

An adsorption and kinetic study of lac dyeing on silk

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Abstract

Adsorption and kinetic studies of lac dyeing of silk were investigated using, as optimal conditions, a pH of 3.0, a material to liquor ratio (MLR) of 1:100, an initial dye concentration of 450 mg/L and 60 min contact time. The progress of dye adsorption was monitored at λ_{max} 487 nm by visible spectroscopy. The experimental data fitted well to the Langmuir and Freundlich isotherms with a high correlation coefficient (R^2). The pseudo second-order kinetic model was indicated with the activation energy of 47.5 kJ/mol. It is suggested that the overall rate of lac dye adsorption is likely to be controlled by the chemical process. The values of the enthalpy (ΔH^\ddagger) and entropy of activation (ΔS^\ddagger) were 44.7 kJ/mol and -175.7 J/mol K, respectively. The free energy of activation (ΔG^\ddagger) at 30 °C was 97.9 kJ/mol. The activation parameters with and without erythrolaccin in the lac dye were similar, consistent with erythrolaccin only having a slight effect on the lac dyeing of silk. The free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) terms for the lac dyeing were also determined, and the negative values of ΔG° and ΔH° obtained indicated that the lac dye adsorption process is a spontaneous and an exothermic one.

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1. Introduction

Lac dye is a natural reddish dyestuff extracted from stick lac which is a secretion of the insect *Coccus lacca* (*Laccifer lacca* Kerr). The insect *C. laccae* is often found in South and Southeast Asia, especially in Thailand and India. In Thailand, the lac insect grows most commonly on the Rain tree, *Samanea saman* (Jacq.) Merr. (*Pithecolobium saman*, Mimosaceae) [1]. Lac dye, which is the soluble part of stick lac, is composed mainly of two major anthraquinone-based components: laccic acids A and B [2–8]; the minor components, laccic acids C, D and E, have also been isolated [9,10] (Fig. 1).

All have an anthraquinone moiety with dicarboxylic acid groups, except for laccic acid D which is a monocarboxylic acid. The quantities of these laccic acid components depend on the locality and the season. Erythrolaccin (Fig. 1) is another component of the lac dye [2], but this can be removed by ethanol extraction.

Lac dye is used extensively as a natural food additive [7,11], and in cosmetics [7], as well as a colourant for silk and cotton dyeing [1]. In the north and the northeast of Thailand, it is used as a natural red dyestuff for cotton and silk dyeing but the fastness properties and reproducibility to give consistency in production are still problems to be solved. As part of the approach to tackle these problems, fundamental physical studies on the dyeing process are important.

The thermodynamics of adsorption of laccic acids on silk has been studied [12], but without pH control

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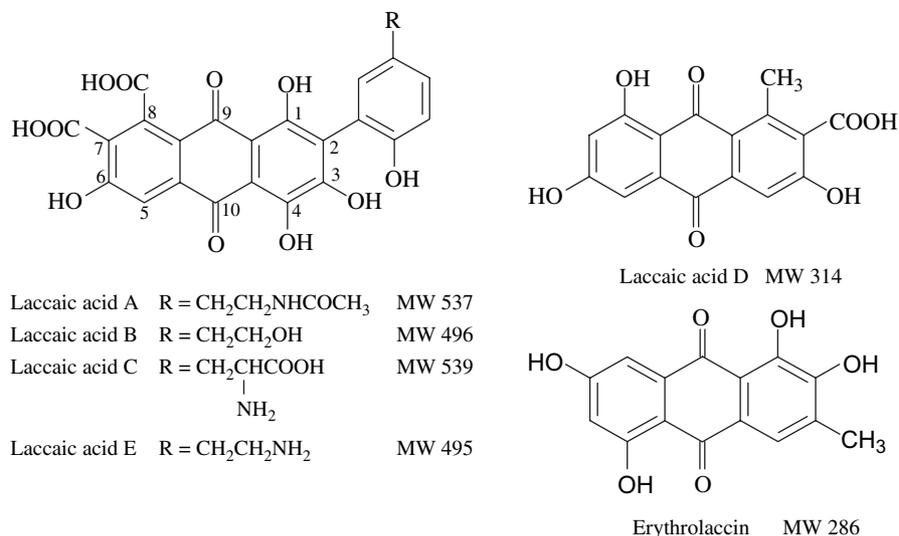


Fig. 1. Chemical structures of the laccic acids and erythrolaccin.

and the results indicated that the adsorption isotherm of silk dyeing with laccic acids, from which the erythrolaccin had been removed, was of the Langmuir type. Also values for the heat and entropy of dyeing were reported [12]. However, there have not been any complementary studies on the kinetics of the dyeing process and such studies are now reported in this paper. The adsorption rates were measured and determined quantitatively in relation to dye solution pH values, contact time, initial dye concentration, and material to liquor ratio (MLR). The Langmuir and Freundlich equations were used to fit the equilibria.

2. Experimental

2.1. Materials

2.1.1. Silk yarn

The silk yarn used was purchased from villagers living in Nakhon Ratchasima, Thailand. To remove the sericin gum, the silk yarn (1 kg) was added to boiling water (5 L) to which soap flakes had been added (ca 100 g), sodium silicate (10 g), sodium carbonate (50 g) and 40% hydrogen peroxide (100 mL). The mixture was then boiled for 2 h. The silk was then removed, washed with water, squeezed to remove excess liquor and air dried. Finally, it was treated with 1 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.

2.1.2. Stick lac

Stick lac (500.48 g) from the Rain tree, *S. saman* (Jacq.) Merr. (*P. 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 °C for 1 h. The aqueous solution was filtered and the filtrate concentrated under reduced pressure (rotary evaporator) to give a crude lac dye extract (38.33 g), which was then used without further purification.

Erythrolaccin-free lac dye was also prepared. Stick lac (300 g) was extracted with ethanol (900 mL) for 15 min at room temperature and then filtered to remove the erythrolaccin solution. The stick lac remaining was then treated with deionized water (3.0 L) for 24 h at room temperature with stirring. The resultant aqueous dye solution was filtered and then the filtrate was concentrated under reduced pressure to obtain the erythrolaccin-free lac dye (9.9628 g). It was used without further purification.

2.2. Instruments

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

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

A thermostatted shaker bath (Heto-Holten A/S Denmark, Type SBD-50 cold), operated at 75 rpm, was used to study the adsorption and kinetics of lac dye onto silk yarn.

2.3. Methods

2.3.1. Batch kinetic experiments

Lac dye was dissolved in deionized water to the required concentrations. The pH of the dye solutions was adjusted to 3.0 with glacial acetic acid. The dye

solution (50 mL) in each conical flask (125 mL) was shaken in a thermostatted shaker bath operated at 75 rpm. After 30 min, the silk yarn (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 based on absorbance at λ_{\max} 487 nm (Cary 1E UV–Visible spectrophotometer) versus dye concentration in standard lac dye solutions. The amount of dye adsorbed per gram of silk (q_t) (mg/g silk) at any time was calculated by a mass–balance relationship (Eq. (1)) as follows:

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

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 solutions (mL) and W is the weight of silk yarn (g) used.

2.3.2. Batch equilibrium experiments

Different lac dye concentrations were freshly prepared in deionized water. The pH of the dye solution was adjusted to 3.0 with glacial acetic acid. The experiments were carried out by shaking silk yarn (0.5 g) with different concentrations of dye solution (50 mL) in a conical flask at 30 and 60 °C in a thermostatted shaker bath operated at 75 rpm. The amount of dye in the solution was monitored by UV–Visible absorption spectroscopy (Cary 1E UV–Visible spectrophotometer) until the absorbance values at λ_{\max} 487 nm remained constant. The initial and equilibrium dye concentrations were determined using a calibration curve based on absorbance at λ_{\max} 487 nm versus dye concentration in standard lac dye solutions. Eq. (2) was used to calculate the amount of dye adsorbed at equilibrium (q_e) (mg/g silk)

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

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

3. Results and discussion

3.1. Optimal conditions for lac dye onto silk

In order to investigate the adsorption of lac dye onto silk, the experiment parameters including pH, material to liquor ratio (MLR), contact time, initial dye

concentration and temperature were determined to find the optimal conditions for adsorption.

3.1.1. The effect of pH on the adsorption of lac dye onto silk

Lac dye, is composed mainly of two major anthraquinone-based components: laccic acids A and B [2–8] and the minor components, laccic acids C, D and E [9,10], and is classified an acid dye [13]. The pH of the dye solution is one of the most important parameters controlling the adsorption capacity of dye onto silk [1,14]. The effect of pH on the adsorption of lac dye onto silk at 30 °C with the initial dye concentration of 450 mg/L and the MLR of 1:100 is shown in Fig. 2. It indicated that the adsorption capacity increased with decreasing pH over the pH range 4.5–3.5, and remained constant in the pH range 3.5–3.0, but dropped gradually at pH values lower than 3.0. The highest adsorption capacity was observed to be in the pH range of 3.5–3.0. This is due mainly to an increase in the protonation of the amino ($-\text{NH}_2$) groups of amino acids in the silk protein, while the carboxyl groups in the side chains are essentially unionized at lower pH. From a model of the electrostatic map of laccic acid A (Spartan Program; AM1; Wavefunction Inc.; '02 Linux/Unix) as shown in Fig. 3, it was found that it has higher negative potential at the 9-quinone carbonyl oxygen group compared with the potential at the other quinone group because of the delocalization of the lone pairs of electrons from the phenolic groups at positions 3 and 6. Therefore, the positive charge on silk most probably attracts laccic acids by electrostatic ion–dipole forces. In addition, laccic acids can form hydrogen bonds with silk because these structures contain hydroxyl groups. Therefore, it was concluded that lac dye onto silk would

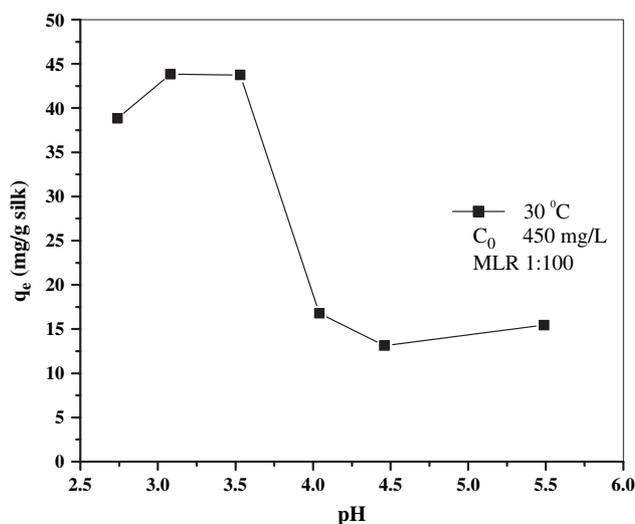


Fig. 2. The effect of pH on the adsorption of lac dye onto silk at 30 °C and 1 h contact time.

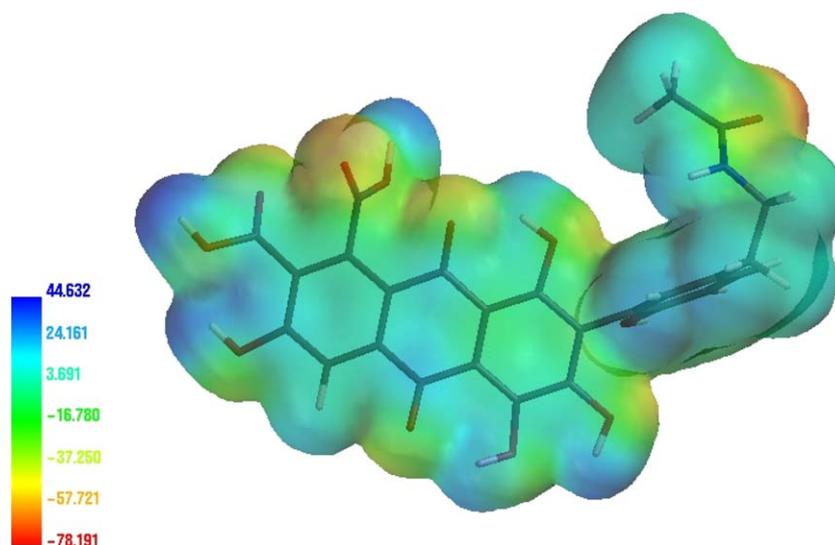


Fig. 3. Electrostatic map of laccase acid A (Spartan Program; AM1; Wavefunction Inc.; '02 Linux/Unix).

be favourable under acidic conditions. The pH of the dye solution in all experiments on the adsorption kinetics was fixed at 3.0. From Table 1, the adsorption of lac dye onto silk at pH 3.0 and 4.0 could be described by the second-order kinetic model. In addition, the initial dye adsorption rate (h_i) at pH 3.0 was higher than that at pH 4.0, consistent with the dyeing process being favoured under acidic conditions.

3.1.2. The effect of material to liquor ratio (MLR) on the adsorption of lac dye onto silk

The aim of dyeing is to transfer the dye molecules from the dye liquor to the fiber in a uniform and efficient manner. The rate of dye uptake by the fiber is significantly increased by the movement of the dye liquor relative to the fiber [14]. The effect of material to liquor ratio (MLR) on the adsorption of lac dye onto silk is shown in Fig. 4. It was found that an increase in

volume of dye solution resulted in an increase of the dye adsorbed onto silk. It indicated that silk yarn is loosely packed in the higher volume of dye solution and the dye solution readily moves past any surface transferring dye molecules to the silk surface in the process. On reaching the silk surface the dye molecules will be adsorbed into the surface and then diffuse into the interior of the silk yarn. Since an MLR of 1:100 or 1:150 showed only a small difference in the amount of the dye adsorbed onto the silk, the MLR of 1:100 ratio was used for all the kinetic experiments.

3.1.3. The effect of contact time and initial dye concentration on the adsorption lac dye onto silk

The adsorption of lac dye at different initial dye concentrations onto silk was investigated as a function of contact time in order to determine the equilibrium time for maximum adsorption. A plot of the amount of

Table 1

Comparison of the pseudo first- and second-order adsorption rate constants and the calculated and experimental q_e values for different temperatures

Parameters	$q_{e,exp}$ (mg/g silk)	Pseudo first-order model			Pseudo second-order model			
		k_1 (min^{-1})	$q_{e,cal}$ (mg/g silk)	R^2	k_2 (g silk/mg min)	$q_{e,cal}$ (mg/g silk)	h_i (mg/g silk min)	R^2
<i>pH: initial dye concentration (C_0) 450 mg/L, contact time 60 min, MLR 1:100, Temp. 30 °C</i>								
3.0	44.0	9.04×10^{-2}	34.0	0.9939	4.85×10^{-3}	45.8	10.2	0.9969
4.0	12.4	4.51×10^{-2}	10.3	0.9743	1.29×10^{-2}	10.8	1.5	0.9921
<i>Initial dye concentration; C_0 (mg/L): contact time 60 min, MLR 1:100, Temp. 30 °C (pH 3.0)</i>								
120	11.1	8.85×10^{-2}	7.8	0.9791	2.42×10^{-2}	11.2	3.0	0.9940
228	23.0	1.08×10^{-2}	14.6	0.9722	1.50×10^{-2}	24.0	8.6	0.9989
450	44.0	9.04×10^{-2}	34.0	0.9939	4.85×10^{-3}	45.8	10.2	0.9969
<i>Temperature (°C): initial dye concentration (C_0) 450 mg/L, contact time 60 min, MLR 1:100 (pH 3.0)</i>								
30	44.0	9.04×10^{-2}	34.0	0.9939	4.85×10^{-3}	45.8	10.2	0.9969
40	42.0	1.28×10^{-1}	26.7	0.9732	9.37×10^{-3}	44.2	18.3	0.9985
60	38.0	1.54×10^{-1}	17.2	0.9603	2.70×10^{-2}	38.0	39.0	0.9996

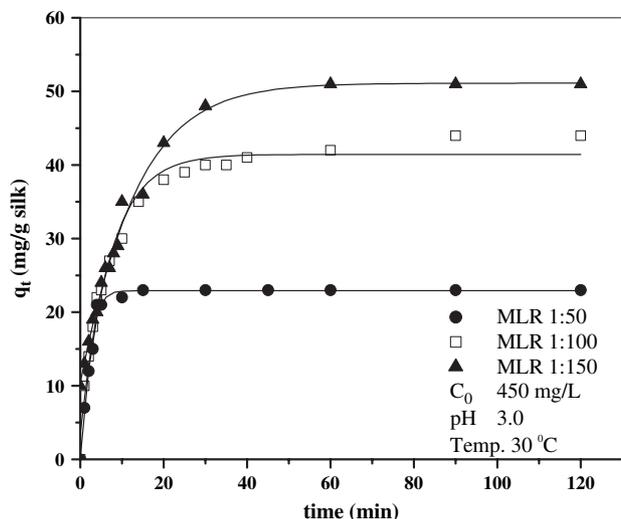


Fig. 4. The effect of material to liquor ratio on the adsorption of lac dye onto silk.

dye adsorbed per gram silk (q_t) (mg/g silk) at any time versus contact time (t) is shown in Fig. 5. It was found that the adsorption capacity was concentration dependent and increased with initial concentration of the lac dye. An increase in the initial dye concentration led to an increase in the amount of dye adsorbed onto silk. This may be a result of an increase in the driving force of the concentration gradient with the increase in the initial dye concentration [15]. This indicated that the initial dye concentration plays an important role in the adsorption capacity of lac dye onto silk. The results of rate constant studies for different initial dye concentrations by using the pseudo-first order and second-order kinetic models are listed in Table 1. The second-order kinetic model well described the adsorption of lac dye onto silk with a high correlation coefficient ($R^2 > 0.99$) as shown in

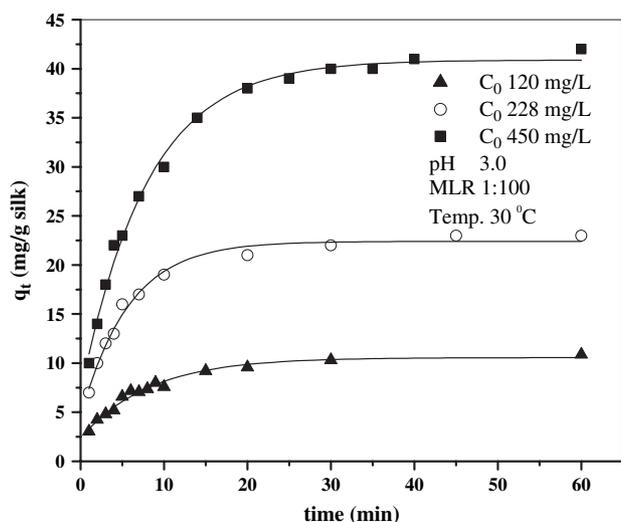


Fig. 5. Adsorption of lac dye onto silk at different initial dye concentrations.

Fig. 6; calculated equilibrium adsorption capacities ($q_{e,cal}$) were only slightly different from the experimental data. This suggested that the overall rate of the lac dye adsorption onto silk is controlled by the chemisorption. From Table 1, the rate constant (k_2) for the pseudo second-order kinetic model decreased with increasing initial dye concentration whereas the initial dye adsorption rate (h_i) increased with an increasing initial dye concentration. The equilibrium time is the time taken for the maximum adsorption of dye onto the silk surface, above which the adsorption remains constant. The equilibrium time was found to be about 30 min for 450, 228 and 120 mg/L dye concentration at pH 3.0 and 30 °C. The adsorption was very fast at the initial stages of contact time and gradually decreased with time until it remained constant. An initial dye concentration of 450 mg/L was used throughout this study. Using different initial concentrations in the temperature range 30–60 °C showed similar trends.

3.1.4. The effect of temperature on the adsorption of lac dye onto silk

The results of the studies on the influence of temperature on the adsorption of lac dye onto silk are shown in Fig. 7. It was carried out under the optimal conditions of pH 3.0, MLR 1:100 and an initial dye concentration of 450 mg/L. Before and after the equilibrium time, the amount of dye adsorbed per gram of silk (q_t) showed different trends at different temperatures. Before the equilibrium time, the initial dye adsorption rate (h_i) increased with increasing temperature which indicated a kinetically controlled process as shown in Table 1. This result may reflect an increase in the mobility of the large dye ions with temperature and thus an increase in the number of molecules interacting with the active sites at the surface. After the equilibrium

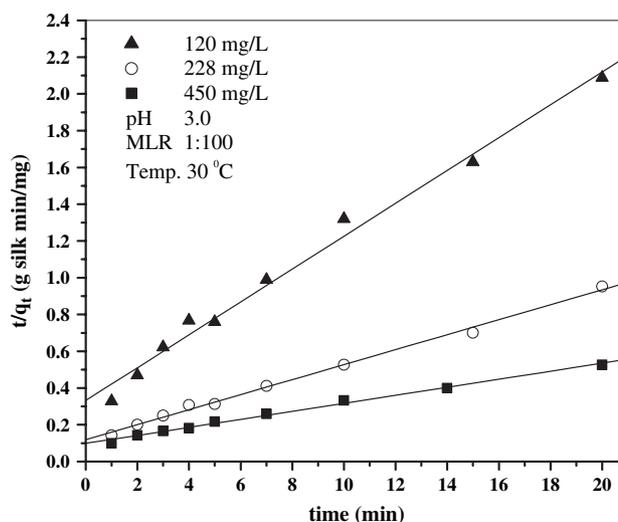


Fig. 6. Plot of the pseudo second-order equation at different initial dye concentrations.

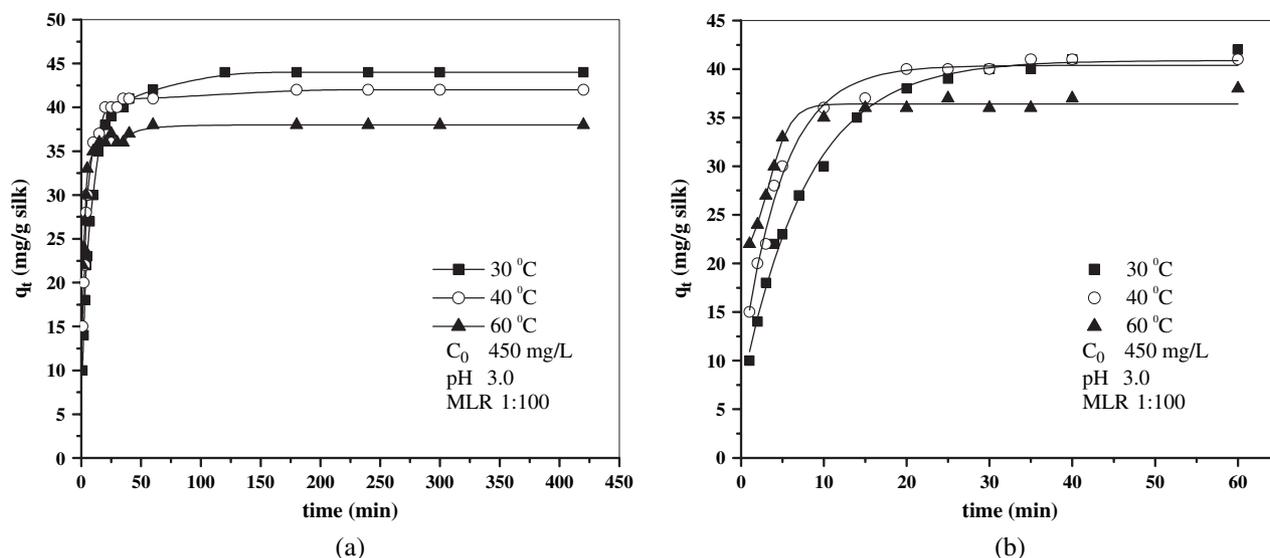


Fig. 7. The effect of contact time and temperature of lac dyeing on silk at the initial lac dye concentration of 450 mg/L, MLR 1:100 and pH 3.0. (a) The effect of contact time and temperature in the period of 0–420 min. (b) The effect of contact time and temperature in the period of 0–60 min (expansion of graph 'a').

time, the decrease of the amount of the dye adsorbed per gram of silk with increasing temperature indicated that the adsorption of lac dye onto silk was controlled by an exothermic process. The equilibrium of the lac dyeing process was shifted to the left-hand side. Therefore, the amount of dye adsorbed at high temperature was lower than that at low temperature after the equilibrium time. This behaviour is similar to that observed for the adsorption of reactive dye and anionic dye on cross-linked chitosan beads [16,17]. Our data showed that the time to reach the adsorption equilibrium decreased with increasing temperature, i.e. 60, 25, and 15 min at 30, 40 and 60 °C, respectively. This is due to more rapid diffusion to the silk with higher temperatures. However, the contact time in the adsorption experiments was set at 60 min throughout this study.

The optimal conditions obtained from this study at pH 3.0 and MLR 1:100 were subsequently used to study the kinetic and adsorption isotherm of lac dyeing.

3.2. Adsorption isotherm

3.2.1. The Langmuir isotherm

The equilibrium adsorption isotherm is fundamental in describing the interaction behaviour between solutes and adsorbents, and is important in the design of an adsorption system. The Langmuir adsorption isotherm has been successfully applied to many other real sorption processes [15,18]. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a dye molecule occupies a site, no further adsorption can take place at that site. Theoretically, therefore, a saturation value is reached beyond

which no further sorption can take place. The saturated monolayer curve can be represented by the expression:

$$q_e = \frac{QbC_e}{1 + bC_e} \quad (3)$$

A linear form of this expression is:

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{QbC_e} \quad (4)$$

In the above equation, Q (mg/g silk) is the maximum amount of the dye per unit weight of silk 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 gram of silk (mg/g silk) at equilibrium, and b the Langmuir constant related to the affinity of binding sites (mL/mg). The value of Q represents a practical limiting adsorption capacity when the surface is fully covered with dye molecules and assists in the comparison of adsorption performance [15]. The linear plot of $1/q_e$ versus $1/C_e$ is obtained from this model as shown in Fig. 8. The values of Q and b are calculated from the intercepts and slopes of different straight lines representing the different temperatures; Table 2 lists the calculated results. The fit is good for the adsorption data of lac dye onto silk at 30 and 60 °C (correlation coefficient, $R^2 > 0.99$). It is found that the adsorption of lac dye at higher temperature decreased with increasing temperature indicating that the process is exothermic. As expected, the Q values decreased with increasing temperature. The b values indicated that the silk yarn has a maximum affinity for lac dye at lower temperature.

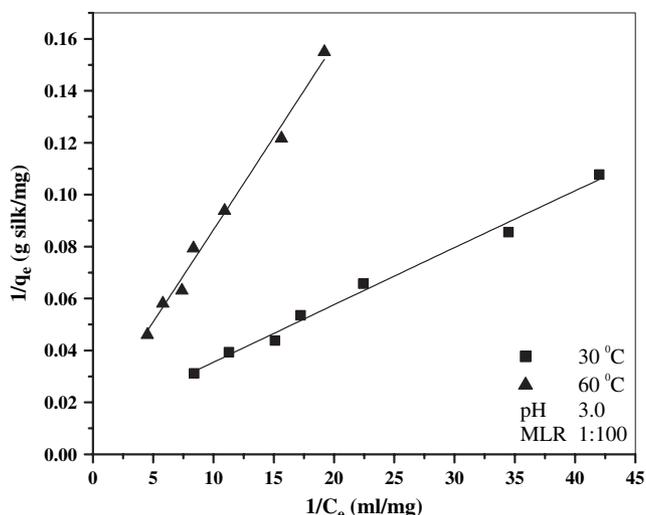


Fig. 8. Langmuir adsorption isotherm of lac dye onto silk at 30 and 60 °C.

The essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor for equilibrium parameter, R_L [19–21], defined as follows:

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

where C_0 is the initial concentration of dye (in ppm or mg/L) and b is the Langmuir constant (L/mg). The values of R_L indicate the type of isotherm to be 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 3) were observed to be in the range of 0–1, indicating that the adsorption of lac dye onto silk was favourable for this study.

3.2.2. Freundlich isotherm

The Freundlich isotherm [15,18] is a special case for heterogeneous surface energy in which the energy in the Langmuir equation varies as a function of surface coverage strictly due to variation of the sorption. The Freundlich equation is given as:

$$q_e = Q_f C_e^{1/n} \quad (6)$$

where Q_f is roughly an indicator of the adsorption capacity and $1/n$ of the adsorption intensity. A linear

Table 3
Data for Langmuir isotherm for lac dyeing of silk

Temperature (°C)	b (L/mg)	Initial dye concentration C_0 (mg/L)	R_L
30	6.14×10^{-3}	443	0.2689
		348	0.3186
		298	0.3532
		250	0.3948
		201	0.4473
		149	0.5221
		120	0.5760
		60	2.06×10^{-3}
348	0.5822		
298	0.6194		
250	0.6604		
121	0.7069		
149	0.7650		
120	0.8020		

form (Eq. (7)) of the Freundlich expression will yield the constants Q_f and $1/n$

$$\ln q_e = \ln Q_f + \frac{1}{n} \ln C_e \quad (7)$$

Therefore, Q_f and $1/n$ can be determined from the linear plot of $\ln q_e$ versus $\ln C_e$. The values are presented in Table 2 and the Freundlich equation isotherms are shown in Fig. 9. The magnitude of the exponent $1/n$ gives an indication of the favourability of adsorption. Values of $n > 1$ obtained represent favourable adsorption conditions [15]. The Q_f values decreased with increasing temperature which again supported an exothermic process. From Table 2, the Freundlich equation can be applied to fit the experiment data as well as the Langmuir equation because it gave a high correlation coefficient ($R^2 > 0.99$).

3.3. Kinetics of adsorption

In order to examine the controlling mechanism of the adsorption process, pseudo first-order and pseudo second-order equations were used to test the experimental data. A simple kinetic analysis of adsorption is the pseudo first-order rate expression of the Lagergren equation [15,22,23]. In this equation the average value of

Table 2
Langmuir and Freundlich isotherm constants of adsorption of dyes onto silk at different temperatures

Temperature (°C)	Langmuir			Freundlich		
	Q (mg/g silk)	b (mL/mg)	R^2	Q_f (mg/g silk)	n	R^2
30	74.0	6.14	0.9956	163.5	1.32	0.9947
60	67.9	2.06	0.9955	75.0	1.22	0.9942

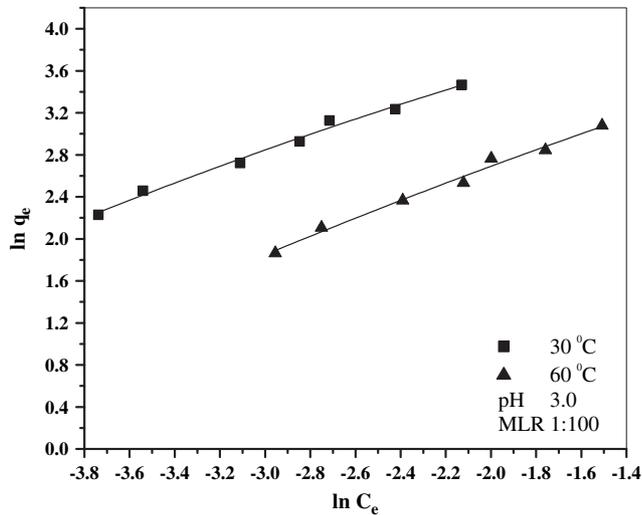


Fig. 9. Freundlich adsorption isotherm of lac dye onto silk at 30 and 60 °C.

the rate constant, k_1 , for adsorption of lac dye onto silk can be calculated in the form:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (8)$$

where k_1 is the rate constant of pseudo first-order adsorption (s^{-1}), and q_e and q_t are the amount of dye adsorbed per gram silk (mg/g silk) at equilibrium and time t , respectively. The first-order kinetics only describes the sorption sites and not the adsorption process as a whole. After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q = q_t$ at $t = t$, Eq. (8) becomes

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (9)$$

A straight line of $\ln(q_e - q_t)$ versus t suggests the applicability of this kinetic model to fit the experimental data. The first-order rate constant k_1 and equilibrium adsorption density $q_{e,cal}$ were calculated from the slope and intercept of this line.

The k_1 values and equilibrium adsorption density q_e at three different temperatures were calculated from these plots (Fig. 10) and are listed in Table 1. A comparison of results with the correlation coefficient (R^2) is shown in Table 1. The correlation coefficients for the pseudo first-order kinetic model are all above 0.96. However, a large equilibrium adsorption density (q_e) difference between the experiment and calculation was observed, indicating a poor pseudo first-order fit to the experimental data.

The pseudo second-order kinetic model [15,22,23] is based on adsorption equilibrium capacity and can be expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (10)$$

where k_2 (g silk/mg min) is the rate constant for pseudo second-order adsorption. Integrating Eq. (10) and applying the initial conditions, we have

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (11)$$

or equivalently,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (12)$$

and

$$h_i = k_2 q_e^2 \quad (13)$$

where h_i [16] is the initial dye adsorption rate (mg/g silk min). The slope and intercept of (t/q_t) versus t were used to calculate the pseudo second-order rate constant k_2 and q_e . It is likely that the behaviour over the whole range of adsorption is in agreement with the chemisorption mechanism being the rate-controlling step [16,17]. From Table 1, lac dyeing onto silk is considered to be pseudo second-order with high correlation coefficients above 0.99 as shown in Fig. 11. In addition, the q_e which is the adsorption capacity, agreed very well with both experiment and calculation as listed in Table 1. These suggested that the pseudo second-order adsorption mechanism is predominant and that the overall rate of the lac dye adsorption process is most likely to be controlled by the chemisorption process [16,17].

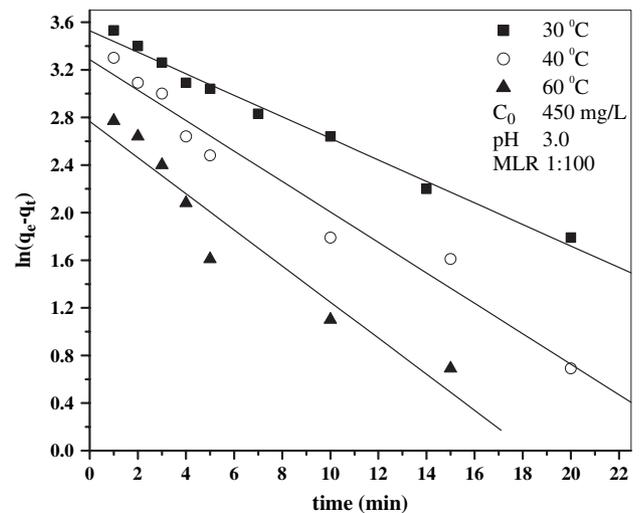


Fig. 10. Plot of the pseudo first-order equation at different temperatures.

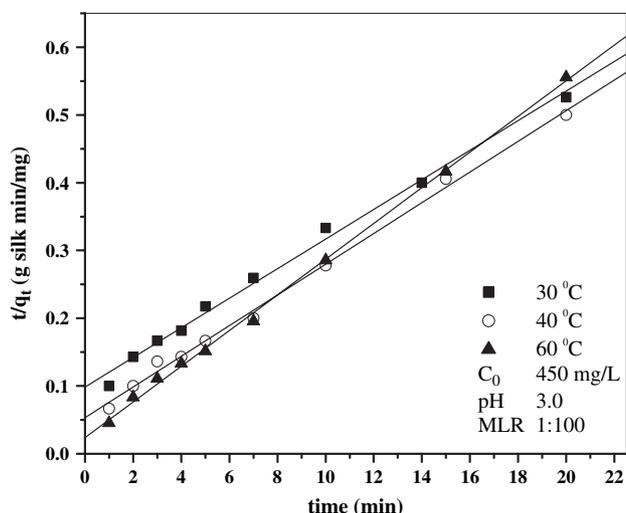


Fig. 11. Plot of the pseudo second-order equation at different temperatures.

3.4. Activation parameters

The rate constant k_2 at different temperatures listed in Table 1 were then applied to estimate the activation energy of the adsorption of lac dye onto silk by the Arrhenius equation [22]:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (14)$$

where E_a , R and A refer to the Arrhenius activation energy, the gas constant and the Arrhenius factor, respectively. The slope of the plot of $\ln k_2$ versus $1/T$ was used to evaluate E_a as listed in Table 4.

The enthalpy (ΔH^\ddagger), entropy (ΔS^\ddagger) and free energy (ΔG^\ddagger) of activation was also calculated using the Eyring equation [22] as follows:

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (15)$$

where k_b and h refer to Boltzmann's constant and Planck's constant, respectively. The enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) of activation were calculated from the slope and intercept of a plot of $\ln(k/T)$ versus $1/T$ as listed in Table 4. Gibbs energy of activation (ΔG^\ddagger) [22]

Table 5
Thermodynamic parameters for the adsorption of lac dyeing at initial dye concentration 450 mg/mL

Temperature (°C)	K_c	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)	R^2
30	12.3	-6.3			
40	11.0	-6.2	-31.4	-81.9	0.9712
60	4.2	-4.0			

can be written in terms of enthalpy and entropy of activation:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (16)$$

The observed activation energy (E_a) and enthalpy of activation (ΔH^\ddagger) for lac dye onto silk yarn shown in Table 4 agreed well with the one calculated from the activated complex theory of reaction in solution, $E_a = \Delta H^\ddagger + RT$. However, the observed activation energy (E_a) seems to be small for adsorption of lac dye onto silk yarn.

The value of ΔG^\ddagger was calculated at 303, 313 and 333 K for initial dye concentration of 450 mg/L by using Eq. (16) and these values are listed in Table 4, while the negative entropy value (ΔS^\ddagger) reflects the interaction between lac dye and silk yarn.

In order to support the exothermic behaviour of lac dye onto silk, after reaching equilibrium, the thermodynamic parameters, ΔG° , ΔH° and ΔS° of lac dye adsorption, were calculated by the following equations [16] and the results are shown in Table 5

$$K_c = \frac{C_{ad,e}}{C_e} \quad (17)$$

$$\Delta G^\circ = -RT \ln K_c \quad (18)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (19)$$

In the above equations, K_c is the equilibrium constant, and $C_{ad,e}$ and C_e are the dye concentration adsorbed at equilibrium (mg/L) and the concentration of dye left in the dye bath at equilibrium (mg/L), respectively.

The negative values of ΔG° and ΔH° indicated that lac dye adsorption is a spontaneous and an exothermic process. The obtained ΔS° is a negative value.

Table 4
Activation parameters for the adsorption of lac dye onto silk

Initial dye conc. (mg/L)	Temp. (°C)	k_2 (g silk/mg s)	E_a (kJ/mol)	R^2	ΔH^\ddagger (kJ/mol)	ΔS^\ddagger (J/mol K)	ΔG^\ddagger (kJ/mol)	R^2
450	30	8.08×10^{-5}					97.9	
	40	1.56×10^{-4}	47.5	0.9985	44.7	-175.7	99.7	0.9985
	60	4.50×10^{-4}					103.2	

Table 6
Activation parameters for the adsorption of crude lac dye with and without erythrolaccin

Crude extract	Temp. (°C)	k_2 (g silk/mg s)	E_a (kJ/mol)	R^2	ΔH^\ddagger (kJ/mol)	ΔS^\ddagger (J/mol K)	ΔG^\ddagger (kJ/mol)	R^2
Erythrolaccin present	30	8.08×10^{-5}	47.5	0.9985	44.7	-175.7	97.9	0.9982
	40	1.56×10^{-4}					99.7	
	60	4.50×10^{-4}					103.2	
Erythrolaccin removed	30	6.97×10^{-5}	50.8	0.9969	48.3	-164.9	98.2	0.9966
	40	1.47×10^{-4}					99.9	
	60	4.48×10^{-4}					103.1	

3.5. Comparison of activation parameters between crude lac dye with and without removing erythrolaccin

Crude lac dyes are composed mainly of laccic acids and a yellow pigment called erythrolaccin [2,24]. They are usually used in dyeing by villagers in northeast Thailand without removing the erythrolaccin [1]. However, in order to study any effect of erythrolaccin on dye uptake, kinetic data with and without erythrolaccin being present was obtained. The results are shown in Table 6.

The activation parameters with and without erythrolaccin in the lac dye are similar indicating only a slight effect of erythrolaccin on lac dyeing onto silk. In particular, ΔH^\ddagger was slightly higher in the latter case while ΔS^\ddagger was smaller.

4. Conclusions

The adsorption isotherm and kinetics of lac dyeing were studied. The following results were obtained:

1. Adsorption data were modeled by using the Freundlich and Langmuir adsorption isotherms. A high correlation coefficient ($R^2 > 0.99$) with both isotherms was obtained.
2. Initially, the rate of adsorption of lac dye onto silk yarn was very fast. This was then followed by a slower rate, and gradually approached a plateau.
3. Before equilibrium was reached, an increase in temperature lead to an increase in the dye adsorption rate which indicated a kinetically controlled process, while the adsorption of lac dye onto silk was controlled by an exothermic process.
4. Adsorption capacity was dependent on the pH of the dye solution and optimal uptake on silk occurred at pH 3.0–3.5.
5. A pseudo second-order kinetic model agreed well with the dynamical behaviour for the adsorption of lac dye on silk yarn under different initial dye concentrations and temperatures, consistent with chemical adsorption being the rate-limiting step.

6. On the basis of the negative ΔG° and ΔH° values, the lac dye adsorption onto silk is a spontaneous and an exothermic process.

The results from this kinetic study will assist in gaining a better understanding of the adsorption mechanism of this dyeing process.

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