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Equilibrium and Kinetic Modeling of the Adsorption of Indigo Carmine onto Silk

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Abstract: Quantitative adsorption kinetic and equilibrium parameters for indigo carmine dyeing of silk were studied using UV-visible absorption spectroscopy. The effect of initial dye concentration, contact time, pH, material to liquor ratio (MLR), and temperature were determined to find the optimal conditions for adsorption. The mechanism of adsorption of indigo carmine dyeing onto silk was investigated using the pseudo first-order and pseudo second-order kinetic models. The adsorption kinetics was found to follow a pseudo-second-order kinetic model with an activation energy (E_a) of 51.06 kJ/mol. The equilibrium adsorption data of indigo carmine dye on silk were analyzed by the Langmuir and Freundlich models. The results indicate that the Langmuir model provides the best correlation. Adsorption isotherms were also used to obtain thermodynamic parameters such as free energy (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o) of adsorption. The negative values of ΔG^o and ΔH^o indicate the overall adsorption process is a spontaneous and exothermic one.

Keywords: Indigo carmine, Adsorption isotherm, Kinetics, Thermodynamics, Silk dyeing

Introduction

Indigo carmine (Figure 1; IUPAC name: disodium (2*E*)-3-oxo-2-(3-oxo-5-sulfonato-1*H*-indol-2-ylidene)-1*H*-indole-5-sulfonate) [1-3] is a blue, water soluble disulfonate derivative of the well known dye indigo, and has major industrial application as a textile coloring agent [4,5]. It has also been employed as an additive in pharmaceutical tablets and capsules and as a coloring agent in confectionery, food items, and cosmetics. It also finds use as a diagnostic aid (e.g. in kidney function tests), as a redox indicator in analytical chemistry, and as a microscopic stain in biology [2,4-6].

Indigo carmine is an acidic dye [7,8] and it has thus been used to dye the protein fibers, wool, and silk [9], including the use of alum as a mordant in the latter case [10]. A limited number of indigo carmine dye adsorption studies have been carried out on silk and wool, particularly in relation to dye removal from textile processing effluents [1,2,11]. However, detailed studies on the kinetics and thermodynamics of the dyeing process of silk with indigo carmine have not been undertaken. As part of our ongoing interest in understanding dye-silk interactions with a view to improving conditions for the dyeing process [12-14] and a need to have basic reference data for later dyeing studies with indigo and derivatives, we have now studied the thermodynamic and kinetic parameters of the dyeing process of silk with indigo carmine. These parameters were determined quantitatively and the results are presented in this paper.

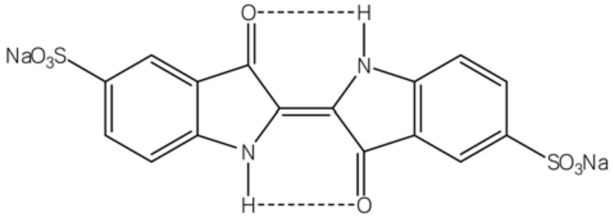

Figure 1. Chemical structure of indigo carmine.

Experimental

Materials and Chemicals

The silk yarn used was purchased from Chul Thai Silk Co., Ltd in Phetchabun, Thailand. Prior to using in the dyeing experiment, the silk yarn (1 kg) 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 [12].

The dye indigo carmine (Acid blue 74, C.I. 73015) is a blue colored, water soluble powder having the molecular formula $C_{16}H_8O_8N_2S_2Na_2$ (molecular weight 466.34). It was obtained from the Acros Organics company. The dye was of analytical reagent grade and of >99 % purity.

Instruments

An Agilent 8453 UV-Vis spectrophotometer was employed to determine the concentration of dye samples through absorbance measurements using quartz cells of path length 1 cm at the characteristic maximum wavelength. A pH meter (Laboratory pH Meter CG 842, SCHOTT, UK) was used to measure the pH values of solutions. A thermostatted shaker bath (Type SBD-50 cold, Heto-Holten A/S, Denmark) operated at 150 strokes/min, was used to study the adsorption kinetics and thermodynamics of indigo carmine onto silk yarn.

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Methods

Batch Kinetic Experiments

The batch technique was used to examine the dyeing process at temperatures of 30, 40, and 50 °C. The dyeing process was scrutinized by taking a series of 125 m*l* conical flasks containing the aqueous solution of indigo carmine over the concentration range 0.5×10^4 to 1.5×10^4 M at a fixed pH (pH range 3.0-5.0; pH adjusted by using acetic acid-acetate buffer). The dye solution in each conical flask was shaken in a thermostatted shaker bath operated at 150 strokes/min and controlled temperature. 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. The concentration of the unadsorbed indigo carmine in the supernatant dye solution was determined at time zero and at subsequent times using a calibration curve based on absorbance at $\lambda_{\max}$=611 nm versus dye concentration. The amount of dye adsorbed per gram of silk (q_t) (mg/g silk) at any time was calculated by a mass balance relationship (equation (1)) as follows:

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

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

Batch Equilibrium Experiments

Indigo carmine was dissolved in deionized water to the required concentrations and the pH of the dye solution was adjusted to 4.0 using acetic acid-acetate buffer. The experiments were carried out by shaking silk yarn (0.50 g) with different concentrations of dye solution (50 m*l*) in a conical flask in a thermostatted shaker bath operated at 150 strokes/min and controlled temperature. The concentration of the unadsorbed indigo carmine in the supernatant dye solution was determined at time zero and at equilibrium times using a calibration curve based on absorbance at $\lambda_{\max}$=611 nm versus dye concentration. The amount of dye adsorbed per gram of silk (q_e) (mg/g silk) at equilibrium time was calculated by a mass balance relationship (equation (2)) as follows:

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

where C_0 and C_e are the initial and equilibrium concentration of dye, respectively (mg/*l*), *V* is the volume of the solution (*l*), and *W* is the weight of the silk yarn used (g).

Results and Discussion

Optimal Conditions for the Adsorption of Indigo Carmine onto Silk

In order to investigate the adsorption of indigo carmine onto silk, the experimental parameters including initial dye concentration, contact time, pH, material to liquor ratio (MLR), and temperature were determined to find the optimal conditions for adsorption. These conditions were a pH of 4.0, an MLR of 1:100, and a temperature of 30 °C. These conditions were then used for the subsequent kinetic and thermodynamic studies.

Kinetics of Adsorption

Effect of Initial Dye Concentration and Contact Time

The adsorption of indigo carmine at different initial dye concentrations onto silk at pH 4.0, MLR=1:100, and temperature was investigated as a function of contact time in order to determine the equilibrium time for maximum adsorption. A plot of the amount of dye adsorbed per gram silk (q_t) (mg/g silk) at any time versus contact time (*t*) is shown in Figure 2. It was found that the dye adsorption rate for each initial dye concentration was quite rapid in the first 15 min, but thereafter the adsorption rate decreased gradually with equilibrium essentially being reached by 60 min (optimum contact time), with only a slight increase being noted over the next 60 min. Hence subsequent experiments were conducted for the optimum contact time only. The higher adsorption rate at the initial period (15 min) may be due to the large number of vacant adsorption sites available on the silk at this stage. Thus an increase in the concentration of indigo carmine in solution and hence on the silk surface (concentration gradient) tends to enhance the dye adsorption rate at the initial stages. As time proceeds, this concentration gradient decreases due to the increased occupation of vacant sites by dye molecules [5,12,15]. Thus the initial dye concentration plays an important role in the adsorption capacity of indigo carmine onto silk.

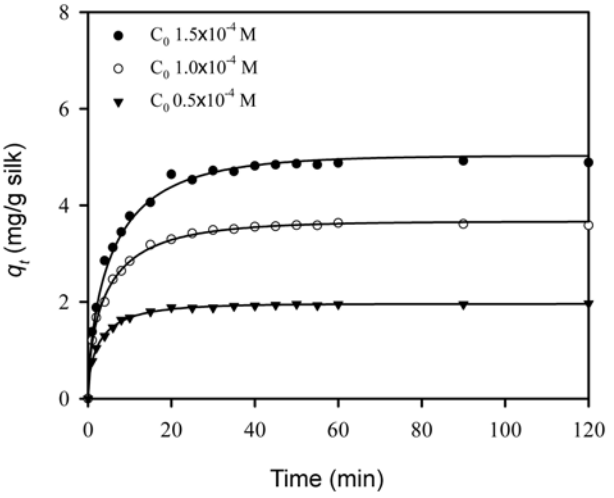

Figure 2. Effect of initial dye concentration on the adsorption of indigo carmine onto silk (under dyeing condition MLR=1:100, pH=4.0, 30 °C).

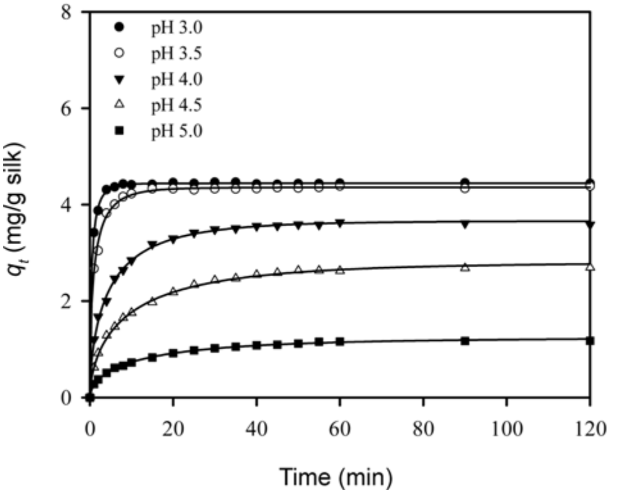

Figure 3. Effect of pH on the adsorption of indigo carmine onto silk (under dyeing condition: C_0=1.0×10^{-4} M, MLR=1:100, 30 °C).

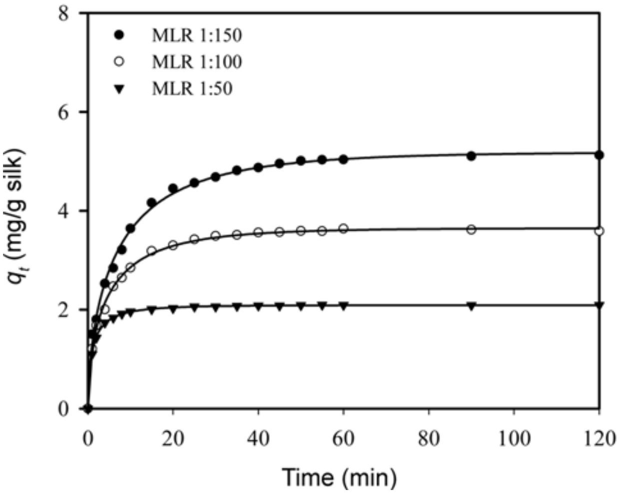

Figure 4. Effect of MLR on the adsorption of indigo carmine onto silk (under dyeing condition C_0=1×10^{-4} M, pH 4.0, 30 °C).

Effect of pH

The pH of the dye solution is one of the most important parameters controlling the adsorption capacity of dye onto silk [16,17]. The effect of pH on the adsorption of indigo carmine onto silk at 30 °C with an initial dye concentration of 1×10^{-4} M and MLR of 1:100 is shown in Figure 3. This showed that the adsorption capacity clearly increased with decreasing pH over the pH range 3.0-5.0. The possible mechanisms for the effect of pH on adsorption of the acid dye indigo carmine [9] are likely to be ionic interactions of the dye anions with the protonated amino groups on the silk fiber [18]. Given the strongly acidic nature of arylsulfonic acids (benzenesulfonic acid pK$_a$-6.5) [19], the anionic sulfonate groups present on dissolution of the sodium salts in water at pH 4.0 would be fully ionized (equation (3)).

$$\text{D-SO}_3\text{Na} \xrightarrow{\text{H}_2\text{O}} \text{D-SO}_3^- + \text{Na}^+ \qquad (3)$$

Also, at pH 4.0, the basic amino groups of silk protein (R-NH$_2$) would be essentially fully protonated (equation (4)) while the acidic carboxylic acid groups in the side chains or the C-termini would be expected to be largely unionized.

$$\text{R-NH}_2 + \text{H}^+ \rightleftharpoons \text{R-NH}_3^- \qquad (4)$$

The adsorption process then proceeds due to the strong electrostatic attractions between the ammonium and sulfonate ion residues (equation (5)).

$$\text{R-NH}_3^+ + \text{D-SO}_3^- \rightleftharpoons \text{R-NH}_3^+ \cdots {}^-\text{O}_3\text{S-D} \qquad (5)$$

Effect of Material to Liquor Ratio

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 increased movement of the dye liquor relative to the fiber [17]. The effect of MLR on the adsorption of indigo carmine onto silk at an initial dye concentration of 1×10^{-4} M at pH 4.0 and 30 °C is shown in Figure 4. It was found that an increase in volume of the dye solution resulted in an increase of the dye adsorbed onto the silk, consistent with the yarn being more loosely packed in such a dye solution. This allows the dye solution to move more readily over the silk surfaces with associated dye molecule binding, and then into the interior of the silk yarn by diffusion [12].

The amount of dye absorbed at MLR=1:150 was higher than for MLRs of 1:100 and 1:50. However, in order to reduce waste from the dyeing process, an MLR of 1:100 was used for all the subsequent experiments.

Effect of Temperature

The dye adsorption process was studied at different temperatures of 30, 40, and 50 °C, and under the optimal conditions of pH 4.0, MLR=1:100, and an initial dye concentration of 1×10^{-4} M in each case. Before (Figure 5(a)) and after (Figure 5(b)) the equilibrium time, the amount of dye adsorbed per gram of silk (q_t) showed different trends at different temperatures. Before the equilibrium time was established, an increase in the temperature leads to an increase in dye adsorption rate indicative of a kinetically controlled process. After the equilibrium time, the amount of the dye adsorbed per gram of silk decreased with increasing the temperature suggesting that the adsorption of indigo carmine onto silk is controlled by an exothermic process.

Rate Constant Studies

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. The best-fit model was selected based on the linear regression correlation coefficient, R^2 values.

A simple kinetic analysis of adsorption is the pseudo first-order rate expression of the Lagergren equation [20]. In this

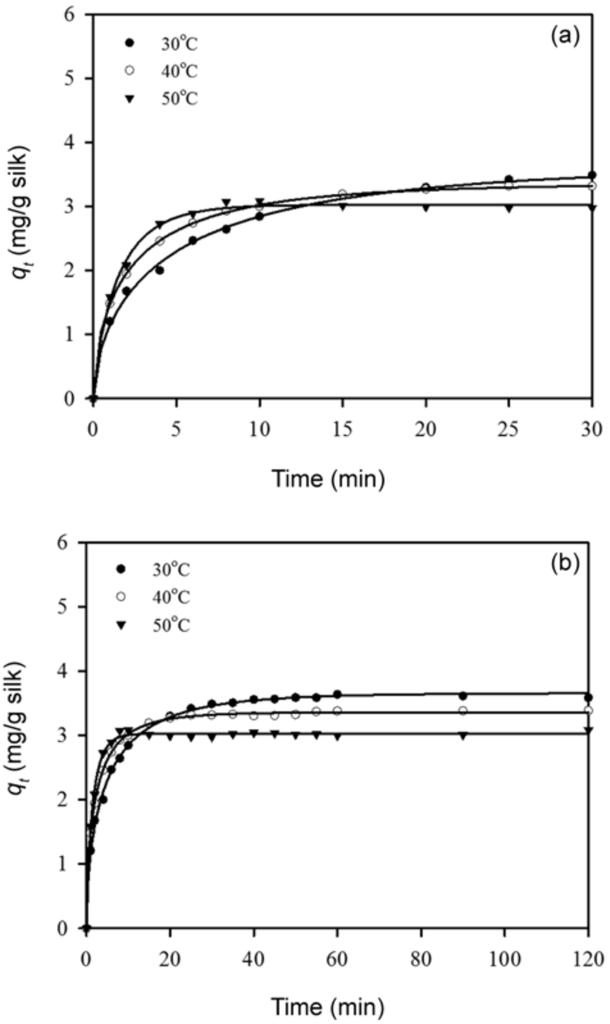

Figure 5. Effect of temperature on the adsorption of indigo carmine onto silk at an initial dye concentration of 1×10^{-4} M, MLR=1:100, and pH 4.0; (a) the effect of contact time and temperature in the period of 0-30 min (expansion of graph (5b)) and (b) the effect of contact time and temperature in the period of 0-120 min.

equation the average value of the rate constant, k_1, for adsorption of indigo carmine onto silk can be calculated in the form:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{6}$$

where k_1 is the rate constant for 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. Integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q = q_t$ at $t = t$, then leads to the following equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{7}$$

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 were calculated from the slope and intercept of this line.

The pseudo second-order kinetic model [5,12,15,21-23] is based on adsorption equilibrium capacity and can be expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{8}$$

where k_2 (g silk/mg min) is the rate constant for pseudo second-order adsorption. Integrating equation (8) and applying the initial conditions gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{9}$$

or equivalently,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{10}$$

and

$$h_i = k_2 q_e^2 \tag{11}$$

where h_i [12,15] is the initial dye adsorption rate (mg/g silk min). If the pseudo second order kinetics is applicable, the plots of t/q_t versus t show a linear relationship. 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.

The best fit values of h_i, q_e k_1, and k_2 along with correlation coefficients for the pseudo-first-order and pseudo-second-order models are shown in Table 1. The $q_{e,\mathrm{exp}}$ and the $q_{e,\mathrm{cal}}$ values from the pseudo-second-order kinetic model were very close to each other, and, the calculated correlation coefficients, R^2 were also closer to unity for pseudo-second-order kinetics than those for the pseudo-first-order kinetics. These suggested that the pseudo second-order adsorption mechanism is predominant and that the overall rate of the indigo carmine dye adsorption process is most likely to be controlled by the chemisorption process [24].

Activation Parameters

In general, the rates of chemical reactions increase with an increase in the temperature. In the rate law, temperature dependence appears in the rate constant and the dependence of rate constants on temperature over a limited range can usually be represented by the empirical van't Hoff and Arrhenius equation [25]:

$$k = Ae^{-E_a/RT} \tag{12}$$

where A is the pre-exponential factor and E_a is the activation energy and R is the gas constant. From the alternative logarithmic form (13) of this equation:

Table 1. Comparison of the pseudo first- and second-order adsorption rate constants and the calculated and experimental q_e values for different initial dye concentrations, pH, MLR and temperature

Parameter	$q_{e,\,exp}$ (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
Initial dye concentration: C_0 (M): pH 4.0, MLR 1:100, temp. 30 °C, contact time 60 min								
0.5×10^{-4}	1.95	0.10	0.99	0.9464	0.26	2.10	1.07	0.9998
1.0×10^{-4}	3.64	0.10	2.67	0.9205	0.09	3.81	1.27	0.9996
1.5×10^{-4}	4.88	0.09	2.99	0.9478	0.06	5.18	1.51	0.9994
pH: C_0 1×10^{-4} M, MLR 1:100, temp. 30 °C, contact time 60 min								
3.0	4.44	0.34	1.10	0.7484	1.80	4.45	35.59	1.0000
4.0	3.64	0.10	2.67	0.9205	0.09	3.81	1.27	0.9996
5.0	1.16	0.06	0.88	0.9842	0.13	1.26	0.20	0.9966
MLR: C_0 1×10^{-4} M, pH 4.0, temp. 30 °C, contact time 60 min								
1:50	2.09	0.11	0.67	0.9317	0.51	2.13	2.314	1.0000
1:100	3.64	0.10	2.67	0.9205	0.09	3.81	1.27	0.9996
1:150	5.03	0.07	3.37	0.9747	0.04	5.42	1.21	0.9990
Temperature: C_0 1×10^{-4} M, pH 4.0, MLR 1:100, contact time 60 min								
30	3.64	0.10	2.67	0.9205	0.09	3.81	1.27	0.9996
40	3.38	0.08	1.13	0.8631	0.25	3.51	3.05	0.9996
50	3.00	0.09	0.91	0.8577	0.37	3.11	3.53	0.9998

$$\ln k = \ln A - \frac{E_a}{RT} \tag{13}$$

E_a can be obtained by plotting (Arrhenius plot) ln k against the reciprocal of the absolute temperature T. The magnitude of E_a may then give an indication of whether a physical or chemical adsorption process is in operation. In physical adsorption (physisorption) the interaction is easily reversible, equilibrium is rapidly attained and its energy requirements are small so E_a is usually no more than 5-40 kJ/mol [26], because usually weak intermolecular forces are involved. However, with chemical adsorption (chemisorption) much stronger bonding forces are involved and E_a values range from 40-800 kJ/mol [26]. In our work, an E_a of 51.06 kJ/mol was determined from the slope of the plot of ln k versus $1/T$ (Table 2). From this it is inferred that the adsorption of indigo carmine onto silk most likely involves a chemisorption process consistent with strong H-bond reinforced salt bridge interactions between the dye sulfonate goups and protonated amino groups on the silk. A similar, though lower, activation energy of 47.5 kJ/mol was noted for the chemisorption of the acidic lac dyes on silk [12].

The enthalpy ($\Delta H^{\#}$), entropy ($\Delta S^{\#}$) and free energy ($\Delta G^{\#}$) of activation for dye adsorption can also be calculated using the Eyring equation [25] as follows:

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S^{\#}}{R} - \frac{\Delta H^{\#}}{RT} \tag{14}$$

where k_b and h refer to Boltzmann's constant and Planck's constant respectively. The enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$) of activation were calculated from the slope and intercept of a plot of ln (k/T) versus $1/T$, and the free energy of activation ($\Delta G^{\#}$) values then calculated [25] from:

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \tag{15}$$

The values thus obtained for indigo carmine adsorption on silk are given in Table 2, with the large negative entropy value ($\Delta S^{\#}$) being consistent with the interaction between the disulfonate dye and the silk.

Equilibrium of Adsorption

Adsorption Isotherms

While the previous discussion focused on the kinetics of

Table 2. Activation parameters for the adsorption of indigo carmine dye onto silk at an initial dye concentration of 1×10^{-4} M and pH 4.0

Temperature (°C)	k_2 (g silk/mg min)	E_a (kJ/mol)	R^2	$\Delta H^{\#}$ (kJ/mol)	$\Delta S^{\#}$ (J/mol K)	$\Delta G^{\#}$ (kJ/mol)	R^2
30	0.09	51.06	0.9824	48.47	-257.72	126.55	0.9815
40	0.25					129.13	
50	0.37					131.71	

dye adsorption, further information on the dyeing process can also be obtained from studies at equilibrium. The relationship between the amounts of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm [27]. Several models have been published in the literature to describe experimental data for adsorption isotherms, with the Langmuir [28] and Freundlich [12,15] models being the most frequently employed. In our work, both models were used to describe the relationship between the amount of indigo carmine adsorbed and its equilibrium concentration.

Langmuir Isotherm

The Langmuir adsorption model is based on the assumption that adsorption takes place at specific homogeneous sites on the surface. 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:

$$q_e = \frac{QbC_e}{1+bC_e} \tag{16}$$

A linear form of this expression is:

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \left(\frac{1}{Q}\right)C_e \tag{17}$$

For lower concentrations, the following form of the Langmuir equation is found to be more satisfactory [29]:

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{QbC_e} \tag{18}$$

In the above equation, Q is the maximum amount of the dye per unit weight of fiber to form 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 fiber at equilibrium, and b the Langmuir constant related to the affinity of binding sites. 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 values of Q and b (from equation (17); Table 3) can be calculated from the intercepts and slopes of different straight lines representing the different temperatures (data not shown). The R^2 values indicated a generally good fit of the equilibrium data in the Langmuir isotherm expression in line with monolayer coverage of indigo carmine onto silk. It was observed that the adsorption of indigo carmine dye at higher temperature decreased with increasing temperature indicating that the process is exothermic. As expected, the Q values decreased with increasing temperature, while the b values indicated that the silk yarn had a maximum affinity for indigo carmine dye at lower temperature.

Freundlich Isotherm

The Freundlich isotherm has also been widely used for many years to model dye adsorption at equilibrium. The isotherm model describes the equilibrium on heterogeneous surfaces and hence does not assume a monolayer capacity [30].

The Freundlich equation is given as:

$$q_e = Q_f\, C_e^{1/n} \tag{19}$$

where Q_f is roughly an indicator of the adsorption capacity and $1/n$ of the adsorption intensity, while the corresponding linear form of the Freundlich expression (equation (20)) is thus:

$$\ln q_e = \ln Q_f + \frac{1}{n}\ln C_e \tag{20}$$

Therefore, Q_f and $1/n$ can be determined from the linear plot of $\ln q_e$ versus $\ln C_e$. The magnitude of the exponent $1/n$ gives an indication of the favourability of adsorption, with values of $n > 1$ being commensurate with favourable adsorption conditions [15]. The determined values of the Freundlich exponent n (Table 3) were greater than 1, representing favorable adsorption conditions [31]. The Q_f values decreased with increasing temperature which again supported an exothermic process. However, this model showed a lower correlation with the experimental adsorption data compared to those derived in the Langmuir model.

Thermodynamic Parameters

The thermodynamic parameters for the adsorption process, namely Gibbs free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) of adsorption can be evaluated using the following equations [32]:

Table 3. Langmuir and Freundlich isotherm constants for the adsorption of indigo carmine dye onto silk at different temperatures

Temperature (°C)	Langmuir $\frac{C_e}{q_e} = \frac{1}{Qb} + \left(\frac{1}{Q}\right)C_e$			Freundlich $\ln q_e = \ln Q_f + \frac{1}{n}\ln C_e$		
	Q (mg/g silk)	b (m*l*/mg)	R^2	Q_f (mg/g silk)	n	R^2
30	15.06	55.33	0.9950	29.44	2.55	0.9163
40	17.99	25.27	0.9758	35.04	2.07	0.9484
50	18.38	22.67	0.9101	42.72	1.77	0.8960

Table 4. Thermodynamic parameters for the adsorption of indigo carmine onto silk at different temperatures

Temperature (^{o}C)	K_C	ΔG^{o} (kJ/mol)	ΔH^{o} (kJ/mol)	ΔS^{o} (J/mol·K)	R^2
30	4.48	-3.82	-27.26	-77.35	0.9919
40	3.34	-3.05			
50	2.29	-2.28			

$$K_C = \frac{C_{ad,e}}{C_e} \tag{21}$$

$$\Delta G^{o} = -RT\ln K_C \tag{22}$$

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} \tag{23}$$

$$\ln K_C = \frac{\Delta S^{o}}{R} - \frac{\Delta H^{o}}{RT} \tag{24}$$

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 remaining in the dye bath solution at equilibrium (mg/*l*), respectively; T is the solution temperature (K) and R is the gas constant. Enthalpy (ΔH^{o}) and entropy (ΔS^{o}) of the adsorption are calculated from the slope and intercept of the van't Hoff plots of ln K_c versus $1/T$. The complete adsorption and thermochemical data for the indigo carmine-silk interaction are given in Table 4. In general, all thermochemical quantities decrease when the temperature increases. This behavior suggests a progressive indigo carmine desorption process when the temperature increases [1]. The negative Gibbs free energy values demonstrated that the indigo carmine dyeing on silk is a thermodynamically favorable process, for the temperature range evaluated. The obtained enthalpy value of −27.26 kJ/mol confirms that the indigo carmine dyeing of silk is an exothermic process, so raising the temperature leads to lower affinity and less dye being adsorbed at equilibrium.

Conclusion

Adsorption kinetic and equilibrium parameters for indigo carmine dyeing of silk were obtained in a batch system. Adsorption capacity was dependent on the initial dye concentration, contact time, pH of the dye solution, MLR and temperature. An increase in the initial dye concentration lead to an increase in the adsorption capacity of indigo carmine dyeing on silk at the optimum contact time (60 min), while an increase in pH and MLR also increased dyeing capacity. The experimental data fitted well to the second-order kinetic model with an activation energy of 51.06 kJ/mol. This indicated that the adsorption of indigo carmine onto silk is likely to be controlled by the chemisorption process. The values of the enthalpy ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) were 48.47 kJ/mol and −257.72 J/mol K, respectively. Langmuir and Freundlich adsorption models were applied to describe the experimental equilibrium isotherms. The Langmuir equation agreed very well with the equilibrium isotherm, while the Freundlich equation gave a poorer fit. The negative values of ΔG^{o} and ΔH^{o} indicated that overall adsorption processes were spontaneous and exothermic.

The results from this study will be used to underpin further work improving the effectiveness of dyeing of silk by villagers in northeast Thailand with indigo extracted from the plant *Indigofera tinctoria* Linn., and of other indigo derivatives.

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