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Adsorption kinetic study of lac dyeing on cotton

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Abstract

Adsorption kinetics study of lac dyeing on cotton were carried out under dyeing conditions of pH 3.0, MLR 1:100 and an initial dye concentration 480 ± 10 mg/L. Pseudo first- and second-order kinetic models were used to examine the adsorption kinetic data. It was found that the adsorption kinetics of lac dyeing on cotton with pH control was found to follow the pseudo second-order kinetic model with an activation energy of 42.4 kJ/mol.

Keywords: Dyeing; Lac dye; Adsorption; Cotton; Kinetics

1. Introduction

There is considerable current interest in dyeing of textile fibres with natural dyes, on account of their compatibility with the environment, and because of their generally lower toxicity and allergic reactions. Lac dye is a natural reddish 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 two major anthraquinone-based components: laccaic acids A and B [2−8]; the minor components, laccaic acids C, D, E and F have also been isolated [9,10]. Erythrolaccin 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 northeast of Thailand, lac dye is a natural red dyestuff extracted for dyeing of cotton and silk [1]. In our previous work, we investigated the adsorption and kinetics of lac dyeing on silk [12]. However, the adsorption kinetics of lac dyeing on cotton with pH control has not been reported. Most studies have focused on qualitative aspects of the modification of cotton for lac dyeing by using chitosan [13], Discofix DBA [14] and poly(ethyleneimine) [15]. Recently, we reported on the thermodynamic parameter of lac dyeing on cotton (with and without chitosan pretreatment) [16], and in this paper we now describe new kinetic facets of this process in untreated cotton.

2. Experimental

2.1. Materials and chemicals

2.1.1. Cotton yarn preparation [16]

The cotton yarn used was purchased from villagers living in Muangphon District, Khon Kaen, Thailand. To remove the wax and impurities, the cotton yarn (100 g) was added to boiling water (2 L) to which were added soap flakes (ca. 7 g) and sodium carbonate (3 g). The mixture was then boiled for 1 h. The cotton was then removed, washed with hot water and cold water in order to avoid breakdown of the emulsion and precipitation of the impurities onto the cotton, squeezed to remove excess liquor and air dried. Finally, it was treated with 1 M HCl (ca. 2 L) at room temperature for 30 min and then removed and washed with deionized water until the rinsed water

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was neutral. The cotton yarn was then dried at room temperature.

2.1.2. Preparation of lac dye [16]

Stick lac (500.90 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 °C for 1 h. The aqueous solution was filtered, the filtrate concentrated under reduced pressure (rotary evaporator) and then dried by using a freeze dryer to give a crude lac dye extract (36.07 g), which was then 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 kinetic adsorption of lac dye onto cotton yarn.

2.3. 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 cotton yarn (0.50 g), which had been pre-warmed in the thermostatted bath for 30 min, was immersed in the dye solution. The cotton 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 $\lambda_{\max}$ 487 nm versus dye concentration in standard lac dye solutions. The amount of dye adsorbed per gram of cotton (mg/g cotton) at any time (q_t) 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 is the initial dye concentration (mg/L) and C_t is the dye concentration after dyeing time t (mg/L), V is the volume of dye solution (mL) and W is the weight of cotton yarn (g) used.

3. Results and discussion

3.1. The effect of temperature on the adsorption of lac dye on cotton

The effect of temperature on the adsorption of lac dye on cotton was investigated. It was found that a higher dyeing temperature resulted in higher initial dye adsorption rate (h_i) on cotton before equilibrium as shown in Fig. 1. These results are similar to those observed for lac dyeing of silk in our previous work [12]. The mobility of the large dye ions would be increased at higher temperature and subsequently the rates of dyeing would be enhanced. A similar observation was also reported in the study on the adsorption of a basic dye on cross-linked cotton [17]. At the equilibrium time, the dye adsorbed by the cotton decreased with increasing temperature, indicating an exothermic process. As can be observed from Fig. 1(a), the time required to reach equilibrium was shorter at higher dyeing temperatures, i.e., 120, 60 and 5 min at 10, 30 and 60 °C, respectively.

The dyeing condition of pH 3.0, initial dye concentration of 480 ± 10 mg/L and MLR of 1:100 was subsequently used to study the adsorption kinetics of lac dye on cotton.

3.2. Kinetics of adsorption

In order to analyze the adsorption kinetics of lac dye on cotton, the pseudo first- and second-order kinetic models were used to analyze the experimental data.

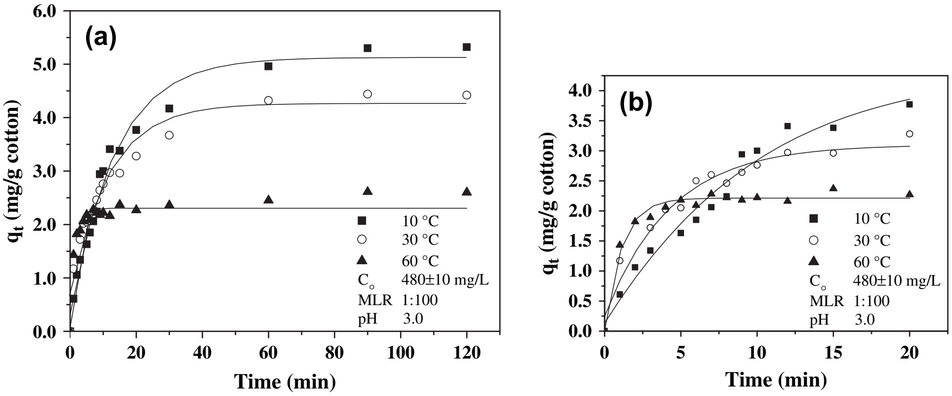

Fig. 1. The effect of contact time and temperature of lac dye on cotton at an initial dye concentration 480 ± 10 mg/L, MLR 1:100 and pH 3.0. (a) The effect of contact time and temperature over a period of 0–120 min. (b) The effect of contact time and temperature over a period of 0–20 min.

Table 1
Comparison of the pseudo first- and second-order adsorption rate constants of lac dyeing onto cotton at an initial dye concentration 480 ± 10 mg/L, MLR 1:100 and pH 3.0

Temperature (°C)	$q_{e,exp}$ (mg/g cotton)	Pseudo first-order model		Pseudo second-order model			
		k_1 (min^{-1})	R^2	k_2 (g cotton/mg min)	$q_{e,cal}$ (mg/g cotton)	h_i (mg/g cotton min)	R^2
10	5.32	4.29×10^{-2}	0.9803	1.60×10^{-2}	5.84	0.55	0.9989
30	4.42	5.52×10^{-2}	0.9914	3.39×10^{-2}	4.68	0.74	0.9990
60	2.60	2.66×10^{-2}	0.7893	2.30×10^{-1}	2.62	1.58	0.9996

A simple kinetic analysis of adsorption is the Lagergren equation. The Lagergren equation, a pseudo first-order equation, describes the kinetics of the adsorption process as follows [18–20]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2}$$

where k_1 is the rate constant of pseudo first-order adsorption (s^{-1}), and q_e and q_t are the amounts of dye adsorbed per gram of cotton (mg/g cotton) at equilibrium and at time t. In many cases, the first-order equation of Lagergren does not fit well for the whole range of contact times and is generally applicable over only the initial stage of the adsorption [21]. After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (2) becomes

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

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 [18,21] is based on adsorption equilibrium capacity and can be expressed as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{4}$$

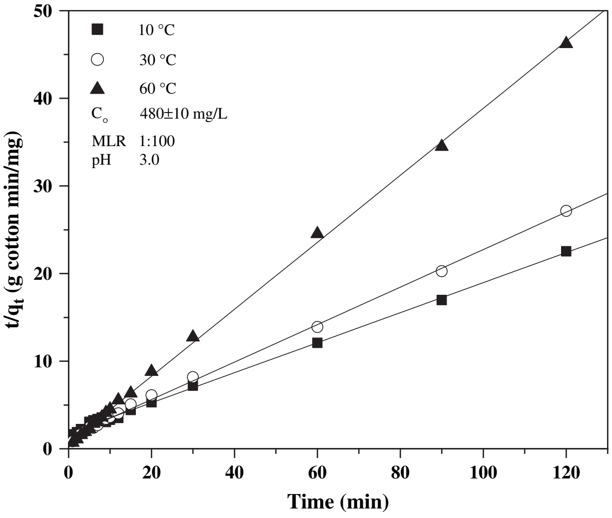

Fig. 2. Plot of the pseudo second-order equation at different temperatures for the adsorption of lac dye on cotton.

where k_2 (g cotton/mg min) is the rate constant for pseudo second-order adsorption. Integrating Eq. (4) and applying the initial conditions give:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{5}$$

or equivalently,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

and

$$h_i = k_2 q_e^2 \tag{7}$$

where h_i [22] is the initial dye adsorption rate (mg/g cotton min). If pseudo second-order kinetics are applicable, the plot of (t/q_t) versus t would 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. It is likely that the behaviour over the whole range of adsorption is in agreement with the chemisorption mechanism being the rate-controlling step [21].

Kinetic data obtained from lac dye adsorption in the present study, was analyzed using the pseudo first-order kinetic model proposed by Lagergren [23] according to Eq. (3). The results are listed in Table 1. Based on the correlation coefficients obtained, the adsorption of lac dye on cotton is not likely to be a first-order reaction.

The pseudo second-order kinetic model was also used to test the experimental data using Eq. (6), and plots of (t/q_t)

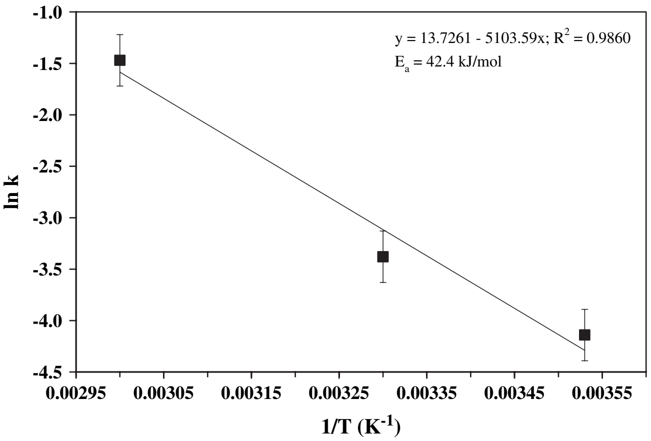

Fig. 3. Arrhenius plot for the adsorption of lac dye on cotton.

Table 2
Activation parameters for the adsorption of lac dye on cotton at an initial dye concentration 480 ± 10 mg/L, MLR 1:100 and pH 3.0

Temperature (°C)	k_2 (g cotton/mg min)	E_a (kJ/mol)	R^2	$\Delta H^\#$ (kJ/mol)	$\Delta S^\#$ (J/mol K)	$\Delta G^\#$ (kJ/mol)	R^2
10	1.60×10^{-2}	42.4	0.9860	39.8	−139.7	79.3	0.9836
30	3.39×10^{-2}					82.1	
60	2.30×10^{-1}					86.3	

against t for the adsorption of lac dye on cotton are given in Fig. 2. The slopes and intercepts of these plots were used to calculate the adsorption capacity ($q_{e,cal}$) and the rate constant (k_2). The experimental data showed a good compliance with the pseudo second-order equation and the correlation coefficients for the linear plots were higher than 0.99 for all the experimental data. Also, the calculated $q_{e,cal}$ values agreed very well with the experimental data. These results suggested that the experimental data for the adsorption kinetics of lac dye on cotton were fitted by the pseudo second-order kinetic model. Similar kinetics were also observed in the dyeing of wool with acid dyes [24], in which the uptake rate of the acid dye on wool was described by a second-order rate expression based on the formation of a protein–dye complex as the rate determining step.

3.3. Activation parameters

From the rate constant k_2 (Table 1), the activation energy (E_a) for the adsorption of lac dye on cotton was determined using the Arrhenius equation (8) [25]:

$$\ln k = \ln A - \frac{E_a}{RT} \qquad (8)$$

where E_a, R and A refer to the Arrhenius activation energy, the gas constant and the Arrhenius factor, respectively.

The Arrhenius plot of $\ln k$ against $1/T$ for the adsorption of lac dye on cotton is shown in Fig. 3 and the activation energy value is listed in Table 2.

The enthalpy ($\Delta H^\#$), entropy ($\Delta S^\#$) and free energy ($\Delta G^\#$) of activation were also calculated using the Eyring equation (9) [25] as follows:

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S^\#}{R} - \frac{\Delta H^\#}{RT} \qquad (9)$$

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 $1/T$ ($y = 6.9551 - 4783.86x$; $R^2 = 0.9836$) while the free energy of activation ($\Delta G^\#$) was obtained from Eq. (10):

$$\Delta G^\# = \Delta H^\# - T\Delta S^\# \qquad (10)$$

The calculated values are listed in Table 2. The negative value of the activation entropy ($\Delta S^\#$) was supportive of an interaction between lac dye and cotton.

4. Conclusion

This study investigated the adsorption kinetics of lac dye on cotton. The initial dye adsorption rates (h_i) onto cotton before equilibrium time increased at higher dyeing temperatures which indicated a kinetically controlled process. The adsorption kinetics of lac dye on cotton was found to follow the pseudo second-order kinetic model and the rate constant indicated a faster adsorption rate than that for lac dye on silk [12]. The activation energy for the adsorption process on cotton was found to be 42.4 kJ/mol.

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