

An adsorption and thermodynamic study of lac dyeing on cotton pretreated with chitosan

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Abstract

Adsorption and thermodynamic studies of lac dyeing on cotton pretreated with chitosan were investigated under dyeing conditions of pH 3.0, a material to liquor ratio (MLR) of 1:100 and a contact time of 3 h. Batch equilibrium studies showed that the adsorption of lac dye on cotton pretreated with chitosan could be described by the Langmuir isotherm with an enthalpy change (ΔH°) of -17.43 kJ. The pretreatment of cotton with chitosan provided a significant enhancement of dye uptake onto the cotton and also a decrease in the dye desorbed from the cotton compared with the results in the absence of chitosan or on lac dyeing in the presence of NaCl. In addition, sodium chloride had no effect on the adsorption of lac dye on cotton at pH 2.5, 3.0 and 3.5. It indicated that hydrogen ions (H^+) play a more important role than sodium ions (Na^+) in the dyeing process.

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1. Introduction

Cotton is an abundant natural fibre which consists of practically pure cellulose (about 88–96%) [1]. Cotton may be described chemically as poly(1,4- β -D-anhydroglucopyranose) (Fig. 1) [2]. Natural cellulose fibres carry a small negative charge ($\zeta_{\text{plateau}} = -11$ mV) due to the presence of some carboxylic acid groups from oxidation at the primary hydroxylic sites [3]. At a pH higher than 8, some of the hydroxyl groups on the hydroxymethyl side chains may also be ionized increasing the negative charge significantly [4]. The negative charges on the surface of cellulose repel anionic dyes and hence the efficiency of dye fixation on cellulosic fibres is generally low. To counter this problem, a number of studies on cotton dyeing have been carried out to improve the dye uptake and fastness properties. Most research focus is on introducing

cationic sites into the cotton fabrics for interactions with anionic dyes [5–8].

Lac dye is used extensively as a natural food additive [9,10], and in cosmetics [9], as well as a colourant for silk and cotton dyeings [11]. In the north and northeast of Thailand, lac dye is a natural red dyestuff extracted for cotton and silk dyeings [11]. However, lac dye has a low affinity for cotton because cotton does not have any cationic sites for the attachment [12]. An alternative way to overcome this problem is the pretreatment of cotton with cationic agents. Rastogi et al. [13] created affinity in cotton for lac dye by introducing cationic sites in the fibre. Cotton fabrics were treated with a cationic agent, Discofix DBA, and then they were dyed with lac dye. It was found that the cationised cotton which was dyed with lac dye exhibited a good colour yield and wet fastness properties even without mordanting. In addition, poly(ethyleneimine) (PEI) has been used as a cationic agent in cotton dyeing with lac dye [14]. It was found that PEI increased the dye adsorbed on cotton and also decreased the dye desorption from the fibre.

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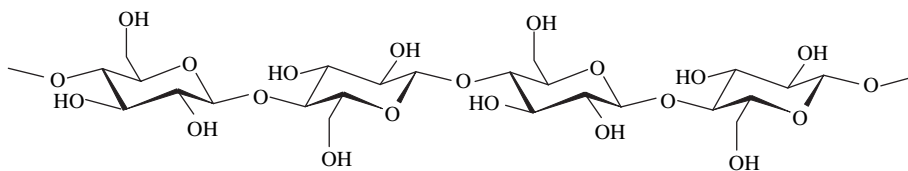


Fig. 1. The chemical structure of cellulose.

Chitosan is a deacetylated derivative of chitin, a natural polymer found in the shell of crabs and shrimps [15]. Structurally, chitosan contains two main functional groups, namely hydroxyl and amino groups, as well as ether linkages (Fig. 2). It has also been used to treat cotton in lac dyeing processes [12]. It was found that chitosan enhanced the uptake of lac dye and increased lac dye sorption on cotton. However, the adsorption isotherm was not reported in the study of Saxena et al. [12].

We have now investigated the adsorption and thermodynamics of lac dyeing of cotton pretreated with chitosan compared with untreated cotton. The effect of sodium chloride (NaCl) on the dyeing process with, and without, pH control was also studied. In addition, the thermodynamics of adsorption of lac dye on cotton in the presence of NaCl was investigated. These results were compared with the results from the lac dyeing of pretreated and untreated cotton with chitosan, and the findings are now reported in this paper.

2. Experimental

2.1. Materials and chemicals

2.1.1. Cotton yarn preparation

The cotton yarn used was purchased from the 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 had been 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 break down of the emulsion and precipitation of the impurities on 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 was neutral. The cotton yarn was then dried at room temperature.

2.1.2. Preparation of lac dye

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 freeze dried to give a crude lac dye extract (36.07 g), which was then used without further purification.

2.1.3. Cotton pretreatment with chitosan

Chitosan (medium molecular weight, viscosity 200,000 cps, CAS 9012-76-4, FW of repeating unit, 161) was purchased from the Aldrich Chemical Company. A 1% (w/v) stock solution of chitosan was prepared by dissolving the required amount of chitosan in a 1% (v/v) aqueous acetic acid solution. The cotton yarn (50 g), prepared as noted in Section 2.1.1., was then immersed directly in 0.3% and 0.6% (v/v) aqueous solutions of chitosan (2 L) (prepared from the stock solution) at room temperature for 1 h. After this time the yarn was removed and dried at 100 °C for 30 min and then cured at 160 °C for 10 min. The cotton yarn, after pretreatment with chitosan, was rinsed with water at 40 °C and allowed to dry in the open air in the laboratory.

2.2. Instruments

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

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

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

2.3. Methods

2.3.1. The effect of sodium chloride on the adsorption of lac dye on cotton with and without pH control

The required dye solutions in the presence of sodium chloride over a concentration range of 4.30×10^{-3} – 17.1×10^{-1} M

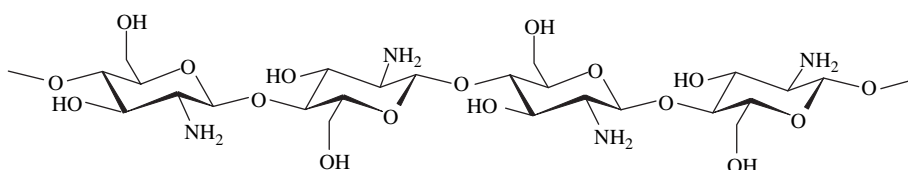


Fig. 2. The chemical structure of chitosan.

at pH 2.5, 3.0, 3.5 and without pH control were freshly prepared in deionized water. The experiments were carried out by shaking cotton yarn (0.5 g) with dye solution (50 mL), containing the different salt concentrations, in a conical flask (125 mL) at 30 °C in a thermostatted shaker bath operated at 75 rpm. The absorbance of lac dye solution for each dyeing time was monitored by UV–visible absorption spectroscopy (Cary 1E UV–visible spectrophotometer) until the absorbance values at λ_{\max} 487 nm remained constant. The initial and equilibrium dye concentrations were determined using a calibration curve based on absorbance at λ_{\max} 487 nm versus dye concentration in standard lac dye solutions. Eq. (1) was used to calculate the amount of dye adsorbed at equilibrium (q_e) (mg/g cotton).

$$q_e = (C_0 - C_e) \frac{V}{W} \quad (1)$$

In Eq. (1), C_0 and C_e are the initial and equilibrium dye solution concentrations (mg/L), respectively, V the volume of the dye solution (mL) and W is the weight of cotton yarn (g) used.

2.3.2. Batch equilibrium experiments

Different lac dye concentrations were freshly prepared in deionized water. The pH of the dye solution was adjusted to 3.0 with glacial acetic acid. The experiments were carried out by shaking pretreated or untreated cotton with a 0.3% (v/v) aqueous solution of chitosan (0.5 g) with different concentrations of dye solution (50 mL) in a conical flask (125 mL) at 10, 30 and 60 °C in a thermostatted shaker bath operated at 75 rpm. The amount of dye in the solution was monitored by UV–visible absorption spectroscopy (Cary 1E UV–visible spectrophotometer) until the absorbance values at λ_{\max} 487 nm remained constant. The initial and equilibrium dye concentrations were determined using a calibration curve based on absorbance at λ_{\max} 487 nm versus dye concentration in standard lac dye solutions. From Eq. (1), the amount of dye adsorbed at equilibrium (q_e) was calculated.

The influence of sodium chloride on the adsorption of lac dye on cotton was investigated in a similar manner. The cotton yarn (0.5 g) was dyed with different dye concentrations (50 mL) in the presence of 0.5 M sodium chloride at 10 and 30 °C. The pH of the dye solution before and after dyeing was measured in each experiment. The absorbance of the dye solution was measured at λ_{\max} 487 nm.

2.3.3. Adsorption and desorption studies of lac dye on cotton pretreated with chitosan and on untreated cotton, and on cotton in the presence of 0.5 M NaCl without pH control

The cotton yarn, prepared as noted in Section 2.1.1., with and without the pretreatment with a 0.3% (v/v) of aqueous solution of chitosan was dyed with an initial dye concentration of 473 mg/L in a thermostatted shaker bath operated at 75 rpm. The adsorption conditions were pH 3.0, MLR of 1:100 and 30 °C. The absorbance of the dye solutions was monitored until constant absorbance values were obtained.

The dyed cotton samples were then taken out and dried at room temperature. To study the desorption of lac dye at 30 °C, deionized water (50 mL) in each conical flask (125 mL) was shaken in a thermostatted shaker bath operated at 75 rpm. After 30 min, the dried cotton sample (0.50 g), which had been pre-warmed in the thermostatted bath at 30 °C for 30 min, was immersed in deionized water. The cotton samples were then rapidly withdrawn after different immersion times. The desorbed dye concentrations (q_{de}) were determined using a calibration curve based on absorbance at λ_{\max} 487 nm (Cary 1E UV–visible spectrophotometer) versus dye concentration in standard lac dye solutions. The amount of dye adsorbed on cotton after desorption was calculated by subtraction.

The adsorption and desorption of lac dyeing onto cotton (initial dye concentration of 479 mg/L) in the presence of 0.5 M NaCl was investigated in a similar way. The absorbance of the dye solution was measured at λ_{\max} 487 nm to monitor the amount of lac dye adsorbed and desorbed from the cotton, respectively.

3. Results and discussion

3.1. Optimal conditions for lac dyeing of cotton

Experiments were undertaken to study the influence of pH, material to liquor ratio (MLR), contact time and initial dye concentration on the adsorption of lac dye on cotton, and the results are discussed separately in the following sub-sections.

3.1.1. The effect of pH on the adsorption of lac dye on cotton

The pH of a dye bath is an important influencing factor for the adsorption of lac dye on cotton. In this study, the pH of lac dye solution was varied in the pH range of 2.0–5.2 by adjustment with glacial acetic acid. The effect of pH on the adsorption of lac dye on cotton at 30 °C, with an initial dye concentration of 430 mg/L and a material to liquor ratio (MLR) of 1:100 was studied. The amount of the dye adsorbed on the cotton increased on decreasing the pH from 4.0–2.5, but decreased gradually at pH values lower than 2.5. Some of the pendant hydroxymethyl ($-\text{CH}_2\text{OH}$) groups in cotton fibres are naturally oxidized to carboxylic acid groups during growth or subsequent processing [4], and hence the cellulosic fibres generally carry a weak negative charge in a dye bath with a pH higher than 4 [4]. If the dye bath pH is raised above 8, some of the hydroxyl groups present on the hydroxymethyl side chains may also ionize, increasing the negative charge significantly. The negative charges on the cellulosic fibre surface repel the laccic acid anion at pH values higher than 4.0. Therefore, the negative charge on the adsorbing surface of cellulose clearly creates a very unfavourable situation for the adsorption of lac dye on cotton at a pH higher than 4.0. At a pH lower than 4.0, carboxyl and hydroxyl groups along the polymer chain of cellulosic fibres are hardly ionized. The dye molecules [16] can reach the surface of the cotton where they can interact with the cotton fibres via hydrogen

bonding together with some ion–dipole interactions. The highest adsorption capacity was observed at pH 2.5. Most organic acids in dilute solution have little effect on cotton, except oxalic, citric and tartaric acids which are liable to cause tendering [2]. However, degradation of cotton may arise from acid hydrolysis of the fibres [2]. Therefore, the pH of the dye solution for the experiment on the adsorption isotherm was fixed at 3.0.

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

Material to liquor ratio (MLR) is another important parameter which influences the exhaustion of dye and the establishment of an equilibrium between the concentration of dye on the fibre and the dye in the dye bath. Shorter liquor ratios shift the equilibrium in favour of the dye on the fibre and the equilibrium is also reached more rapidly. The effect of MLR on the adsorption of lac dye on cotton was investigated under dyeing conditions of pH 3.0, an initial dye concentration of 480 mg/L, 30 °C and a contact time of 2 h. It was found that MLRs of 1:50, 1:100 and 1:150 showed only slight differences in the amount of the dye adsorbed onto cotton due to lac dye having a low affinity for cotton [17]. For this reason, increasing the volume of dye solution showed a slight increment in the dye adsorbed onto cotton at higher material to liquor ratios. The maximum of the dye adsorbed per gram of cotton for MLR 1:100 was 5.00 mg/g cotton. Therefore, the MLR of 1:100 was used for the adsorption isotherm of lac dye on cotton.

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

The adsorption capacity of lac dye on cotton was a function of the initial dye concentration. As expected, the amount of the dye adsorbed on cotton increased with an increase in the initial concentration of dye solution. This is due to the increase in the driving force of the concentration gradient with the higher initial dye concentration [18]. Nearly 60 min were required for the equilibrium adsorption at initial dye concentrations of 137, 272 and 480 mg/L. The maximum of the dye adsorbed per gram of cotton at initial dye concentration of 480 mg/L was 5.00 mg/g cotton. The contact time for the adsorption isotherm study of lac dye of pretreated and untreated cotton with chitosan at pH 3.0 was fixed at 3 and 2 h, respectively.

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

3.2. Adsorption isotherms

The most widely used two-parameter equation describing the adsorption process is the Langmuir equation, which has the linear form [19]:

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \left(\frac{1}{Q}\right)C_e \quad (2)$$

For lower concentrations, the following form of the Langmuir equation is found to be more satisfactory [20]:

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

In the above equations, Q is the maximum amount of the dye adsorbed per unit weight of fibre to form a complete monolayer coverage on the surface bound at high equilibrium dye concentration C_e , q_e is the amount of dye adsorbed per unit weight of fibre at equilibrium, and b 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 and assists in the comparison of adsorption performance [18]. The values of Q and b are calculated from the intercepts and slopes of the straight lines of plot of $1/q_e$ versus $1/C_e$.

The Langmuir constant b is related to the enthalpy of adsorption, ($b \propto (\exp(-\Delta H^\circ/RT))$) [21]. Therefore, the thermodynamic parameters including the free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were also evaluated using the following equations [22,23]:

$$\Delta G^\circ = -RT \ln(b) \quad (4)$$

$$\ln\left(\frac{b_2}{b_1}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (5)$$

$$\ln(b) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

Another empirical isotherm given by the Freundlich equation is often used to describe adsorption data. The linear form of the Freundlich isotherm can be represented in the following form:

$$\ln q_e = \ln Q_f + \frac{1}{n} \ln C_e \quad (8)$$

where Q_f is roughly an indicator of the adsorption capacity and $1/n$ is the adsorption intensity. 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. Values of $n > 1$ represent favourable adsorption conditions [18].

In our work, linear forms of the Langmuir and Freundlich isotherms were used to fit the equilibrium data of lac dye adsorption on cotton in the presence of 0.5 M sodium chloride and on cotton pretreated with chitosan compared to untreated cotton.

3.2.1. Adsorption isotherm of lac dye on cotton at pH 3.0

The isothermal equilibrium data of lac dye on cotton under dyeing conditions of pH 3.0, MLR 1:100 in the dye concentration range 52–1421 mg/L at 10, 30 and 60 °C were described employing the Langmuir isotherm equation as shown in Fig. 3.

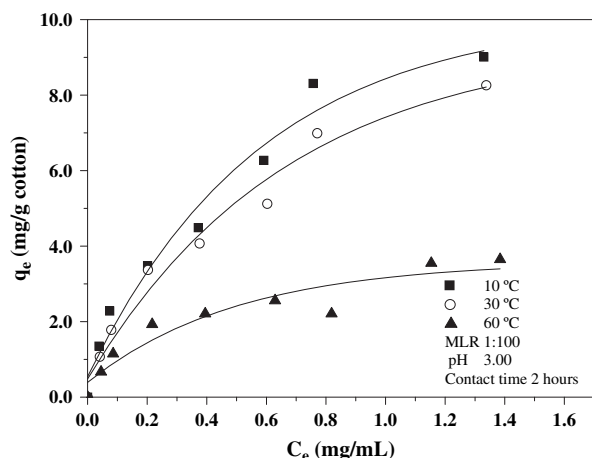


Fig. 3. Adsorption isotherm of lac dye on cotton at pH 3.0 in the initial dye concentration range 52–1421 mg/L.

It was found that the uptake of the dye decreased with increasing temperature, thereby indicating that the process is an exothermic one. This is in agreement with the experimental results of the adsorption of lac dye on cotton without pH control by Janhom et al. [14].

When $1/q_e$ was plotted against $1/C_e$ according to Eq. (3), the Langmuir model fitted the experimental data very well with high correlation coefficients ($R^2 > 0.98$). The values of the Langmuir constants Q and b were calculated from the intercepts and slopes of different straight lines, respectively, at different temperatures. The calculated results are reported in Table 1. It was found that Q values decreased with increasing temperature. Similar observations were reported for the adsorption of lac dye on silk [17].

The free energy (ΔG°) change was evaluated using Eq. (4), while enthalpy (ΔH°) and entropy (ΔS°) changes of the adsorption were calculated (Eq. (6)) from the slope and intercept of the straight line of a graph of $\ln(b)$ versus $1/T$. The results are reported in Table 2. The negative value of the free energy (ΔG°) indicated the spontaneous nature of lac dye adsorption on cotton. The change in enthalpy (ΔH°) was found to be a small negative value. The negative value confirms the exothermic nature of the adsorption. Also, the negative value of the entropy change (ΔS°) was consistent with the decreased randomness after the adsorption of lac dye on cotton. The adsorption of lac dye on cotton in this study was similar to the adsorption of direct dyes on cotton [24]. It was found that the enthalpy for the adsorption of cotton dyeing with direct

Table 1
Langmuir and Freundlich isotherm constants for the adsorption of lac dye on cotton at different temperatures, at the initial dye concentration range 50–550 mg/L, MLR 1:100 and pH 3.0

Temp (°C)	Langmuir			Freundlich		
	Q (mg/g cotton)	b (mL/mg)	R^2	Q_f (mg/g cotton)	n	R^2
10	6.46	6.76	0.9940	8.88	1.79	0.9914
30	4.80	5.98	0.9866	6.63	1.68	0.9915
60	3.44	4.93	0.9961	4.40	1.63	0.9979

Table 2

Thermodynamic parameters for the adsorption of lac dye on cotton at different temperatures, MLR 1:100, at the initial dye concentration range 50–550 mg/L and pH 3.0

Temp (°C)	b (mL/mg)	ΔG° (kJ)	ΔH° (kJ)	ΔS° (J/K)	R^2
10	6.76	−4.50			
30	5.98	−4.51	−4.88	−1.31	0.9986
60	4.93	−4.42			

dyes, namely Yellow 29, Yellow 50, Orange 31, Red 81, Red 75, Red 23, Violet 51, and Blue 71, differed from −0.84 to −6.28 kJ/mol [24].

The Freundlich isotherm model was also used to fit the experimental data for the adsorption of lac dye on cotton at pH 3.0. Linear plots of $\ln q_e$ versus $\ln C_e$ showed that the adsorption follows the Freundlich isotherm model well with high correlation coefficients ($R^2 > 0.99$) (Table 1). The value of Q_f has been used as a relative measure of adsorption capacity, and it was found that Q_f increased with decreasing temperature which again indicated that the process was exothermic. In addition, the n values greater than 1 indicated the favourable adsorption condition.

3.2.2. The effect of sodium chloride on the adsorption of lac dye on cotton with and without pH control

Due to the presence of hydroxyl and some carboxylic acid groups, the natural cellulose fibres carry a negative charge [3] whereas lac dye is an acid dye [12] as a result of the presence of phenolic and carboxylic acid groups in the molecule providing a negative charge on ionization. Therefore, lac dye molecules and cellulose repel one another at pH values higher than 4. This means that electrical repulsion between the lac dye and cellulose fibres in the dyeing process must be overcome by other forces of attraction. For this reason, electrolytes such as sodium chloride have been added into the dye bath to promote the adsorption of anionic dye on cellulose fibres [25]. In addition, many experimental results have been reported where electrolytes such as sulfates and phosphates increased the sorption of acid dyes on nylon and wool and also increased the sorption of basic dyes on acrylic fibres if the salt concentrations are sufficiently high [26]. Therefore, the effect of sodium chloride (concentration range 4.30×10^{-3} – 17.1×10^{-1} M) on the adsorption of lac dye on cotton with and without pH control was investigated in this study and the results are shown in Fig. 4.

It was found that an increase in the sodium chloride concentration over the range 4.31×10^{-3} – 6.84×10^{-1} M led to an increase in the dye adsorbed on cotton and then remained constant in the concentration range 10.3×10^{-1} – 17.1×10^{-1} M when cotton fibres were dyed with lac dye solution without pH control (pH of the dye solutions before and after dyeing varied over the pH range 5.43–4.75 and 6.23–5.53, respectively). Similar results were also obtained by Janhom et al. [14] but no thermodynamic parameters were noted.

The results obtained in our study can be explained by the Donnan model [27]. According to this model, cellulose fibres

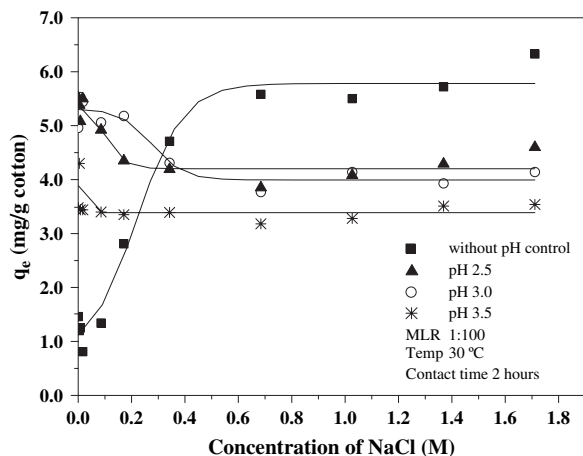


Fig. 4. The effect of NaCl salt on the adsorption of lac dye on cotton with and without pH control.

are negatively charged at a pH higher than 4 [3,4], and dyeing occurs by the transfer of dye from the external to the internal solution. Upon addition of sodium chloride (as an electrolyte) to the dye solution, the sodium ions (Na^+) distribute between the external solution and internal solution so that the negative charge on the cellulose surface is neutralized or shielded, allowing the lac dye molecules to be adsorbed on the cotton [3,23,26]. However, sodium chloride had no effect on the adsorption of lac dye on cotton at pH 2.5, 3.0 and 3.5 (Fig. 4) since the carboxylic acid and hydroxyl groups would not be ionized at these pH values. This indicated that the hydrogen ion (H^+) plays a more important role in the adsorption process than sodium ion (Na^+); the adsorption isotherm of lac dye on cotton in the presence of 0.5 M sodium chloride is reported in the next section.

3.2.3. Adsorption isotherm of lac dye on cotton in the presence of 0.5 M sodium chloride without pH control

The results of the adsorption data were analyzed by using linear forms of the Langmuir and Freundlich isotherms according to the Eqs. (3) and (8), respectively.

It was found that the linear forms of both the Langmuir and Freundlich isotherms fitted well with the experimental data with a high correlation coefficient ($R^2 > 0.99$). The computed parameters of the Langmuir and Freundlich isotherms together with the correlation coefficients in this study are given in Table 3. It was found that the adsorption capacity (Q) values decreased with increasing temperature, and a similar trend was also observed with values of the Freundlich parameter

Table 3

Langmuir and Freundlich isotherm constants for the adsorption of lac dye on cotton in the presence of 0.5 M sodium chloride without pH control at 10 and 30 °C, MLR 1:100 and initial dye concentration range 85–819 mg/L

Temp (°C)	Langmuir			Freundlich		
	Q (mg/g cotton)	b (mL/mg)	R^2	Q_f (mg/g cotton)	n	R^2
10	20.04	2.18	0.9982	18.08	1.41	0.9989
30	16.78	1.51	0.9978	12.26	1.35	0.9903

Q_f . These results clearly indicated that the adsorption of lac dye on cotton in the presence of 0.5 M sodium chloride without pH control is an exothermic process.

The thermodynamic parameters for the adsorption of lac dye on cotton in the presence of 0.5 M sodium chloride without pH control at 10 and 30 °C were also calculated using Eqs. (4), (5) and (7), respectively. The results are reported in Table 4. The small negative value of the enthalpy change (ΔH°) suggests the adsorption to be a physical one [23] and the negative values of the free energy (ΔG°) term indicated the spontaneous nature of this adsorption process.

3.2.4. Adsorption isotherm of lac dye on pretreated cotton with chitosan at pH 3.0

Since lac dye has a low affinity for cotton because of the absence of cationic sites on the cotton for attachment, mordants such as alum, ferrous sulfate and tin have been used for lac dyeing onto cotton thus improving the fastness properties [11,28]. However, the wastewater containing these mordants may affect the environment and public health. To avoid these problems, the pretreatment of cotton with chitosan, derived from a natural polymer and containing amino groups (Fig. 2), has been investigated as an alternative way to introduce cationic sites on cotton. According to Saxena et al. [12], the pretreatment of cotton with chitosan enhanced the affinity of lac dye on cotton. However, the adsorption isotherm was not reported in their study, and thus we investigated the adsorption of lac dye on pretreated cotton with chitosan at pH 3.0 in order to obtain the thermodynamic parameters and a better understanding of the process. The cotton yarn was treated with a 0.3% (v/v) aqueous solution of chitosan.

The Langmuir and Freundlich isotherm models were examined in this study to describe the adsorption equilibrium and the adsorption isotherms of lac dye on pretreated cotton are shown in Fig. 5. The linear plots of C_e/q_e versus C_e following Eq. (2) confirmed good fits for the adsorption with the Langmuir isotherm model (Fig. 6).

The correlation coefficients (R^2) were higher than 0.98. Adsorption capacity (Q) and the Langmuir constant (b) were then determined from the slope and intercept of this plot (Table 5). It was found that the adsorption capacity decreased with an increase in the temperature, indicating an exothermic process. Based on the correlation coefficient (R^2) shown in Table 5, the equilibrium data could not be described by the isotherm of Freundlich (Fig. 7).

To obtain the thermodynamic parameters, Eq. (4) was used to calculate the free energy (ΔG°) term. Enthalpy (ΔH°) and entropy (ΔS°) changes of the adsorption were calculated

Table 4

Thermodynamic parameters for the adsorption of lac dye on cotton in the presence of 0.5 M sodium chloride without pH control at 10 and 30 °C, MLR 1:100 and initial dye concentration range 85–819 mg/L

Temp (°C)	b (mL/mg)	ΔG° (kJ)	ΔH° (kJ)	ΔS° (J/K)
10	2.18	-1.83	-13.09	-39.79
30	1.51	-1.04		-39.77

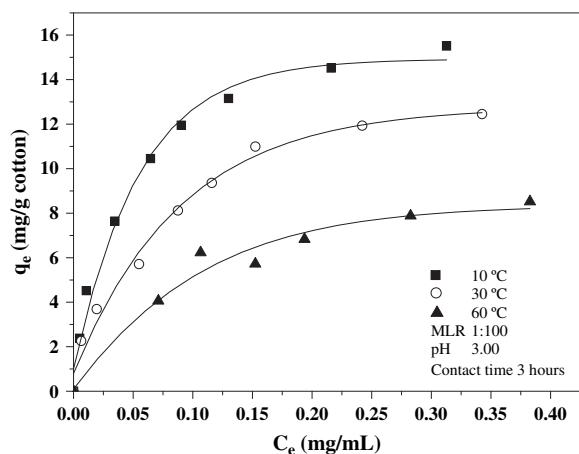


Fig. 5. Adsorption isotherm of lac dye on pretreated cotton with chitosan in the initial dye concentration range 29–469 mg/L.

(Eq. (6)) from the slope and intercept of a straight line of a plot of $\ln(b)$ versus $1/T$. The calculated results are reported in Table 6. Based on these results, it can be concluded that the adsorption of lac dye on pretreated cotton with chitosan at pH 3.0 is a spontaneous and exothermic process.

The chitosan contains amine groups, $-\text{NH}_2$, which would be in the protonated cationic form ($-\text{NH}_3^+$) in acidic solution [15]. At a pH lower than 4, the carboxylic acid and hydroxyl groups on cellulose would not be ionized. After pretreatment of the cotton with chitosan under acidic conditions, the protonated amino ($-\text{NH}_3^+$) groups of chitosan could interact with the surface of the cellulose via hydrogen bonding and ion–dipole interactions. The pretreated cotton was then dyed with lac dye under acidic conditions. The neutralization of laccic acid A, in water containing 4% of dimethyl sulfoxide by volume, by 0.1 M sodium hydroxide gave $\text{p}K_{\text{a}2}$ and $\text{p}K_{\text{a}3}$ values to be about 4.4 and 6.5, respectively, whilst the most strongly acidic group was completely ionized below pH 4.0 [29]. Laccic acid A, the major lac dye component [30,31], may then bind to the pretreated cotton via hydrogen bonding and ionic interactions under acidic conditions. Chitosan could then act as an organic

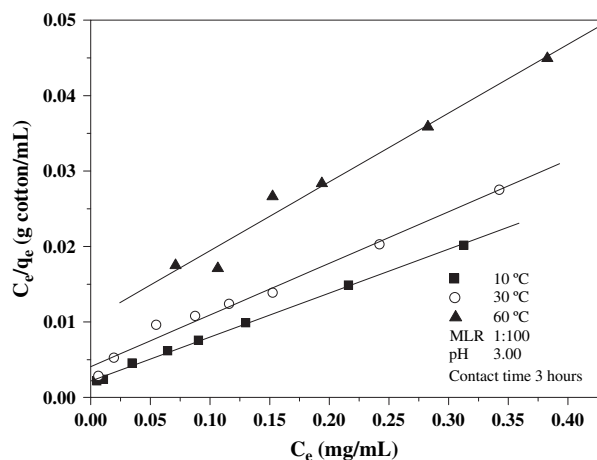


Fig. 6. A plot of C_e/q_e versus C_e for the adsorption of lac dye on pretreated cotton with chitosan in the initial dye concentration range 29–469 mg/L.

Table 5

Langmuir and Freundlich isotherm constants of the adsorption of lac dye on pretreated cotton with chitosan at different temperatures; dyeing at the initial dye concentration range 29–469 mg/L, MLR 1:100 and pH 3.0

Temp (°C)	Langmuir			Freundlich		
	Q (mg/g cotton)	b (mL/mg)	R^2	Q_f (mg/g cotton)	n	R^2
10	17.16	26.73	0.9990	31.38	2.23	0.9770
30	14.61	16.78	0.9918	23.24	2.18	0.9910
60	10.97	8.82	0.9868	12.89	2.51	0.9366

mordant to enhance the uptake of lac dye on the cellulose surface resulting in lac dye sorption on the cotton. The calculated enthalpy change was higher than that from the lac dyeing in the presence of 0.5 M NaCl without pH control and lac dyeing on cotton at pH 3.0, respectively. The comparative results are given in Table 7.

3.2.5. Comparison of thermodynamic parameters between the adsorption of lac dye on untreated and pretreated cotton with chitosan

Under the same conditions, the amount of the dye adsorbed on pretreated cotton with a 0.3% (v/v) aqueous solution of chitosan was higher than that on the untreated cotton as shown in Fig. 8. This may be due to the protonated amino group of chitosan interacting with both cellulose and the lac dye, and acting like a binder between the two which results in higher dye adsorption. In addition, the amount of the dye adsorbed on pretreated cotton with chitosan was also higher than that on the untreated cotton in the presence of 0.5 M NaCl without pH control, supporting the important binding role played by the chitosan.

Under the same dyeing conditions, the thermodynamic parameters of the adsorption of lac dye on untreated cotton with chitosan were compared with those for the adsorption of lac dye on pretreated cotton with chitosan at pH 3.0 (Table 7). The free energy values in both were consistent with a spontaneous process. The enthalpy value obtained from the

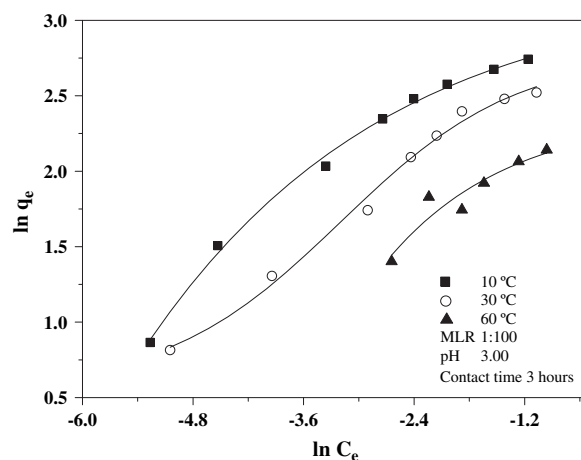


Fig. 7. Freundlich isotherm for the adsorption of lac dye on pretreated cotton with chitosan in the initial dye concentration range 29–469 mg/L.

Table 6

Thermodynamic parameters for the adsorption of lac dye on pretreated cotton with chitosan at different temperatures; dyeing at the initial dye concentration range 29–469 mg/L, MLR 1:100 and pH 3.0

Temp (°C)	<i>b</i> (mL/mg)	ΔG° (kJ)	ΔH° (kJ)	ΔS° (J/K)	R^2
10	26.73	−7.73			
30	16.78	−7.10	−17.43	−34.13	0.9999
60	8.82	−6.03			

adsorption of lac dye on pretreated cotton with chitosan was higher than that for the untreated cotton, further supporting the dual binding role proposed for chitosan. Therefore, the pretreated cotton with chitosan enhanced the adsorption capacity of lac dye on cotton.

3.2.6. Adsorption and desorption studies of lac dye on untreated and pretreated cotton with chitosan at pH 3.0 and on cotton in the presence of 0.5 M NaCl without pH control

As seen from Fig. 9, cotton pretreated with chitosan showed a higher dye uptake than the untreated cotton. Also, the cotton dyeing of the pretreated cotton with chitosan enhanced dye uptake compared with cotton dyed in the presence of sodium chloride. This indicated that the modification of cotton by pretreatment with chitosan can create an affinity between cotton and the lac dye [12]. After 180 min, the dye bath was replaced with deionized water and desorption of lac dye was observed. At 420 min, the amount of the dye adsorbed on pretreated and untreated cotton with chitosan at pH 3.0 and in the presence of NaCl was 8.8, 2.4 and 1.1 mg/g cotton, respectively (Fig. 9). It was found that lac dye could be desorbed easily from the cotton which was dyed in the presence of NaCl and at pH 3.0 without the pretreatment with chitosan. These data supported the belief that the pretreatment of cotton with chitosan in the lac dyeing process increased the amount of dye adsorbed and also decreased the dye desorption from the cotton.

4. Conclusions

This study is the first to investigate the thermodynamics of lac dye adsorption on cotton. The adsorption capacities were

Table 7

Thermodynamic parameters for the adsorption of lac dye on untreated and pretreated cotton with chitosan at pH 3.0, and lac dye on cotton in the presence of 0.5 M NaCl without pH control

Temp (°C)	<i>b</i> (mL/mg)	ΔG° (kJ)	ΔH° (kJ)	ΔS° (J/K)	R^2
<i>Lac dye on untreated cotton with chitosan at pH 3.0</i>					
10	6.76	−4.50			
30	5.98	−4.51	−4.88	−1.31	0.9986
60	4.93	−4.42			
<i>Lac dye on pretreated cotton with chitosan at pH 3.0</i>					
10	26.73	−7.73			
30	16.78	−7.10	−17.43	−34.13	0.9999
60	8.82	−6.03			
<i>Lac dye on untreated cotton in the presence of 0.5 M NaCl without pH control</i>					
10	2.18	−1.83	−13.09	−39.79	
30	1.51	−1.04		−39.77	

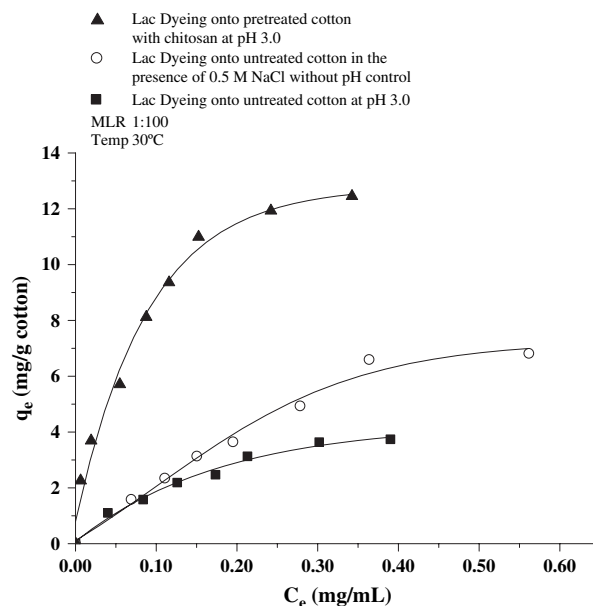


Fig. 8. Comparison of the adsorption isotherms of lac dye on pretreated and untreated cotton with chitosan at pH 3.0 and lac dye on cotton in the presence of 0.5 M NaCl without pH control.

significantly affected by the pH, the initial dye concentration, and the material to liquor ratio (MLR). It was found that dye uptake increased with decreasing pH. Also, the dye uptake increased at higher initial concentrations of the lac dye and was influenced by the material to liquor ratio (MLR). Batch isotherm studies showed that the adsorption of lac dye on cotton was described by the Langmuir and Freundlich isotherms. The enthalpy (ΔH°) for the adsorption of lac dye on cotton at pH 3.0 was found to be -4.88 kJ indicating that the process is an exothermic one. The small negative value of ΔH° suggested the adsorption to be a physical one.

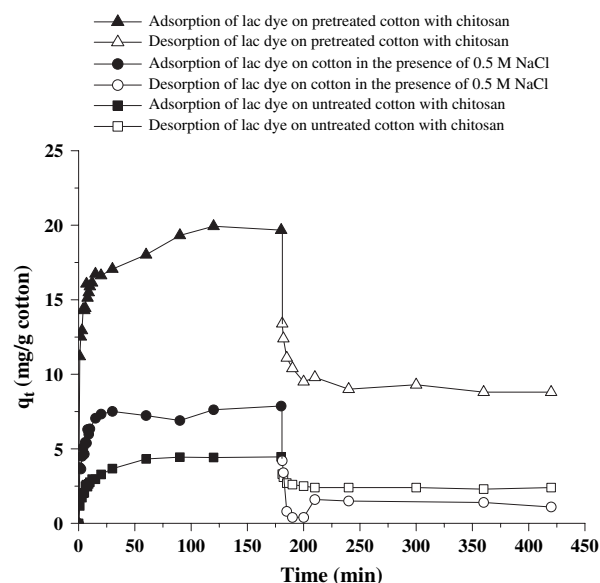


Fig. 9. Adsorption and desorption of lac dye on cotton.

The effect of sodium chloride, and pretreatment of cotton with chitosan, on the adsorption of lac dye was also studied. An increase in the sodium chloride concentration over the range 4.31×10^{-3} – 6.84×10^{-1} M led to an increase in the dye adsorbed onto the cotton and this remained constant in the concentration range 10.3×10^{-1} – 17.1×10^{-1} M when cotton fibres were dyed with lac dye solution without pH control. It is believed that the sodium ion (Na^+) can distribute between the external solution and internal solution so that the negative charge on the cellulose surface is neutralized or shielded, allowing the lac dye molecules to be adsorbed onto the cotton [3,16,17]. The adsorption isotherm for lac dye on cotton in the presence of 0.5 M NaCl agreed well with both the Langmuir and Freundlich isotherms with an enthalpy (ΔH°) of -13.09 kJ. However, sodium chloride had no effect on the adsorption of lac dye on cotton at a pH 2.5, 3.0 and 3.5, indicating that hydrogen ions (H^+) play a more important role than sodium ions (Na^+). The pretreatment of cotton with a 0.3% aqueous (v/v) solution of chitosan showed a significant enhancement of dye uptake onto cotton and also a decrease in the dye desorbed from cotton compared with the results in the absence of chitosan or on lac dyeing in the presence of NaCl. The experimental data for lac dyeing on cotton pretreated with chitosan fitted very well to the Langmuir isotherm with an enthalpy change (ΔH°) of -17.43 kJ. Pretreatment of cotton with chitosan is thus an alternative way to create cationic sites on cotton and to subsequently increase the affinity between lac dye and the fibre. The results from this study should help to underpin future improved practical applications of lac dyeing of cotton.

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