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Research Article

Adsorption Properties of Lac Dyes on Wool, Silk, and Nylon

Bo Wei,[1] Qiu-Yuan Chen,[1] Guoqiang Chen,[1] Ren-Cheng Tang,[1] and Jun Zhang[2]

[1] *National Engineering Laboratory for Modern Silk, College of Textile and Clothing Engineering, Soochow University, Suzhou 215123, China*
[2] *Suzhou Institute of Trade and Commerce, 287 Xuefu Road, Suzhou 215009, China*

Correspondence should be addressed to Ren-Cheng Tang; tangrencheng@suda.edu.cn

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There has been growing interest in the dyeing of textiles with natural dyes. The research about the adsorption properties of natural dyes can help to understand their adsorption mechanism and to control their dyeing process. This study is concerned with the kinetics and isotherms of adsorption of lac dyes on wool, silk, and nylon fibers. It was found that the adsorption kinetics of lac dyes on the three fibers followed the pseudosecond-order kinetic model, and the adsorption rate of lac dyes was the fastest for silk and the slowest for wool. The activation energies for the adsorption process on wool, silk, and nylon were found to be 107.15, 87.85, and 45.31 kJ/mol, respectively. The adsorption of lac dyes on the three fibers followed the Langmuir mechanism, indicating that the electrostatic interactions between lac dyes and those fibers occurred. The saturation values for lac adsorption on the three fibers decreased in the order of wool > silk > nylon; the Langmuir affinity constant of lac adsorption on nylon was much higher than those on wool and silk.

1. Introduction

Natural dyes generally exhibit better biodegradability and compatibility with the environment and lower toxicity and allergic reaction [1–3]. In recent years, there has been growing interest in the dyeing of textiles with natural dyes, and a lot of natural dyes from different resources have been explored to be applied in textile dyeing [4]. On the basis of origins, natural dyes are broadly classified into three categories: vegetable, mineral, and animal origins. Animal origin lac, cochineal, and kermes bearing anthraquinone structures have been the principal natural dyes yielding from the insects [5, 6]; these insect red dyes can dye textiles to purple and red colors and have good color fastness to light in comparison with most of vegetable dyes [6, 7]. Up to the present, there have been a lot of published studies about the application of vegetable dyes to the dyeing of textiles [1, 3–5, 7] but relatively few reports about the exploitation of insect dyes in the field of textile dyeing.

Lac dyes (laccaic acid) consisting of polyphenolic anthraquinone compounds are a natural, weakly acidic, and reddish colorant produced by the insect *Coccus lacca* or *Laccifer lacca* and can be obtained in large amounts as a by-product of shellac industry [8, 9]. Over the past years, there have been a few studies highlighting the dyeing of lac for cotton and silk [8–10]. Chairat and Rattanaphani reported the adsorption kinetics of lac dyeing on cotton and silk, which have been found to follow the pseudosecond-order kinetic model [9, 10]. However, little research has so far been undertaken on the dyeing of nylon and wool with lac dyes. Taking into consideration the fact that the research about the adsorption properties of natural dyes helps to understand their adsorption mechanism and to control their dyeing process, this study is mainly concerned with the kinetics and isotherms of lac adsorption on wool, silk, and nylon fibers.

2. Experimental

2.1. Materials. The scoured, woven wool fabric (warp and weft thread, 156 dtex×2) for color fastness tests up to the standard GB/T 7568.1-2002 was purchased from Shanghai Textile Industry Institute of Technical Supervision. The scoured, woven silk fabric (warp and weft thread, 23.3 dtex×2) and the scoured, woven semidull nylon fabric (warp thread, 55.6 dtex/48F; weft thread, 50.0 dtex/34F) were obtained from Wujiang Zhiyuan Textile Co. Ltd., China. All of the fabrics were plain woven and used as received.

Table 1: Kinetic parameters for the adsorption of lac dyes on wool, silk, and nylon.

Temperature (°C)	Fibers	q_e (mg/g)	$t_{1/2}$ (min)	k ($\times 10^{-2}$ g/[mg·min])	h_i (mg/[g·min])	R^2
70	Wool	42.92	22.498	0.104	1.91	0.9968
	Silk	30.21	0.737	4.490	40.98	0.9999
	Nylon	23.87	3.313	1.265	7.20	0.9992
80	Wool	40.65	7.268	0.339	5.59	0.9971
	Silk	27.55	0.457	7.938	60.24	0.9999
	Nylon	22.42	2.357	1.893	9.51	0.9998
90	Wool	39.37	3.094	0.821	12.72	0.9993
	Silk	25.00	0.163	24.615	153.85	0.9994
	Nylon	21.65	1.522	3.036	14.22	0.9987

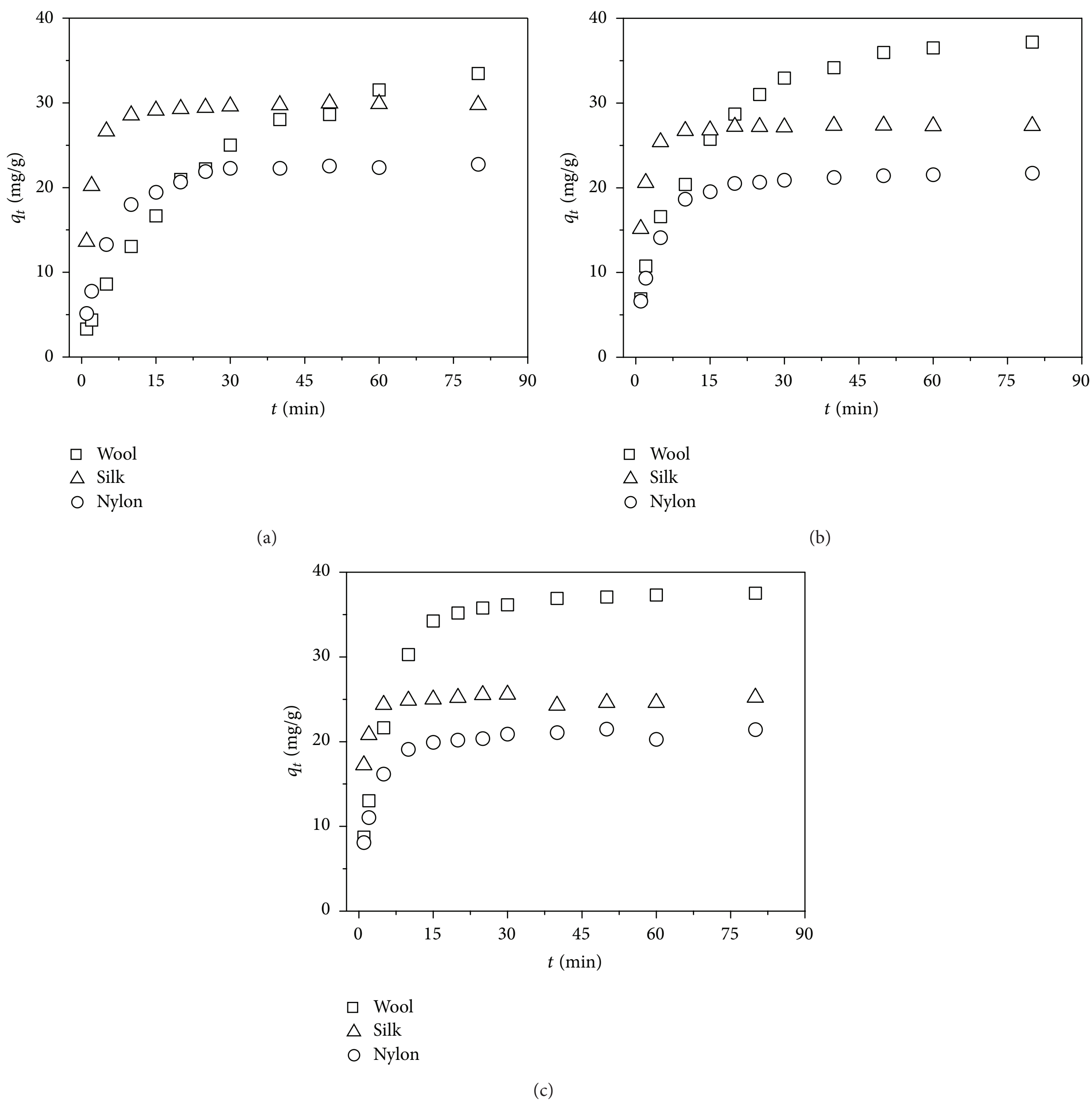

Figure 1: Adsorption rates of lac dyes for wool, silk, and nylon at 70°C (a), 80°C (b) and 90°C (c).

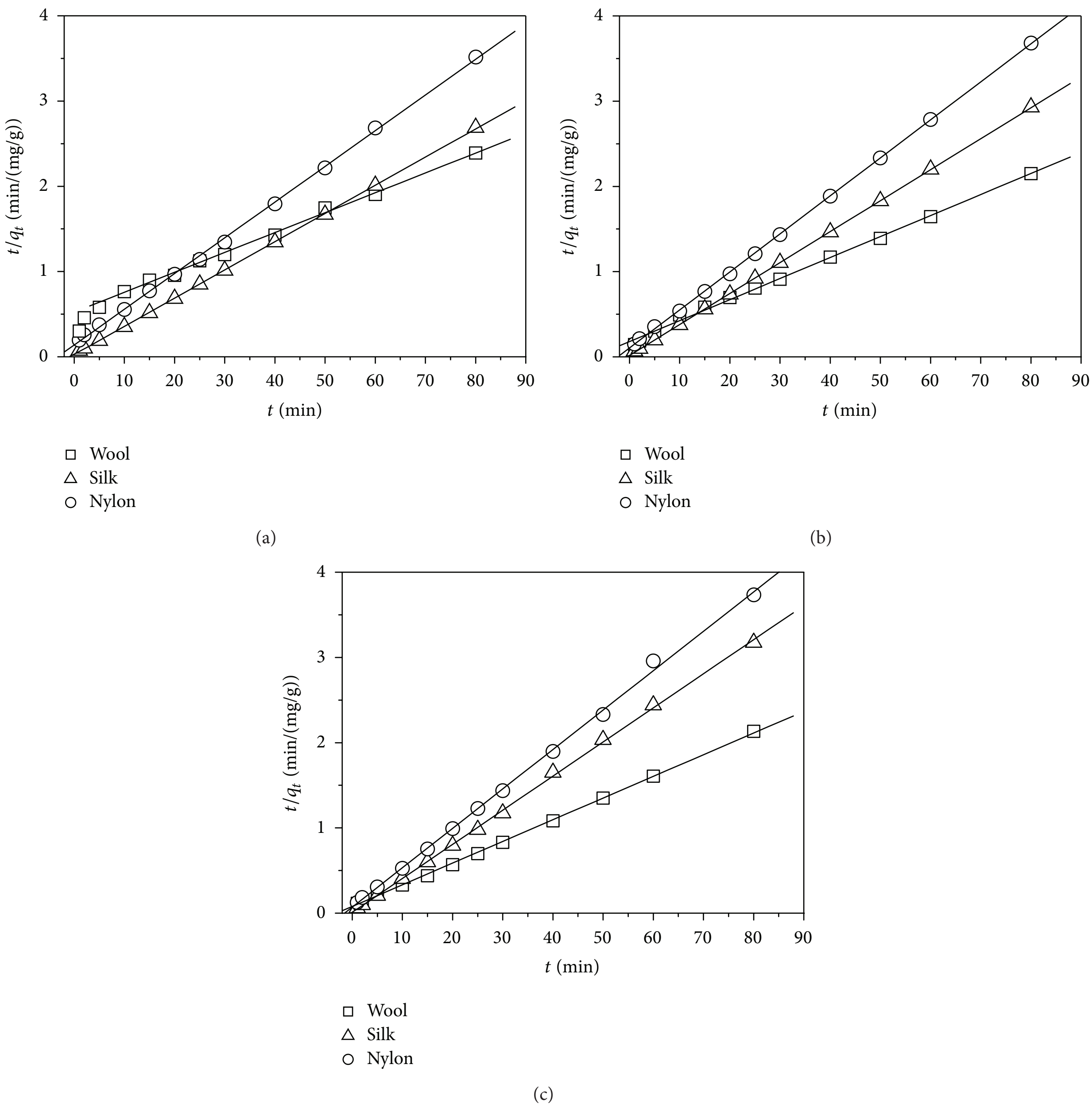

Figure 2: Plots of t/q_t against t for the adsorption of lac dyes on wool, silk, and nylon at 70°C (a), 80°C (b), and 90°C (c).

A commercial lac dye was obtained by Yunnan Tonghai Yang Natural Products Co. Ltd., China. *Leveler O* used as a leveling agent is the commercial product. Citric acid and disodium hydrogen phosphate used to adjust the pH of dyeing solutions were of analytical reagent grade.

2.2. Adsorption of Lac Dyes. All experiments of adsorption were carried out in sealed conical flasks immersed in the universal dyeing machine. The liquor ratio was 60 : 1.

(1) Adsorption rates. The silk, wool, and nylon fabrics were dyes with 4% owf lac dyes and 0.5 g/L *Leveler O* at pH 3 and at constant temperature for different times.

(2) Adsorption isotherms. The adsorption isotherms for lac dyes on the silk, wool, and nylon fabrics were measured in a series of lac dye solutions of various concentrations (1~21% owf) at pH 3 at 90°C for 80 min.

2.3. Determination of Lac Dye Concentration. At the end of each dyeing, the concentration of lac dyes remained in the dye-bath was determined by reference to the extinction coefficient of a calibration plot of lac dyes at the maximum adsorption wavelength. The absorbance of the dye solution was measured using a *Shimadzu* 1800 UV/VIS spectrophotometer. The quantity of lac dyes on the fibers was calculated

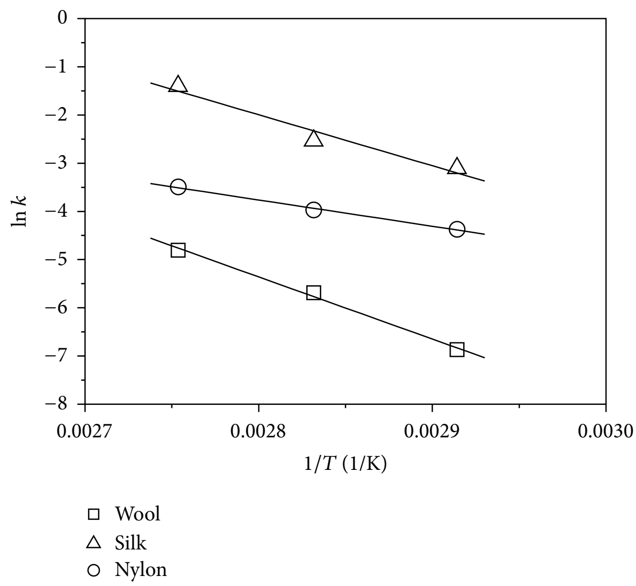

Figure 3: Plots of $\ln k$ versus $1/T$ for the adsorption of lac dyes on wool, silk, and nylon.

by taking into account the initial and final concentration of lac dyes in solution and the weight of the dried fabrics.

3. Results and Discussion

3.1. Adsorption Kinetics of Lac Dyes. The adsorption kinetics is important as it controls the process efficiency. Figure 1 depicts the effect of time (t) on the quantity (q_t) of the adsorption of lac dyes on wool, silk, and nylon at two temperatures. As shown in Figure 1, the initial rates of the adsorption of lac dyes on silk were the fastest, and the quantity of adsorption reached a very high value in short times, indicating that some measures should be taken to control the levelness of silk dyeing. The initial rate of lac adsorption on wool was the slowest, which can be explained by the poor ability of dye diffusion into wool substrate owing to the tight structure of epicuticle layer existing on wool surface. The rate of lac uptake by nylon was between those of wool and silk.

In this study, the pseudosecond-order kinetic model was used to investigate the adsorption process of lac dyes on three fibers. The pseudosecond-order kinetic model is based on both chemisorption and adsorption equilibrium capacity and can be expressed as follows [11, 12]:

$$\frac{dq_t}{dt} = k\left(q_e - q_t\right)^2, \tag{1}$$

where k is the rate constant for pseudosecond-order adsorption and q_t and q_e are the adsorption amounts of lac dyes at time t and at equilibrium.

Integrating (1) and applying the initial conditions give

$$\frac{1}{q_e - q_t} - \frac{1}{q_e} = k \cdot t \tag{2}$$

or, equivalently,

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{3}$$

and [9, 12]

$$h_i = kq_e^2, \tag{4}$$

where h_i is the initial adsorption rate the following:

If the pseudosecond-order kinetics is 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 pseudosecond-order rate constant (k) and the quantity of equilibrium adsorption (q_e).

The half adsorption time ($t_{1/2}$) was calculated using the following [13]:

$$t_{1/2} = \frac{1}{k \cdot q_e}. \tag{5}$$

The pseudosecond-order kinetic model was also used to test the experimental data using (3), and the plots of (t/q_t) against t for the adsorption of lac dyes on the three fibers are given in Figure 2. The kinetic parameters along with the correlation coefficients (R^2) of the kinetic model are shown in Table 1. From Table 1, it is clear that the correlation coefficients for the linear plots were higher than 0.996 for all the experimental data, indicating that the pseudosecond-order kinetic model might be suitable to describe the adsorption process of lac dyes onto wool, silk, and nylon.

As can be seen from Table 1, the kinetic parameters for the adsorption of lac dyes varied according to fiber categories and temperature. For the adsorption of lac dyes on silk, the highest rate constant (k) and initial adsorption rate (h_i) were found with the shortest half adsorption time ($t_{1/2}$), which might be ascribed to the looser surface structure of silk than those of wool and nylon. The adsorption of lac dyes on wool showed the lowest k and h_i values with the longest $t_{1/2}$, which could be explained by the existence of the epicuticle layer on the surface of wool and the corresponding barrier action to the diffusion of dyes into fiber interior.

From the rate constant k (Table 1), the activation energies (E_a) for the adsorption of lac dyes on the three fibers were determined using the following Arrhenius equation [9]:

$$\ln k = \ln A - \frac{E_a}{RT}, \tag{6}$$

where E_a, R, A, and T refer to the Arrhenius activation energy, the gas constant, the Arrhenius factor, and the temperature in K, respectively. E_a can be estimated from the slope of the plots of $\ln k$ versus $1/T$ shown in Figure 3.

The calculated activation energies of the adsorption of lac dyes were 107.15 kJ/mol for wool, 87.85 kJ/moL for silk, and 45.31 kJ/mol for nylon, respectively. The physisorption processes usually have energies in the range of 5–40 kJ/moL, while higher activation energies (40–800 kJ/moL) suggest chemisorptions [14, 15]. Therefore, it can be concluded that the adsorption of lac dyes has the characteristic of chemisorptions which is a consequence of the ion-ion interaction between the protonated amino groups in three fibers and the carboxyl groups in lac dyes.

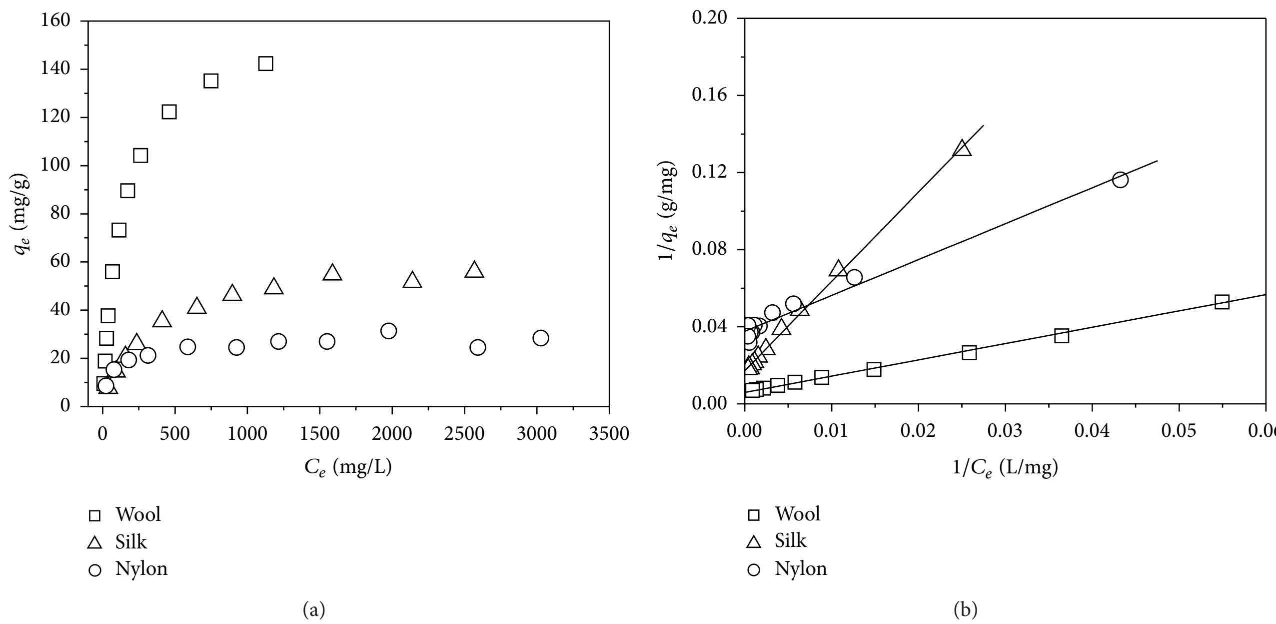

Figure 4: Plots of q_e against C_e (a) and $1/q_e$ against $1/C_e$ (b) of adsorption isotherms of lac dyes on wool, silk, and nylon.

Table 2: Langmuir adsorption parameters of lac dyes on wool, silk and nylon.

Fibers	Q (mg/g)	b (mL/mg)	R^2
Wool	169.49	6.97	0.9994
Silk	58.14	3.71	0.9984
Nylon	26.60	20.19	0.9789

3.2. Adsorption Isotherms of Lac Dyes. The adsorption isotherms of lac dyes on three fibers at 90°C are given in Figure 4. Here, C_e is the concentration of lac dyes in the solution at the end of dyeing. Clearly, within a certain range of concentration, the amount of lac uptake by fibers (q_e) increased with increasing concentrations of lac dyes in the solutions. As the C_e increased further, the q_e would approach a maximum value. The adsorption isotherm curves had the characteristics of Langmuir type. As a result, the dyeing mechanism of lac dyes on three fibers could be explained by Langmuir model. The Langmuir affinity constants and saturation values could be calculated according to the following linearity equation of $1/q_e - 1/C_e$ [9, 16] and are listed in Table 2:

$$\frac{1}{q_e} = \frac{1}{bQC_e} + \frac{1}{Q}, \tag{7}$$

where q_e and C_e are the concentrations of lac dyes on fibers and in solution at the end of dyeing, respectively; b is the Langmuir affinity constant; Q is the saturation concentration of dyes on fibers by Langmuir.

It is clear from Table 2 that the Q values for lac adsorption on the three fibers decreased in the order of wool > silk > nylon, with this being directly relevant to the content of amino groups in the three fibers. Lac dyes showed the much higher Langmuir affinity constant (b) for nylon than those for wool and silk, which was due to their stronger nonionic interactions with nylon such as van der Waals forces.

4. Conclusions

This study discussed the adsorption properties of lac dyes on wool, silk, and nylon fibers. The adsorption process of lac dyes on the three fibers was in accordance with the pseudosecond-order kinetic model. The adsorption rate of lac dyes was the fastest for silk and the slowest for wool. The activation energies of the adsorption of lac dyes were 107.15 kJ/moL for wool, 87.85 kJ/moL for silk, and 45.31 kJ/moL for nylon, respectively, showing the chemisorption characteristic. The adsorption of lac dyes on the three fibers followed the Langmuir model, indicating that the ion-ion interaction between lac dyes and those fibers occurred. The saturation values for lac adsorption on the three fibers decreased in the order of wool > silk > nylon, with this being directly relevant to the content of amino groups in those fibers. Lac dyes showed the higher Langmuir affinity constant for nylon than those for wool and silk.

Acknowledgments

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