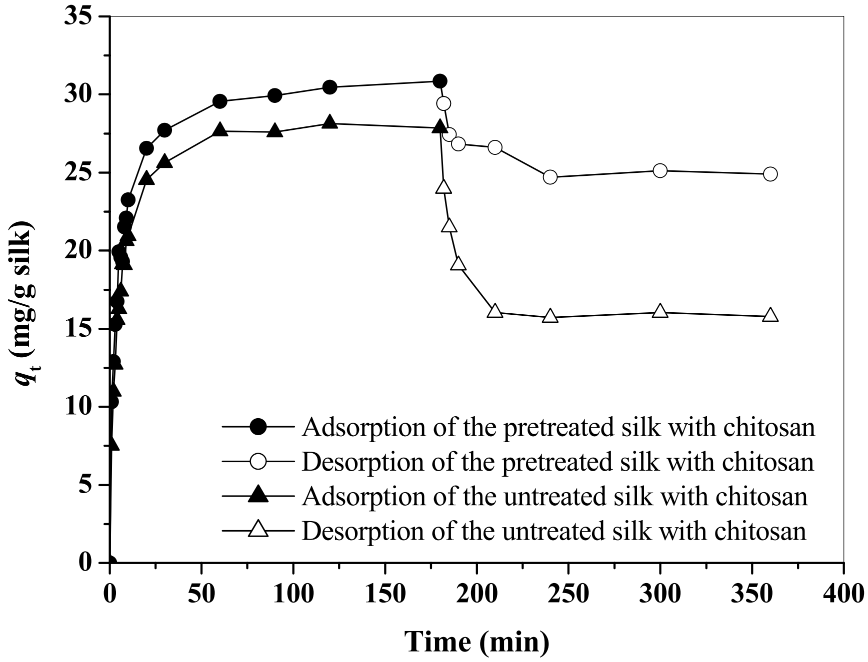


Figure 4 Effect of chitosan on adsorption-desorption of lac dye on/from silk.

As seen from **Figure 4**, the pretreatment of silk yarn with a 0.3 % (v/v) aqueous solution of chitosan enhanced the dye uptake and also decreased the dye desorption from silk yarn compared to the untreated silk yarn. The results supported the fact that the silk fibroin chains can form hydrogen bonds with chitosan and use the protonated amino ($-NH_3^+$) groups of chitosan to hold the lac dye. Chitosan could then act as an organic mordant to enhance the dye uptake of the silk surface resulting in lac dye sorption on the silk. Similar observations were reported for the adsorption of acid, direct and disperse dyes onto tussah silk fabric pretreated with chitosan [16,17].

Adsorption Isotherm

The Langmuir model is used to describe equilibrium adsorption isotherms. The most widely used Langmuir equation, which is valid for monolayer adsorption onto a surface with a finite number of identical sites, is expressed as [19]:

$$q_e = \frac{QbC_e}{1+bC_e} \tag{3}$$

where Q (mg/g silk) is the maximum amount of the dye per unit weight of silk sample to form a complete monolayer coverage on the surface bound at high equilibrium dye concentration C_e, q_e is the amount of dye adsorbed per unit weight of silk samples at equilibrium, and b is the Langmuir constant related to the affinity of binding sites. **Figure 5** shows the experimental isotherms for adsorption of lac dye on silk pretreated with chitosan at different temperatures.

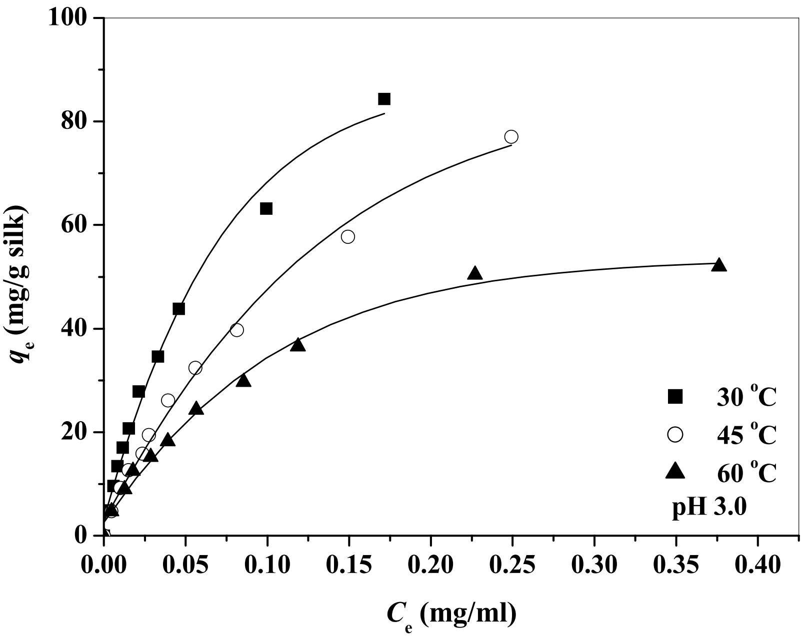


Figure 5 Adsorption isotherm of lac dye on silk pretreated with chitosan in an initial dye concentration range 52 - 1,022 mg/l.

The linear form of the Langmuir equation can be represented in the following form:

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \left(\frac{1}{Q}\right)C_e \tag{4}$$

From Eq. (4) a linearized plot of (C_e/q_e) versus C_e is obtained as shown in **Figure 6**, and Q and b are computed from the slope and intercept of Eq. (4). **Table 1** lists the calculated values of the parameters Q and b. It was found that the equilibrium data fitted well with the Langmuir model ($R^2 > 0.99$) in the entire concentration range (52 - 1,022 mg/l). The adsorption capacity (Q) values decreased with increasing temperature. The results indicate that the adsorption of lac dye onto silk pretreated with chitosan is an exothermic process.

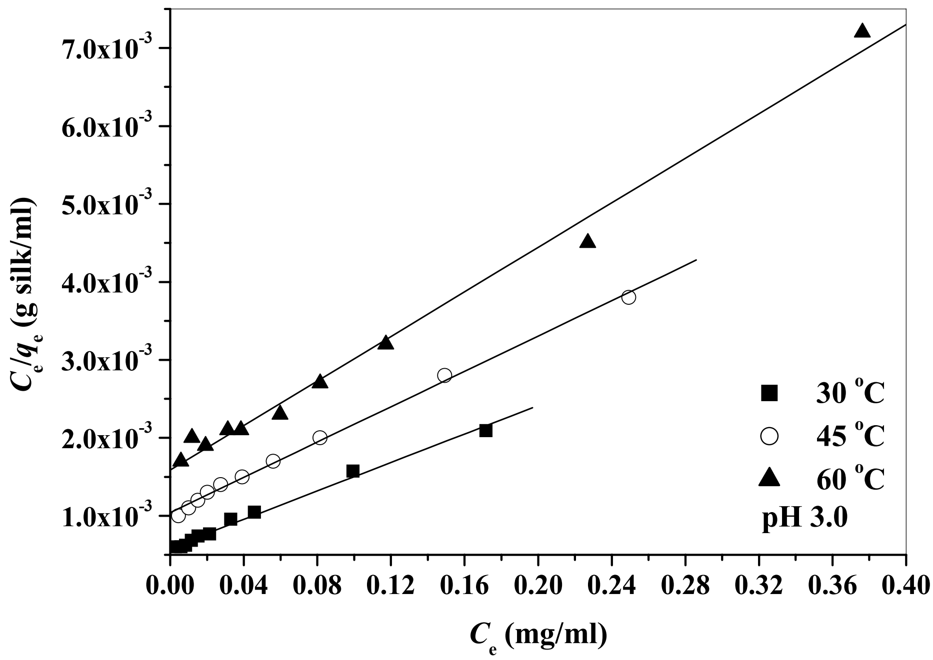


Figure 6 The linearized Langmuir adsorptions for the adsorption of lac dye onto silk pretreated with chitosan in the initial dye concentration range 52 - 1,022 mg/l.

Table 1 Langmuir isotherm constants for the adsorption of lac dye onto silk pretreated with chitosan at different temperatures.

Temperature (°C)	Langmuir		
	Q **(mg/g silk)**	***b*** **(mg/ml)**	R^2
30	109.65	15.17	0.9909
45	86.96	11.55	0.9954
60	69.44	9.00	0.9900

The essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor for equilibrium parameter, R_L, defined as follows:

$$R_L = \frac{1}{(1 + bC_0)} \tag{5}$$

where C_0 is the initial concentration of lac dye (in mg/l), and b is the Langmuir constant (l/mg). The value of R_L indicates the type of isotherm, i.e. irreversible (R_L= 0), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$).

In the present study, the values of R_L (**Table 2**) were observed to be in the range of 0 - 1, indicating that the adsorption of lac dye onto silk pretreated with chitosan was favourable for this study.

Before reaching equilibrium, the relationship between the amount of dye adsorbed per unit weight of silk sample at equilibrium (q_e) and the equilibrium dye concentrations (C_e) can be considered as a linear function. Therefore, its slope is constant and it yields a partition ratio (K). Thus, the standard affinity ($\Delta\mu°$) can be computed using the Eq. (6) [20]:

$$\Delta\mu° = -RT \ln K \tag{6}$$

where R is the gas constant. **Table 3** lists the calculated values of the partition ratio (K) and the standard affinity ($\Delta\mu°$) of lac dye on silk pretreated with chitosan. The data showed that the partition ratio (K) decreased with increasing temperature, thereby indicating that the process is an exothermic one. The negative value of the standard affinity ($\Delta\mu°$) indicated the spontaneous nature of dye adsorption on silk pretreated with chitosan. Similar observations were reported for the adsorption isotherm of silk dyeing with laccaic acids, from which the erythrolaccin had been removed, without pH control [21].

Table 2 Langmuir isotherm data for the adsorption of lac dye onto silk pretreated with chitosan at different temperatures.

Temperature (°C)	*b* (l/mg)	Initial lac dye concentration C_0 (mg/l)	R_L
30	15.17×10^{-3}	52	0.560
		103	0.390
		143	0.315
		183	0.264
		223	0.228
		303	0.179
		383	0.147
		485	0.120
		734	0.082
		1,022	0.061
45	11.55×10^{-3}	52	0.626
		103	0.457
		143	0.377
		183	0.321
		223	0.280
		303	0.222
		383	0.184
		485	0.151
		734	0.106
		1,022	0.078
60	9.00×10^{-3}	52	0.682
		103	0.519
		143	0.437
		183	0.377
		223	0.333
		303	0.268
		383	0.225
		485	0.186
		734	0.132
		1,022	0.098

Table 3 Partition ratio (K) and standard affinity ($\Delta\mu°$) of the adsorption of lac dye onto silk pretreated with chitosan.

Temperature (°C)	Partition ratio (K)	Standard affinity ($\Delta\mu°$) (kJ/mol)
30	1,448.00	–18.33
45	828.59	–17.77
60	484.44	–17.11

Furthermore, the thermodynamic parameters including the heat of dyeing ($\Delta H°$) and entropy of dyeing ($\Delta S°$) were evaluated using the following equations:

$$\ln\frac{K_2}{K_1} = \frac{-\Delta H^{\circ}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{7}$$

$$\Delta\mu^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{8}$$

The heat of dyeing ($\Delta H°$) was calculated from the slope of the plot of ln K versus $1/T$ as shown in **Figure 7**. The values of $\Delta H°$ and $\Delta\mu°$ were then used together in Eq. (8) to calculate $\Delta S°$. The results are listed in **Table 4**.

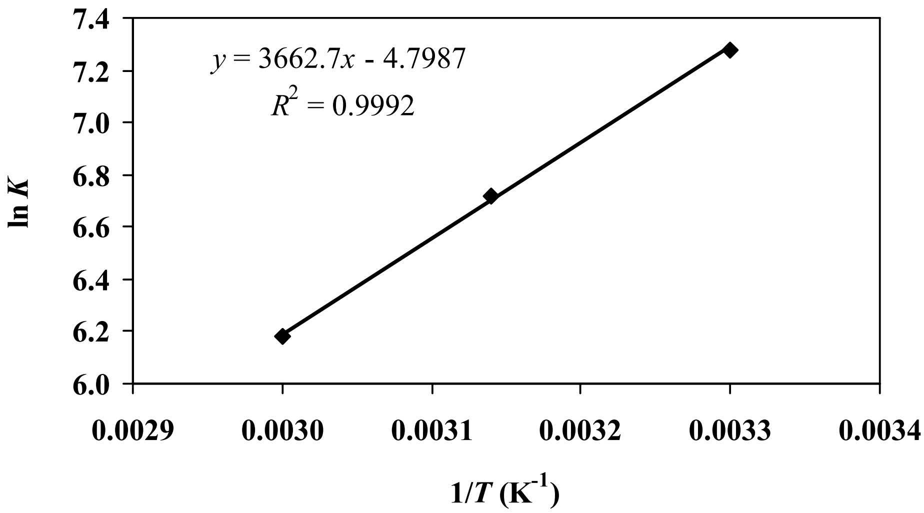


Figure 7 Plot of ln K against $1/T$ for the adsorption of lac dye onto silk pretreated with chitosan.

The negative value of $\Delta H°$ indicates that the adsorption of lac dye on silk pretreated with chitosan is an exothermic process. In addition, the negative value of entropy of dyeing ($\Delta S°$) also indicates that the randomness decreases at the solid-solution interface during the adsorption of lac dye on silk pretreated with chitosan.

Table 4 Heat of dyeing ($\Delta H°$) and entropy of dyeing ($\Delta S°$) for the adsorption of lac dye onto silk pretreated with chitosan.

Temperature (°C)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol·K)
30		–40.00
45	–30.45	–39.87
60		–40.06

Future work will be performed on the study of the thermodynamics of the adsorption of lac dye onto silk pretreated with chitosan in the presence of a crosslinking agent or alum. The resulting thermodynamic parameters will be compared with those for the adsorption of lac dye onto silk pretreated with chitosan at pH 3.0 from this study.

CONCLUSIONS

A thermodynamic study of lac dyeing of silk pretreated with chitosan has been conducted. It was found that the adsorption of lac dye on silk pretreated with chitosan could be described by the Langmuir isotherm ($R^2 > 0.99$). The adsorption capacity was found to be dependent on the pH of the dye solution and the optimal dye uptake of silk pretreated with chitosan occurred at pH 3.0 - 2.5. The negative values of $\Delta\mu°$ and ΔH^o indicated that the lac dye adsorption on silk pretreated with chitosan was a spontaneous and an exothermic process. Therefore, the pretreatment of silk yarn with a 0.3 % (v/v) aqueous solution of chitosan enhanced the dye uptake and also decreased the dye desorption from silk yarn compared with untreated silk yarn.

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บทคัดย่อ

มนตรา ไชยรัตน์

อุณหพลศาสตร์ของการย้อมสีครั่งบนเส้นไหมที่เคลือบด้วยไคโตซาน

งานวิจัยนี้ได้ศึกษาอุณหพลศาสตร์ของการย้อมสีครั่งบนเส้นไหมที่เคลือบด้วยไคโตซานที่พีเอช 3.0 โดยพบว่าการดูดซับของการย้อมสีครั่งบนเส้นไหมที่เคลือบด้วยไคโตซานเป็นการดูดซับแบบแลงเมียร์ (Langmuir isotherm) ผลการทดลองแสดงให้เห็นว่าการเคลือบเส้นไหมด้วยไคโตซานช่วยเพิ่มการดูดซับสีครั่งบนเส้นไหมและยังช่วยลดการหลุดของสีออกจากเส้นไหมเมื่อเปรียบเทียบกับเส้นไหมที่ไม่ได้เคลือบด้วยไคโตซาน ค่าลบของการเปลี่ยนแปลงเอนทัลปี (ΔH^{o}) สำหรับการย้อมสีครั่งบนเส้นไหมที่เคลือบด้วยไคโตซานชี้ให้เห็นว่ากระบวนการดูดซับเป็นปฏิกิริยาคายความร้อน

สาขาวิชาเคมี สำนักวิชาวิทยาศาสตร์ มหาวิทยาลัยวลัยลักษณ์ อำเภอท่าศาลา จังหวัดนครศรีธรรมราช 80161