

ADSORPTION KINETICS AND THERMODYNAMIC STUDIES OF LAC DYE ON POLYDOPAMINE-COATED SILK YARN

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In this study, silk yarn was treated with polydopamine nanoparticles (PDA) formed *in situ* by oxidation of a dopamine solution in the presence of oxygen. The adsorption kinetics of lac dye on the PDA-coated silk yarn at different temperatures was investigated. The values of the dye adsorption rate constant (k) at different temperature were calculated using the modified Cegarra-Puente equation. The results showed that the dye adsorption rate constant (k) and the diffusion coefficient (D) increased with an increasing temperature, which was consistent with a kinetically controlled diffusion process. The activation energy (E_a) was found to be 51.2 kJ mol^{-1} . The adsorption isotherm of lac dye on the PDA-coated silk yarn at pH 2.50 was studied in a batch system. The findings revealed that the adsorption isotherm could be described by the Langmuir isotherm ($R^2 > 0.99$). The results indicated that the pretreatment of silk yarn with PDA, followed by dyeing with an aqueous solution of lac dye and then post-mordanting with alum, exhibited color fastness to light and washing at rating levels of 4 and 3-4, respectively.

Keywords: polydopamine, lac dye, natural dye, silk, dopamine, thermodynamic

INTRODUCTION

Lac dye, which is the soluble part of stick lac secreted by the insect *Coccus laccae* (*Laccifer lacca* Kerr), is mainly composed of two major anthraquinone-based components: laccaic acids A and B;¹ but three other minor components, laccaic acids C, D and E, have also been isolated (Fig. 1). Lac dye has very high potential for use as a natural food additive and in cosmetics,² but also as a natural dyestuff for textile dyeing.³ In the north and northeast of Thailand, lac dye is used as a natural red dyestuff for cotton and silk dyeing.¹ However, the color fastness to washing of the dyed silk yarn is quite low because of the presence of many free polar groups in the anthraquinone of the dye molecule. An alternative way to overcome this problem, the pretreatment of silk yarn with chitosan before lac dyeing, was reported.⁴ As a result, the lac dye displayed high adsorption capacity on silk yarn coated with chitosan and also decreased the dye desorption from silk yarn, compared with the untreated silk

yarn. Chimprasit *et al.* studied lac dye adsorption on silk yarn coated with microcrystalline chitosan.⁵ It was found that a significant enhancement of dye uptake onto microcrystalline chitosan coated silk yarn was achieved, compared with the untreated silk yarn. In addition, a *Memecylon* extract from the dried leaves of the plant (*Memecylon scutellatum* Naud.) was used as a bio-mordant for silk dyeing with lac dye.⁶ It revealed that the *Memecylon* extract promoted the adsorption of lac dye onto the silk and increased the attraction between the lac dye and the silk surfaces because this extract contains tannin and can act as a fixing agent. Moreover, the use of different metal salts (*e.g.* alum, copper sulphate, stannous chloride) as mordants for silk dyeing with lac dye showed a better fastness to washing, compared to dyeing without mordant.^{7,8} This may be due to the fact that metal ions can act as acceptors to electron donors to form co-ordinate

bonds with dye molecules, resulting in their

insolubility in water.

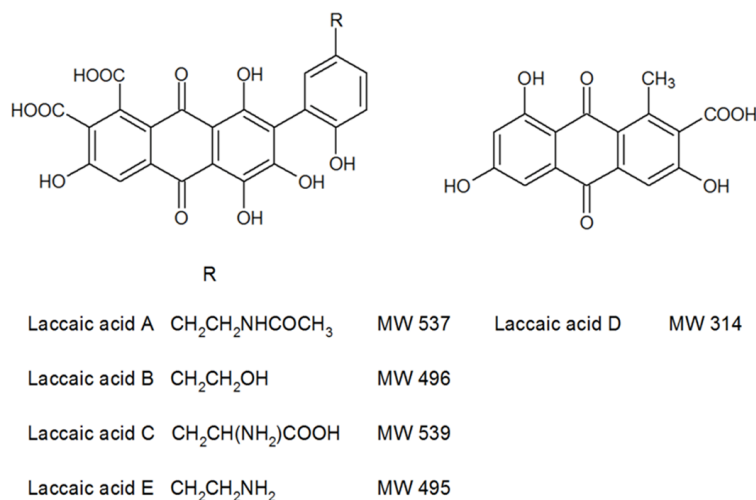


Figure 1: Chemical structure of lac dye components

In order to further increase dyeability, one possibility is to use polydopamine (PDA) in the dyeing of textiles. PDA is a biocompatible synthetic mimic of mussel adhesive protein, which is a non-toxic and biodegradable compound.⁹ It is a major pigment of naturally occurring melanin (eumelanin). It is synthesized via polymerization of dopamine (DA) monomer under alkaline conditions (pH 8.5) in the presence of oxygen. This self-polymerization reaction proceeds under mild conditions without the need for any complicated instrumentation or hazardous reaction conditions.¹⁰ PDA is widely used for many coating applications,¹¹ as a grafting material, as well as an antimicrobial agent.¹⁰⁻¹² More importantly, it has been reported that PDA can also be used as a photo-protective agent.¹³ For example, Sheng *et al.* used the PDA as a coating agent on avermectin.¹² It was found that the PDA coating exhibited remarkable UV-shielding properties for avermectin. Yang *et al.* studied the effect of PDA coating on improving the photostability of poly(1,3,4-oxadiazole)s (POD) fiber.¹³ Their results showed that PDA could efficiently capture the superoxide anion radical, thus reducing the photodegradation of POD fibers, due to its catechol structure. Silk fabric dyed with PDA produced *in situ* has also been shown to have good anti-UV properties.¹⁴ In addition, PDA was also used in the dyeing of

wool, cotton and polybenzimidazole (PBI) fabrics in the presence of a model dyestuff, rhodamine B. It showed that the color yield (*K/S*) values of the dyed cotton and PBI fabrics in the presence of PDA were obviously higher than those in the absence of PDA, which indicated improved dyeability of the fabrics.¹⁵ Recently, PDA has been used to pretreat silk yarn, followed by dyeing with a *P. macarthurii* extract.¹⁶ It was found that the color yield (*K/S*) values as well as the color fastness to light and washing of the *P. macarthurii* dyed PDA-treated silk yarn were better than those of the untreated dyed silk yarn.

As far as we are aware, there are no reports in the literature on the adsorption kinetics and thermodynamic studies of natural dye on polydopamine-coated protein fiber. Therefore, we were interested in investigating the potential of PDA to improve the dyeability of silk yarn in lac dyeing. In order to gain a clearer understanding of the process at a molecular level, we investigated the kinetic and thermodynamic aspects of the adsorption of lac dye on PDA-coated silk, as well as the effect of initial dye solution pH on the adsorption, and the results are reported in this paper.

EXPERIMENTAL

Chemicals and materials

Dopamine hydrochloride (H8502, Sigma-Aldrich, USA) and tris(hydroxymethyl)aminomethane (99+%,

for biochemistry, ACROS Organics, Thermo Fisher Scientific, USA) were purchased. Degummed silk yarn (Luangpirot species) and stick lac were bought from Ruenmail-Baimon Part. Ltd. (Thailand). Analytical grade monopotassium phthalate, hydrochloric acid, sodium carbonate, ethanol and sodium hydroxide were purchased from Merck (Germany).

Instruments

An ultrasonic cleaner (Elmasonic P 30 H, 50/60 Hz, 230-240 V, Germany) was used to extract lac dye solution from stick lac. A thermostatted shaker bath (SWB 5050 shaking water bath; National Labnet Company, USA) was employed to coat silk yarn with PDA and for dyeing. A pH meter (Orion 420A; Thermo Scientific, USA) was used to measure the pH values of the solutions. The particle sizes and particle size distribution index of the obtained PDA solution (0.10 mg mL^{-1}) were determined with a Malvern Nano ZS light-scattering instrument (Malvern Instruments, UK). The measurement was performed in a 1 mL quartz cuvette, using a 4 mW helium-neon laser, operating at a wavelength of 633 nm, at 25°C , with the scattering angle fixed at 173° . Surface morphology and the average diameter of PDA particles were observed using field emission scanning electron microscopy (FE-SEM, JEOL JSM-7800F, Japan) and transmission electron microscopy (TEM, JEOL JEM-2100 microscope, JEOL Inc., MA, USA). The PDA sample was coated with gold by sputtering for 60 s before observation and operated with an accelerating voltage of 120 kV for FE-SEM and TEM, respectively. All the samples were coated with gold by sputtering for 60 s before observation. A colorimeter (LabScan XE 0/45, Hunter Lab, USA) was used to measure the CIELab values of all the samples. A Unicam 310 UV-Vis spectrophotometer (Unicam Instruments, UK) was employed for absorbance measurements using quartz cells of 1 cm path length. A universal testing machine (Lloyd Instruments Ltd, UK) was used to determine the ultimate tensile strength, initial modulus and percentage of strain of the PDA-coated silk and degummed silk yarns.

Average particle size and characterisation of polydopamine

A PDA solution (0.10 mg mL^{-1}) was prepared by dissolving the required amount of DA hydrochloride powder in a mixture of ethanol and distilled water (1:1), and then adjusting the solution pH to 8.5 using Tris buffer. The particle size and polydispersity index (PDI) of the obtained PDA particles were measured by dynamic light scattering (DLS). In addition, the morphology of the obtained PDA particles was characterized using a field emission scanning electron microscope (FE-SEM) and a transmission electron microscope (TEM) in order to ensure they had been formed properly, with suitable dispersivity, prior to the silk coating process.

Preparation of PDA-coated silk

The degummed silk yarn used in this study was sonicated sequentially with distilled water and then with an ethanol solution in an ultrasonic bath for 5 min at room temperature, keeping the material to liquor ratio at 1:50. This process was repeated three times. The silk samples were squeezed to remove excess solvent, dried at room temperature and then used for the next step. To obviate too marked a color change in the dyed silk yarn, the PDA-coated silk yarn used in the dyeing experiments was prepared using an initial dopamine (DA) concentration of 0.10 mg mL^{-1} . The PDA solution (0.10 mg mL^{-1}) was prepared by dissolving the required amount of DA hydrochloride powder in a mixture of ethanol and distilled water (1:1), and then adjusting the solution pH to 8.5 using Tris buffer. The silk samples were immersed directly into the freshly prepared DA solution, keeping the material to liquor ratio at 1:100, and then shaken at room temperature for 24 h in a thermostated shaker operated at $150 \text{ strokes min}^{-1}$ to aerobically polymerize the DA. The PDA-coated silk yarn was removed and thoroughly washed with ethanol at room temperature to remove non-adhering PDA until the ethanol was colorless and then washed with distilled water. The PDA-coated silk yarn was then allowed to air-dry at room temperature, prior to use in the further studies.

PDA-coated silk and degummed silk yarns were then tested for strength using the universal testing machine. The universal testing machine provided Young's modulus, ultimate tensile strength, initial modulus and percentage of strain of the yarns, given an average diameter of 0.05 mm, gauge length of 10 mm, and pulling speed of 50 mm min^{-1} . The test provided information on mechanical characteristic changes in the PDA-coated silk yarn, compared with the degummed silk yarn.

Dyeing of untreated and treated silk yarn with lac dye

Dyeing was carried out by shaking the silk yarn coated with PDA and the untreated silk yarn with lac dye solution (500 mg L^{-1}) at pH 2.50 in a conical flask at 60°C for 60 min in a thermostated shaker bath operated at $150 \text{ strokes min}^{-1}$, keeping a material to liquor ratio of 1:00. After dyeing, the silk yarn was washed with tap water to remove the unfixed dye and then air dried.

The dyed silk yarn coated with PDA was immersed directly in an aqueous solution of alum (0.25% w/v; distilled water) at room temperature for 30 min. It was then removed, washed with tap water to remove the unfixed dye, and then air dried.

Color measurement

The sample was wound around the skein holder twice in taut layers and an average of three readings was taken for each measurement. The reflectance of dyed yarn and the values of the CIE $L^*a^*b^*$

coordinates were measured on a LabScan XE 0/45 spectrophotometer, using D65 illuminant and 10° standard observer. The tristimulus values, X , Y and Z under illuminant were converted to CIE $L^*a^*b^*$ coordinates. The color indices derived from the CIE $L^*a^*b^*$ measurement depict the color. ' L^* ' describes lightness, ' a^* ' measures redness (+positive) or greenness (−negative) and ' b^* ' measures yellowness (+positive) or blueness (−negative).

The dyed yarn samples were tested in terms of fastness properties following standard methods; specific tests were for color fastness to washing, ISO 105-C10: 2006 (E) Method A(1) (40 °C, 30 min) and color fastness to light, ISO 105-B02: 2014(E) using ATLAS XENON ARC WEATHER-OMETER MODEL Ci 3000+. The rating scale of wash fastness (both color change and color staining to adjacent fiber) is from 1 (poor) to 5 (excellent). The rating scale of light fastness is from 1 (poor) to 8 (excellent).

Preparation of lac dye solution

Lac dye powder was prepared from stick lac according to the procedure described earlier.¹⁷ A lac dye solution can be obtained by extracting crushed stick lac (240 g) with distilled water (1.5 l) at 80 °C for 1 hour in an ultrasonic cleaning bath, operated at a frequency of 37 kHz, 100 W and sweep mode. The aqueous dye solution was filtered and then the filtrate was freeze dried to give a red dye powder (20.48 g). The red dye powder was then used without further purification.

Influence of initial pH of lac dye solution on the adsorption of lac dye on PDA-coated silk

An initial lac dye concentration of 550 mg L^{−1} was freshly prepared by diluting from the stock solution (1000 mg L^{−1}) in a buffer system of monopotassium phthalate/hydrochloric acid solution at pH 2.00, 2.50, 2.80, 3.20, 3.70, 4.40 and 5.00. The experiments were carried out by shaking PDA-coated silk with an initial dye concentration of 550 mg L^{−1}, keeping a material to liquor ratio of 1:100 in a conical flask with a screw cap in a thermostated shaker bath, operated at 150 strokes min^{−1} and 60 °C for 120 min. After 120 min of contact time, the silk samples were withdrawn, washed with tap water to remove the unfixed dye and then air-dried at room temperature. The residual dye in the dye bath was monitored by a UV-Visible spectrophotometer at λ_{max} 488 nm, using a dye standard calibration curve ($y = 0.0053x$, $R^2 = 0.998$). The amount of dye adsorbed per gram of PDA-coated silk (q_t , mg g silk^{−1}) at any time t was calculated using the mass balance equation:

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

where C_i and C_t are the initial dye concentration and the dye concentration (mg L^{−1}) after dyeing time t , respectively. V is the volume of the dye solution (L) and W is the weight of silk yarn coated with PDA (g).

Batch kinetic experiments

A lac dye solution (500 mg L^{−1}) was freshly prepared by diluting from the stock solution (1000 mg L^{−1}) in a buffer system of monopotassium phthalate/hydrochloric acid solution at pH 2.50. The required dye solution in a screw-capped conical flask (500 mL) was shaken in a thermostated shaker bath operated at 150 strokes min^{−1}. After 30 min, the PDA-coated silk, which had been pre-warmed in a thermostated bath for 30 min, was directly immersed in the dye solution, keeping a material to liquor ratio of 1:100. After the selected time intervals, 1.00 mL of the dye solution was pipetted into a volumetric flask (5.00 mL) and then diluted with distilled water to 5.00 mL to measure its absorbance at λ_{max} 488 nm. Dye concentrations in the dye bath were determined at time zero and at subsequent times using a calibration curve based on the absorbance at λ_{max} 488 nm *vs* dye concentrations in standard lac dye solutions ($y = 0.0053x$, $R^2 = 0.998$). The amount of dye adsorbed per gram of PDA-coated silk yarn (q_t , mg g silk^{−1}) at any time was calculated using the mass balance equation (Eq. 1). Bath temperatures of 30, 45, 60 and 80 °C for batch kinetic experiments were used.

Batch isotherm experiments

Lac dye solutions at different concentrations (200–2300 mg L^{−1}) were freshly prepared in a buffer system of monopotassium phthalate/hydrochloric acid solution at pH 2.50. The experiments were carried out by shaking PDA-coated silk with different concentrations of dye solution, keeping a material to liquor ratio of 1:100, in a conical flask with a screw cap, at 30, 60 and 80 °C, in a thermostated shaker bath operated at 150 strokes min^{−1} for 2 h. Dye concentrations were determined at time zero and at equilibrium time using a dye standard calibration curve ($y = 0.0053x$, $R^2 = 0.998$) based on the absorbance at λ_{max} 488 nm *versus* dye concentrations in standard lac dye solutions. The amount of dye adsorbed per gram of PDA-coated silk yarn at equilibrium time (q_e , mg g silk^{−1}) was calculated using:

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

where C_i and C_e are the initial and equilibrium dye solution concentrations (mg L^{−1}), respectively. V is the volume of the dye solution (L) and W is the weight of silk yarn coated with PDA (g) used.

RESULTS AND DISCUSSION

PDA characterization

In this study, PDA (0.10 mg mL^{−1}) was synthesized in a water-ethanol system at room temperature by the reported procedures,^{17–19} exposing DA hydrochloride to air under basic conditions in Tris buffer. DLS analysis of the PDA formed in a dopamine solution showed

monodisperse particles, with average diameters of 354.9 ± 3.54 nm and narrow PDI value (0.068 ± 0.03) (Fig. 2). To confirm the DLS technique, the morphology and the average diameter of PDA were revealed by FE-SEM and TEM. The result indicated that uniform spherical particles were obtained, with an average size of 100 nm (Fig. 3). Considering that DLS relies on Rayleigh scattering from the suspended nanoparticles that undergo Brownian motion, it is therefore unable to distinguish between nanoparticles with slight differences in diameter or to precisely resolve polydisperse samples. In comparison with the FE-SEM and TEM techniques, DLS measures the hydrodynamic diameter of the particles in solution, which includes the hydration layer or agglomerates of smaller particles, leading to a larger particle size in general. This is the reason why the average diameters of PDA determined using DLS is

significantly larger than the size measured by the FE-SEM and TEM techniques.

PDA-coated silk yarn

The silk yarn, after immersion in a DA solution at 0.10 mg mL^{-1} for 24 h, changed to a brown color due to PDA adsorption, as shown in Figure 4. Adsorption could be due in part to PDA being attached to the silk yarn *via* a Schiff base reaction/Michael addition process involving amino group components in the silk protein.^{11,20} Non-covalent interactions are also likely to occur. It was found that the PDA coating on silk yarn decreased the color brightness (L^*) of the PDA-coated silk yarn.

In addition, the PDA-coated silk yarn was also tested for Young's modulus, ultimate tensile strength and percentage of elongation to evaluate any physical changes occurring in the yarn after pretreatment with PDA under basic condition in a weak base (Tris buffer).

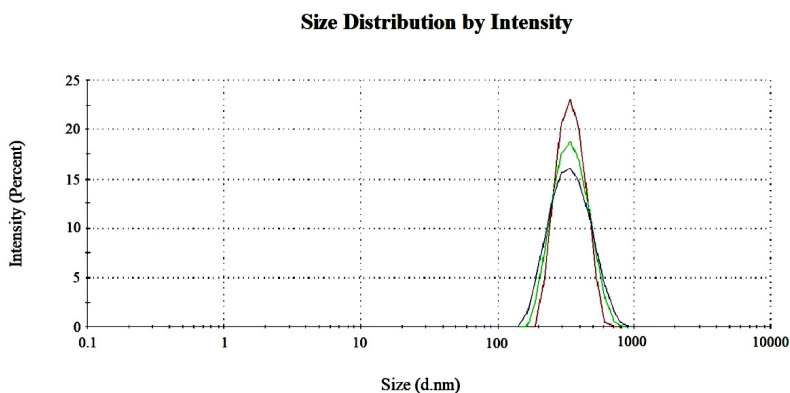


Figure 2: Particle size distribution analysis of PDA by DLS

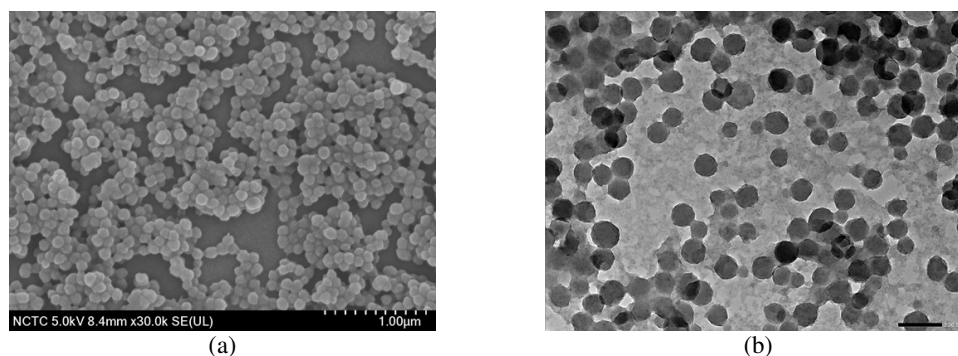


Figure 3: FE-SEM (a) and TEM (b) images of PDA at a concentration of 0.10 mg mL^{-1}

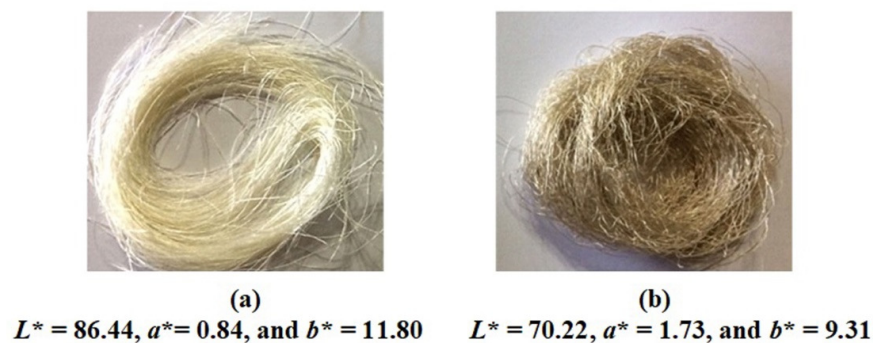
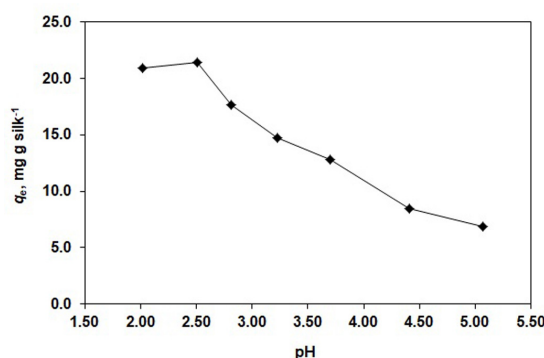


Figure 4: Images of degummed silk yarn (a) and PDA-coated silk yarn (b)

Table 1
Tensile properties of PDA-coated silk and degummed silk yarns

| Sample | Young's modulus (GPa) | Ultimate tensile strength (MPa) | Elongation (%) |
|----------------------|-----------------------|---------------------------------|----------------|
| Degummed silk yarn | 7.9 | 1279 | 32.1 |
| PDA-coated silk yarn | 7.7 | 1133 | 31.6 |

Figure 5: Influence of initial pH of lac dye solution on adsorption of lac dye on PDA-coated silk (initial dye concentration of 500 mg L⁻¹, contact time of 120 min, temperature of 60 °C)

It was found that Young's modulus, ultimate tensile strength and percentage of elongation of the PDA-coated silk yarn remained similar to those of the degummed silk yarn (control), as listed in Table 1. Therefore, alkaline hydrolysis of peptide bonds is hardly destroyed under this condition, when compared to strong basic condition, using sodium hydroxide or potassium hydroxide. Based on this principle, the tensile properties of the silk yarn before and after pretreatment with PDA did not show significant differences in values.

Influence of initial pH on dye uptake

The initial pH of the lac dye solution is one of the most important parameters controlling the

adsorption capacity of dyeing.³ The effect of different initial pH values on the adsorption of lac dye on PDA-coated silk yarn at constant initial dye concentration, temperature, and contact time is shown in Figure 5. It was found that the amount of the dye adsorbed on PDA-coated silk increased with decreasing the pH from 5.00 to 2.50, and remained constant in the pH range of 2.00-2.50, where the highest dye adsorption was observed. Since PDA contains both catechol/quinone and amine groups, the interactions between PDA and the silk yarn surface occurred by hydrogen bonding and Michael addition/Schiff base reaction with amino and carboxylic groups of proteins on the silk yarn surface. The weakly acidic groups in laccic acids A and B, which are

the major laccaic acid components in lac dye, could interact with the PDA-coated silk *via* hydrogen bonds, and π - π stacking interactions under acidic conditions. The schematic illustration of some of the possible interactions

between PDA-coated silk yarn and lac dye is shown in Figure 6. The initial pH of the lac dye solution was fixed at 2.50 for the adsorption kinetic and thermodynamic studies.

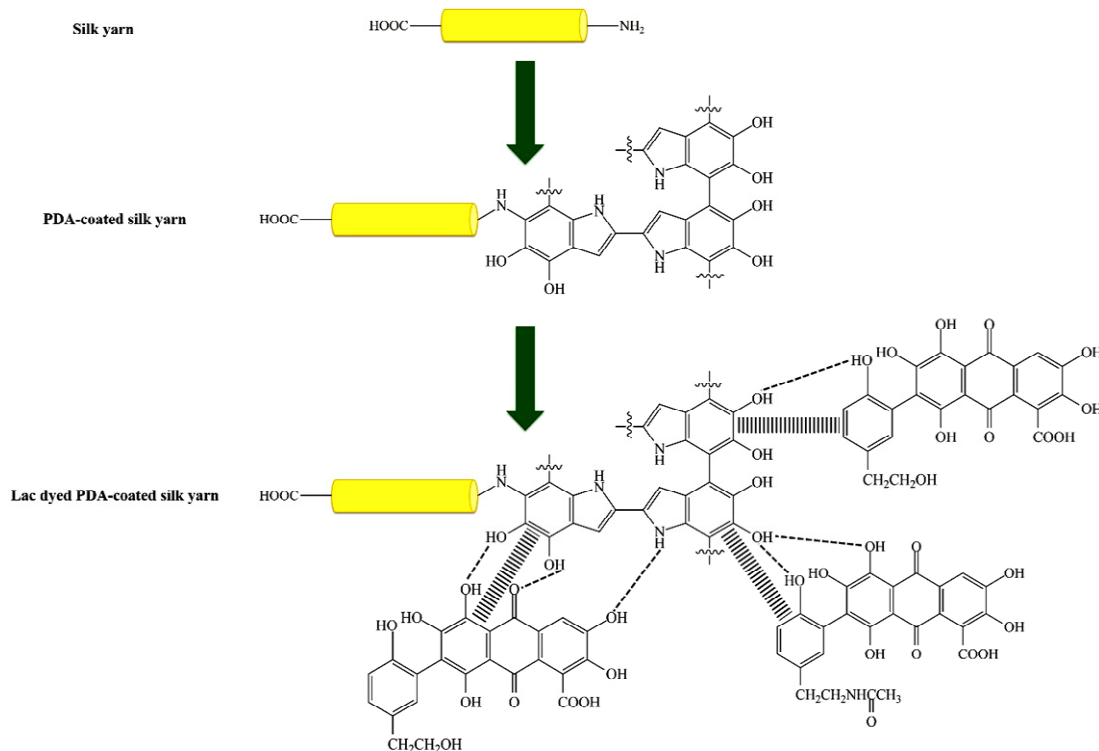


Figure 6: Schematic illustration of some of the possible interactions between PDA-coated silk yarn and lac dye

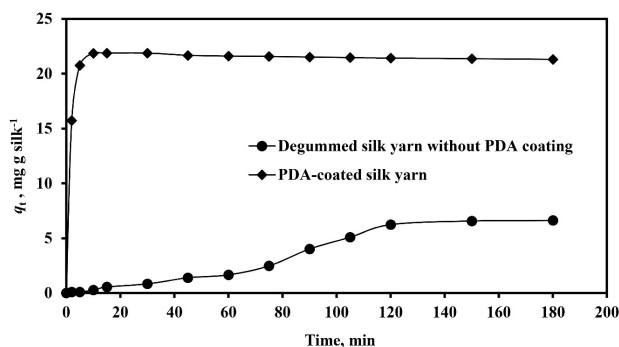


Figure 7: Amount of dye adsorbed (q_t) on PDA-coated silk yarn and degummed silk yarn without PDA coating (initial dye concentration of 500 mg L^{-1} , initial pH of the dye solution 2.50, temperature of 60°C)

Comparison of dye uptake of PDA-coated silk yarn and degummed silk yarn without PDA coating

Under the same conditions, the PDA coating on silk yarn showed a higher dye uptake than the

degummed silk yarn without PDA coating in the range of 0-180 min, as shown in Figure 7. This indicates that the coating of silk yarn at 0.10 mg mL^{-1} of DA solution enhanced the dye uptake. Therefore, PDA coating of silk yarn increased the

binding sites for the adsorption of the dyes, resulting in better dye adsorption on the silk yarn.

Rate of dyeing

The effect of temperature on the adsorption of lac dye on PDA-coated silk yarn over a period of 0-180 min was investigated (Fig. 8 (a)). It was found that a higher dyeing temperature resulted in a higher initial dye adsorption rate in the first stage of dye adsorption, as shown in Figure 8 (b). The mobility of dye molecules would be increased at higher temperature and, subsequently, the rate of dyeing would be enhanced. In the final stage of dye adsorption, the amount of dye molecules adsorbed at equilibrium decreased with increasing temperature (Fig. 8 (a)), owing to the exothermic nature of the dyeing process.²¹

The modified Cegarra-Puente equation can be adapted to dye baths with varying exhaustion. This equation covers the full range of the exhaustion values.²¹ It was used to calculate the dye adsorption rate constant (k) at different temperatures of the lac dye on PDA-coated silk

yarn. The modified Cegarra-Puente equation is expressed as:^{21,22}

$$\ln \left[-\ln \left(1 - q_t^2 / q_e^2 \right) \right] = a \ln t + a \ln k \quad (3)$$

where a is a coefficient depending on exhaustion, t is the dyeing time, and k is the dye adsorption rate constant. The coefficient and the dye adsorption rate constant (k) at different temperatures can be estimated from the slopes and intercepts of these lines of the linear plot of $\ln \left[-\ln \left(1 - q_t^2 / q_e^2 \right) \right]$ vs $\ln t$ as shown in Figure 9.

The sequence of the dyeing process falls into four stages. In the initial stage, the dye molecules diffuse through the aqueous dyebath to the fiber surface and then through the diffusional boundary layer present on the surface of the fiber. When the external surface of the fiber becomes saturated, the dye molecules diffuse to and then adsorb within the fiber in the final stage of dye adsorption. The slow final stage ultimately has the greatest influence on the overall rate of dyeing, with this being the rate-controlling step.²¹

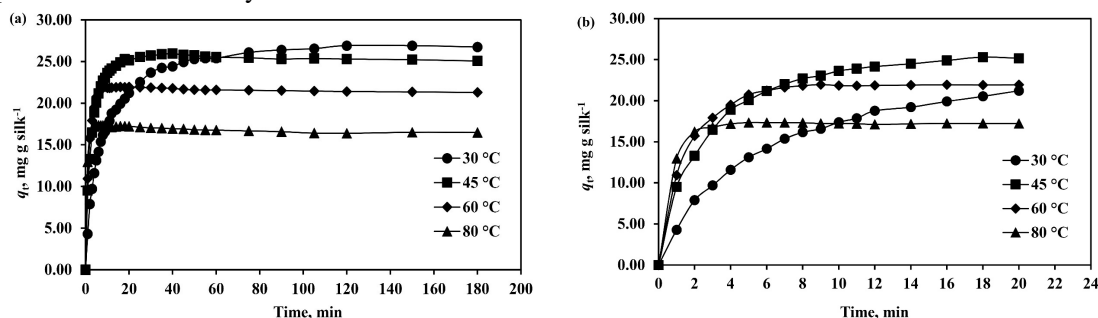


Figure 8: Effect of temperature on adsorption of lac dye on PDA-coated silk (initial dye concentration of 500 mg L⁻¹, initial pH of the dye solution 2.50); the effects of temperature over the time period of 0-180 min (a) and 0-20 min (b)

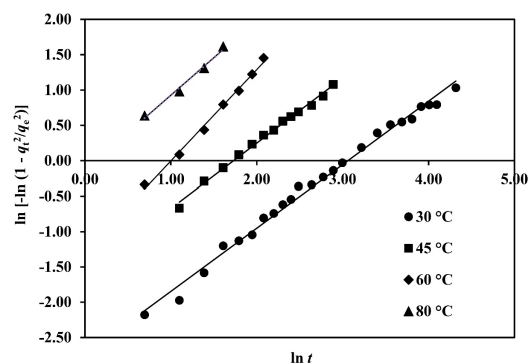


Figure 9: A plot of $\ln \left[-\ln \left(1 - q_t^2 / q_e^2 \right) \right]$ vs $\ln t$ of adsorption of lac dye on PDA-coated silk

From the results, the dye adsorption rate constant (k) values at 30, 45, 60 and 80 °C of the adsorption of lac dye on PDA-coated silk are listed in Table 2. It was apparent that the dye adsorption rate constant (k) increased with increasing temperature, owing to a diffusion controlled process. This result corresponds to the

known increase in the rate of dye diffusion with temperature.²¹ The a values obtained at different temperatures were > 0.8 , describing the finite dye bath kinetics of Fickian diffusion on the adsorption of lac dye on PDA-coated silk, where neither adsorption delay nor rapid adsorption occurs in the early stages.²³

Table 2
Dye adsorption rate constant (k) at different temperatures for adsorption of lac dye on PDA-coated silk (initial dye concentration of 550 mg L⁻¹, initial pH of the dye solution 2.50)

| Temperature (K) | K (min ⁻¹) | A | D ($\times 10^{-12}$ m ² min ⁻¹) | E_a (kJ mol ⁻¹) |
|--------------------|-----------------------------|------|---|----------------------------------|
| 303 | 4.70×10^{-2} | 0.90 | 3.45×10^{-11} | 51.2 |
| 318 | 1.78×10^{-1} | 0.92 | 6.93×10^{-10} | |
| 333 | 3.68×10^{-1} | 1.29 | 9.93×10^{-10} | |
| 353 | 8.82×10^{-1} | 1.06 | 1.43×10^{-9} | |

The dye adsorption rate constant (k) at different temperatures from the modified Cegarra-Puente equation, as listed in Table 2, was then applied to estimate the activation energy (E_a) of the adsorption of lac dye on PDA-coated silk by the Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (4)$$

where E_a , R and A refer to the Arrhenius activation energy, the gas constant (8.314 J K⁻¹ mol⁻¹) and the Arrhenius factor, respectively. The slope from the plot of $\ln k$ vs $1/T$ ($R^2 = 0.981$) was used to calculate E_a . The activation energy (E_a) for the adsorption of lac dye on PDA-coated silk was found to be 51.2 kJ mol⁻¹, as shown in Table 1. It was found that the activation energy of lac dye on PDA-coated silk at pH 2.5 was higher than that of the lac-dyed silk yarn without PDA coating at pH 3.5 ($E_a = 47.5$ kJ mol⁻¹), which was reported by Chairat *et al.*³

The diffusion coefficient (D) values of the lac dye on PDA-coated silk at different temperatures were obtained using Equation (5):²⁴

$$\frac{q_t}{q_e} = 4 \left[\frac{Dt}{\pi r^2} \right]^{1/2} \quad (5)$$

where D is the diffusion coefficient (m² min⁻¹) and r is the average radius of PDA-coated silk (5.0×10^{-5} m). Diffusion coefficient (D) values of dye adsorption at 30, 45, 60, and 80 °C were calculated from the slope of straight lines from the plot of q_t/q_e vs $t^{1/2}$. As can be seen in Table 1, the diffusion coefficient (D) increased with increasing temperature. This was because lac dye

molecules moved faster both in the solution and in the silk yarn at higher temperatures.

Adsorption isotherm studies

The isotherm equations used in this study for analyzing adsorption equilibrium data were the Langmuir and Freundlich isotherms. The obtained coefficients of determination (R^2) values from these models were used as criteria for comparing the applicability of the isotherms.

The most widely used Langmuir equation, which is valid for monolayer adsorption onto a surface with a finite number of identical sites,²⁵ is expressed as:

$$q_e = \frac{QbC_e}{1 + bC_e} \quad (6)$$

For lower concentrations, Langmuir adsorption parameters were determined by transforming the Langmuir equation (6) into a linear form as follows:

$$\frac{1}{q_e} = \frac{1}{QbC_e} + \frac{1}{Q} \quad (7)$$

where Q (mg g silk⁻¹) is the maximum amount of the dye adsorbed per unit weight of fiber to form complete monolayer coverage on the surface bound at high equilibrium dye concentration C_e (mg L⁻¹), q_e (mg g silk⁻¹) is the amount of dye adsorbed per unit weight of fiber at equilibrium, and b (l mg⁻¹) is the Langmuir constant related to the affinity of the binding sites. The value of Q represents a practical limiting adsorption capacity when the surface is fully covered with dye molecules. The values of Q and b can be

calculated from the intercepts and slopes of the straight lines of plot of $1/q_e$ vs $1/C_e$.

Another empirical isotherm given by the Freundlich equation is often used to describe adsorption data. This isotherm is commonly used to describe the adsorption characteristics of a heterogeneous surface. The linear form of the Freundlich isotherm is given as:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (8)$$

where K_F (mg g silk^{-1}) is an approximate indicator of adsorption capacity and $1/n$ is the adsorption intensity. Therefore, K_F and $1/n$ can be determined from the linear plot of $\log q_e$ versus $\log C_e$. The magnitude of the exponent $1/n$ gives an indication of the favorability of adsorption. Values of $n > 1$ represent favorable adsorption conditions.

In our work, the linear forms of the Langmuir and Freundlich isotherms were used to fit the equilibrium data of lac dye on PDA-coated silk. Based on the correlation coefficient shown in Table 3, the Langmuir isotherm agreed well with a high correlation coefficient ($R^2 > 0.99$) for the

three dyeing temperatures of 30, 60 and 80 °C. As seen in Figure 10, lower temperatures led to higher lac dye adsorption in the range of 30-80 °C. This was due to the exothermic adsorption of lac dye on PDA-coated silk. However, the low correlation coefficient ($R^2 < 0.96$) indicated poor agreement of the Freundlich isotherm with the experimental data.

The linear plot of $1/q_e$ vs $1/C_e$ was obtained from the Langmuir isotherm, as shown in Figure 11. The values of Q and b can be calculated from the intercepts and slopes of different straight lines, representing the different temperatures (Table 3). The fit is good for the adsorption data of lac dye on PDA-coated silk at 30, 60 and 80 °C (correlation coefficient $R^2 > 0.99$). It was found that the adsorption of lac dye on PDA-coated silk 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 PDA-coated silk has a maximum affinity for lac dye at lower temperature.

Table 3
Langmuir and Freundlich isotherm constants for adsorption of lac dye on PDA-coated silk

| Temperature (K) | Langmuir | | | Freundlich | | |
|--------------------|------------------------------------|-------------------------------|-------|--------------------------------------|------|-------|
| | Q (mg g silk^{-1}) | B (l mg^{-1}) | R^2 | K_F (mg g silk^{-1}) | n | R^2 |
| 303 | 222 | 1.38×10^{-3} | 0.995 | 0.775 | 1.30 | 0.954 |
| 333 | 145 | 1.25×10^{-3} | 0.993 | 0.621 | 1.84 | 0.965 |
| 353 | 100 | 1.14×10^{-3} | 0.995 | 0.669 | 3.22 | 0.968 |

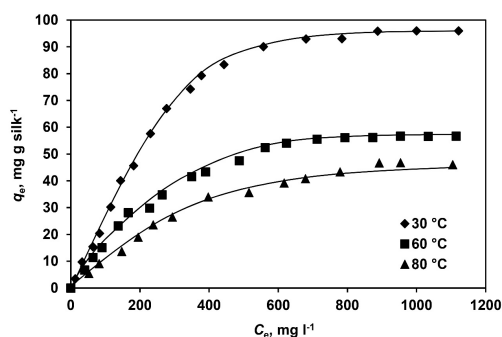


Figure 10: Langmuir adsorption isotherm of lac dye on PDA-coated silk yarn at 30, 60 and 80 °C (contact time 120 min, pH 2.50)

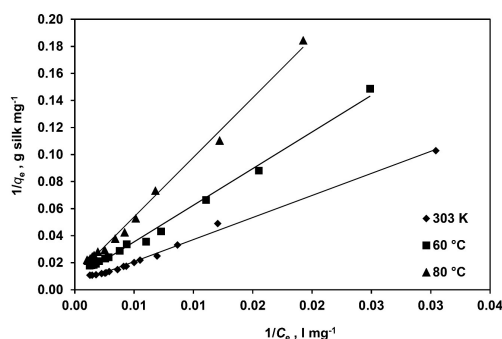


Figure 11: Linear plot of $1/q_e$ vs $1/C_e$ from Langmuir isotherm of lac dye on PDA-coated silk at 30, 60 and 80 °C (contact time 120 min, pH 2.50)

Color hue and fastness properties of the dyed yarn

Table 4 lists the color obtained and CIE $L^*a^*b^*$ values of the dyed silk yarn samples. The pretreatment of silk yarn with PDA, followed by dyeing with lac dye solution, resulted in an auburn color and significant changes in L^* and b^*

values. In addition, the silk yarn coated with PDA, followed by dyeing with an aqueous solution of lac dye and then post-mordanting with alum, showed a shade of violet with significant changes in L^* and b^* values, compared with the lac dyed untreated silk yarn (control).

Table 4
Color measurements of dyed silk yarn samples





| Silk yarn | CIE | | | Color obtained |
|--|-------|-------|-------|--|
| | L^* | a^* | b^* | |
| Degummed silk yarn | 86.50 | 1.33 | 7.89 |  |
| Lac dye on untreated silk yarn (control) | 55.57 | 27.60 | 16.95 |  |
| Lac dye on PDA-coated silk yarn | 49.54 | 25.74 | 21.29 |  |
| Lac dye on PDA-coated silk yarn and then post-mordanting with alum | 33.43 | 21.94 | 0.63 |  |

Table 5
Fastness properties of silk dyed with an aqueous extract of lac dye

| Silk yarn | Wash fastness | | | Light fastness |
|--|---------------|----------|--------|----------------|
| | Color change | Staining | | |
| | | Silk | Cotton | |
| Silk coated with PDA | 4 | 4-5 | 4-5 | 4 |
| Lac dye on untreated silk yarn (control) | 1 | 4-5 | 4-5 | 3 |
| Lac dye on PDA-coated silk yarn | 1-2 | 4 | 4 | 4 |
| Lac dye on PDA-coated silk yarn post-mordanted with alum | 3-4 | 4-5 | 4-5 | 4 |

The fastness properties of the dyed silk yarn samples are summarized in Table 5. It was observed that the pretreatment of silk yarn with PDA afforded a material with good light fastness, compared to the lac dyed untreated silk yarn (control). This is due to the fact that PDA has the ability to serve as physical barrier that scatters UV radiation for this dye.¹³ Therefore, PDA coating can absorb an amount of ultraviolet light and diminish the damage to the dyed silk. The

wash fastness of lac dye on the PDA-coated silk yarn was not affected. The color fastness to light and washing of the silk yarn coated with PDA, followed by dyeing with an aqueous solution of lac dye and then post-mordanting with alum, was found to be good, compared with that of the other samples. This may be explained by complexing of the laccic acids from lac dye to aluminum (III) and the OH groups of the PDA-coated silk yarn

chain, which would lead to higher color fastness to light and washing.

CONCLUSION

The adsorption kinetic and thermodynamic parameters for lac dye on PDA-coated silk were investigated in this work. It was found that the adsorption capacity was dependent on the pH of the dye solution and an optimal uptake occurred at pH 2.5. In the initial stage of dye adsorption, an increase in temperature led to an increase in the dye adsorption rate constant (k) and diffusion coefficient (D), which is consistent with a kinetically controlled diffusion process. The experimental data fitted well the Langmuir isotherm, with a high correlation coefficient ($R^2 > 0.99$). From our study, it could be concluded that the combination of PDA coating and post-mordanting with alum for lac dyeing gave better color fastness to light and washing than lac dye on untreated silk yarn (control) and lac dye on PDA-coated silk yarn.

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