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Comparative study of lac dye adsorption on cotton fibre surface modified by synthetic and natural polymers

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Abstract

Poly(ethyleneimine) (PEI) and bovine serum albumin (BSA) were investigated as pretreating agents for surface modification of the cotton fibres. The measurement of zeta potential was initially used to indicate the effectiveness of the pretreatment. It was found that the PEI largely developed the positive charge whereas the BSA slightly enhanced the positive charge on cotton fibres following a decrease in the pH. Adsorption studies of lac dye on these pretreated cotton fibres show that both PEI and BSA enhance adsorption capacity of lac dye on cotton fibres. The zeta potential results and adsorption studies reveal that the uptake of lac dye on treated cotton fibres occurs via electrostatic attractions between the anion of the dye and cationic segments on the treated cotton fibres. The wash fastness of the dyeing is slightly increased by pretreatment while light fastness is unaffected.

Keywords: Cotton; Lac dye; Poly(ethyleneimine); Protein; Zeta potential

1. Introduction

Natural cotton fibres possess only hydroxylic groups in its structure that cause problems of fibre–dye bonding (especially with natural dye). Many works have aimed to improve dye bonding and dye adsorption on materials through chemical modification. In order to improve the dyeability of cellulosic substrates, a variety of functional compounds in the form of secondary, tertiary and quaternary amines were suggested for using in the pretreatment of cotton [1,2]. Burkinshaw et al. used three commercially available cationic polymers as fixing agents for direct dyeing on natural cellulosic fibres to raise its colour strength. Enhancement of the colour strength of treated cellulosic fibres can be described via ion–ion forces of interaction operating between anionic groups in the dye molecule and cationic group in the pretreated fibre [3]. Lewis and McIlroy synthesised and applied nicotinoyl thioglycollate (NTG) to cotton, producing a cellulosic fibre containing tertiary amine residues in order to improve its dyeability [4]. Cotton fabric modification with photo-modification using a methacryloyl quaternary ammonium compound has also been studied to enhance cationicity and dyeability on the fabric [5]. Uniqema's new polymer for pretreating cotton, containing many cationic sites permits the ready adsorption of the dye without the need to add salt. The polymer also contains large numbers of primary amino groups ($-NH_2$) which are much more reactive than the hydroxyl groups on cotton and able to bind the dye even at neutral pH [6].

The effect of various proteins, natural polymers, on dyeing affinity for the cellulose fibres has also been

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studied. Cellulose fibres, cotton, ramie, viscose, and cuprammonium rayon were all treated with the aqueous solution of four different proteins to study the effect of the protein on dyeing affinity. The four proteins used were soybean, egg albumin, milk casein, and wheat gluten. It was observed that milk casein pretreatment gave the highest uptake for all cellulose fibres, while soybean followed the milk casein for its effectiveness on binding with cotton [7]. Moreover the effect of three different proteins (gelatin, soybean protein powder, and bovine Hb) and six different amino acids on the dyeing of cellulose fibres with cochineal dye was also determined. It was found that, except gelatin, protein pretreatment increased dye affinity for cellulose, while the pretreatment of amino acid increased the affinity slightly [8].

In previous work the effect of poly(ethyleneimine) (PEI), a synthetic polymer, on the adsorption and desorption of lac dye on cotton fibres was reported [9]. It was found that PEI enhanced the dye adsorption and decreased any subsequent desorption of lac dye from the cotton fibres. In order to understand how PEIs work on the cotton fibres, the characteristic surface charge of untreated cotton fibres and also treated with synthetic polymer has been investigated through zeta potential measurement. In addition, bovine serum albumin (BSA), a natural polymer was also used as a surface modifier in comparison with PEI in terms of its dyeability improvement on cotton fibres. Moreover, colour fastness of dyed cotton fibres has also been tested to quantify the effects of washing and light fastness on dyeing lac dye on untreated and treated cotton fibres.

2. Experimental

2.1. Materials

2.1.1. Cotton fibres

The bleached cotton yarn type of 10/1 (8400 yds/lb) obtained from a local market in Chiang Mai, Thailand was used. The cotton fibres (100 g) were first washed in a bath containing 10 g of a long chain fatty acid sodium soap ($C_{18}H_{37}COONa$), 16 g of sodium carbonate, and 1000 ml of water at 80–90 °C for 1 h. Repeated rinsing under distilled water was followed, the cotton fibres were then air-dried.

2.1.2. Lac dye

Stick lac was finely ground and heated in distilled water at the ratio 1:5 of stick lac to distilled water for 1 h, at 80 °C to obtain the red solution of lac dye.

2.1.3. Poly(ethyleneimine) (PEI)

Aldrich $M_w \sim 2000$ (LS) 50 wt.% solution in water was used as received.

2.1.4. Bovine serum albumin (BSA)

United States Biochemical, Purity (Albumin) > 98% protein > 96%, pH 7.

2.2. Instrumentation

Dyeing experiments were also carried out in a custom-built reactor designed for this study [9]. The temperature was controlled via a hot plate and a circulating bath in conjunction with a magnetic stirrer. After removing the treated cotton, an aliquot of the residual lac dye solution was buffered and the concentration was measured using an UV–vis spectrophotometer (6400, Jenway) at 495 nm in order to quantify the amount of lac dye adsorbed on the treated cotton fibres. Zeta potential of the untreated and the treated cotton fibres was measured using a zeta meter (Zeta meter 3+, USA). Colour of the samples was determined using a colour difference meter (X-Rite®).

2.3. Methodology

2.3.1. Adsorption of lac dye onto the treated cotton fibres

PEI, a synthetic polymer and BSA, a natural polymer, were used as surface modifiers of cotton fibres. The cotton fibres were treated separately with various concentrations of PEI and also BSA. Then both treated cotton fibres were dyed in 75 mg/ml of lac dye solution at various times up to 3 h at 40 °C and 60 °C, respectively. At the optimum concentration of each polymer, the treated cotton fibres were dyed in lac dye solution at the concentration range of 20–160 mg/ml for 3 h at 60 °C to determine the adsorption isotherm.

2.3.2. The effect of NaCl on lac dye adsorption onto treated cotton fibres

The cotton fibres were treated with the polymers at the optimum amounts obtained as described in Section 2.3.1. Then the untreated and the treated cotton fibres were dyed in lac dye solutions prepared in various NaCl concentrations for 3 h at 60 °C. The absorbance of lac dye solutions was measured using UV–vis spectrophotometer to monitor the effect of NaCl on lac dye adsorption.

2.3.3. Zeta potential measurements

Zeta potential values of the untreated and the treated cotton fibres were measured in order to verify the charge on the cotton fibre's surface before and after pretreatment with polymer and understand the interaction of dye molecule, polymer, and cotton fibres. At the optimum amounts of polymer given at the maximum lac dye adsorbed on cotton fibres, the treated and also the untreated cotton fibres were cut to the length of approximately 1 mm. The 0.10% solids were prepared in 0.0010 M KCl at various pH and stirred with magnetic stirrer for 10 min. Then the zeta potentials were measured using zeta meter.

2.3.4. Colour measurement and fastness testing (washing fastness and light fastness)

Each dyed sample at the optimum condition was washed three times with 5 l of tap water. Colour measurement was carried out in CIELAB system 1976 using colour difference meter that follows the standard test. Then the dyed cotton fibres were tested for washing fastness (ISO 105-C01:1989 and ISO 105-C03:1989) and light fastness (ISO 105-B02:1994) by comparison to gray scale.

3. Results and discussion

Adsorption of lac dye on the untreated and treated cotton fibres by PEI and BSA at various times was studied and these results are shown in Fig. 1. It revealed that the equilibration time for dyeing decreased with the increase in temperature. Moreover the treated cotton fibres require a longer equilibration time than the untreated one. Increasing the temperature slightly increased the amount of lac dye adsorbed on PEI-treated cotton fibres and largely increased in the case of BSA-treated cotton fibres, but the opposite effect occurred on untreated cotton fibres. The temperature-independence of adsorption of lac dye on PEI-treated cotton fibres could be attributed to the characteristic of modified surface discussed via zeta potential. However, these results might affect the interaction time of the dye molecule and the surface of cotton fibres and also thermodynamics of the adsorption. In addition, the PEI-treated cotton fibres demonstrated the highest amount of lac dye adsorption with respect to the BSA-treated and the untreated cotton fibres.

The adsorption of lac dye onto cotton fibres at various temperatures was studied from the previous work [9]. It was found that an increase in temperature led to a reduction in the adsorbed amount, while the adsorbed amount of lac dye on PEI-treated cotton fibres did not depend on the temperature and it increased with the increase in PEI concentration which became constant around 1000 ppm. At a given BSA, an increase in BSA concentration showed an opposite effect on lac dye adsorption onto BSA-treated cotton with respect to the untreated cotton fibres as shown in Fig. 2, whilst the amount of lac dye adsorbed on BSA-treated cotton increased with the increase in temperature. A maximum amount of lac dye adsorbed on cotton fibres was observed at a BSA concentration of 200 ppm. Besides, the adsorbed amount of lac dye decreased as the BSA concentration increased, when the cotton fibres, treated with BSA of a concentration higher than 200 ppm are employed.

Fig. 3 revealed that the adsorption isotherms of lac dye on the untreated and the treated cotton fibres at the optimum temperature of 60 °C were similar to the Langmuir type. This figure also showed that the PEI-treated cotton fibres possessed the highest adsorbed amount of lac dye followed by the BSA-treated cotton fibres and the untreated cotton fibres, respectively.

Given a probable electrostatic mechanism, the effect of electrolyte concentration on lac dye adsorption on treated cotton fibres was studied. In this case, NaCl a widely used electrolyte in dyeing process was chosen [10]. As shown in Fig. 4, it was observed that adsorption of lac dye on both the untreated and the BSA-treated cotton fibres was influenced in the presence of NaCl, but not for the PEI-treated case.

In terms of the salt concentration, it was found that the increase in NaCl concentration significantly raised the amount of adsorbed dye in the untreated and the BSA-treated cotton fibres due to the diminishing

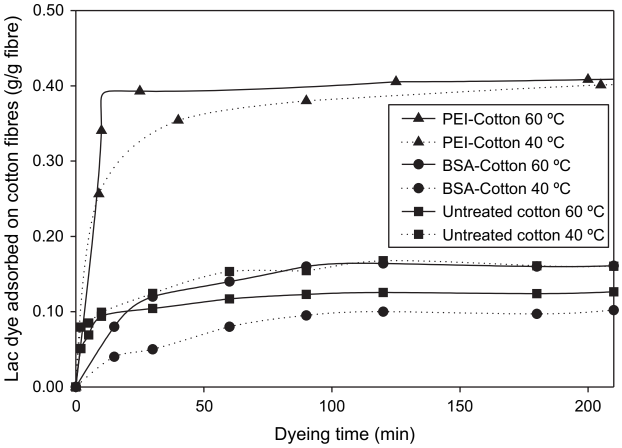

Fig. 1. The effect of dyeing time on lac dye adsorption on untreated and treated cotton fibres at various temperatures.

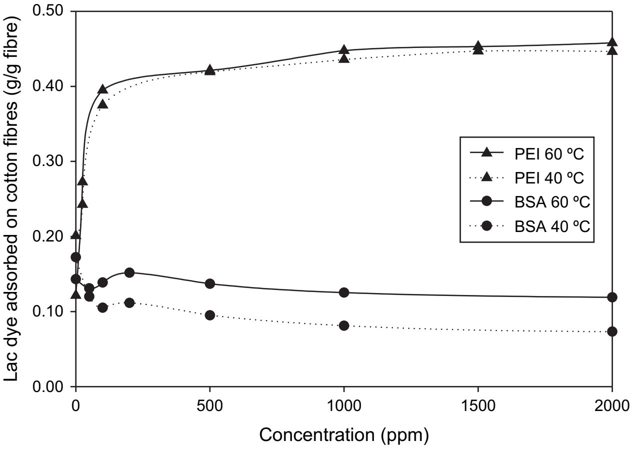

Fig. 2. The effect of polymer concentration on lac dye adsorption at various temperatures.

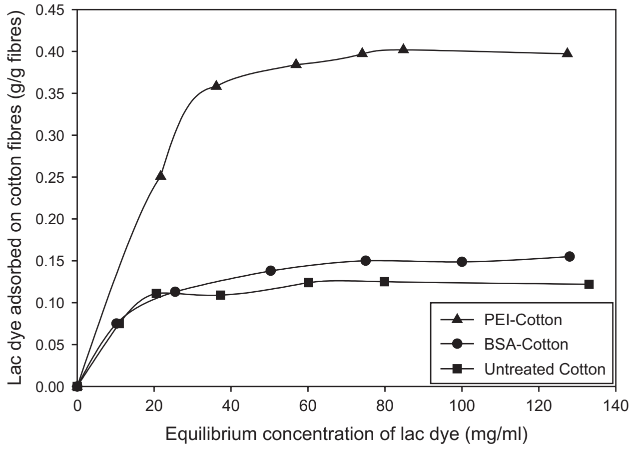

Fig. 3. Adsorption isotherm of lac dye on the untreated and treated cotton fibres at 60 °C.

electronegative potential of cotton fibres caused by Na^+ ions [11]. The amount of lac dye adsorbed on the BSA-treated cotton tended to reach the equilibrium more rapidly than on the untreated cotton fibres. On the other hand, an increase in NaCl concentration had no effect on lac dye adsorption for the PEI-treated cotton fibres. This is due to the surface of cotton fibres that was modified by a highly branched aliphatic poly(imine) which concealed the effect due to the presence of Na^+. Moreover, it could be seen that although Na^+ has no effects on lac dye adsorption on PEI-treated cotton fibres the amount of lac dye adsorbed on the PEI-treated cotton remained high with respect to that on the untreated and the BSA-treated cotton fibres.

In Fig. 5, the zeta potential values (ζ) of the untreated cotton and the cotton modified by PEI and protein were presented. The results showed that the untreated cotton exhibited a negative charge ($\zeta_{\text{plateau}} = -20$ mv) on the surface over the pH range of 4–11. The BSA-treated cotton fibres showed a similar trend.

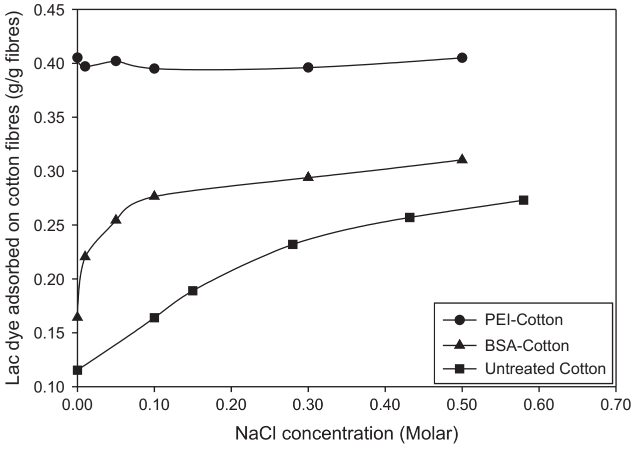

Fig. 4. The effect of NaCl on lac dye adsorption on untreated and treated cotton fibres at 60 °C.

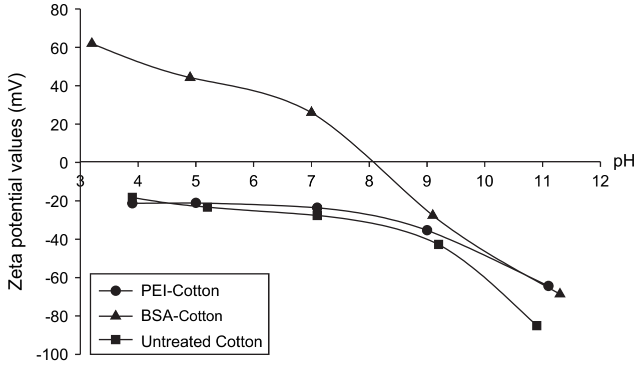

Fig. 5. The zeta potential values of the untreated and treated cotton fibres.

Although BSA consisted of positive charge of amino groups that might adsorb onto the cotton fibres, it also carried negative charge of the acid that counteracted the positive charge causing the loss of the total positive charge. Therefore, the final result of this interaction should increase the positive charge on the surface of cotton fibres slightly as shown in Figs. 6 and 7. On the other hand, PEI a highly branched aliphatic polyimine increased the zeta potential values over the entire pH range, rendering the surfaces to be positively charged at low pH. This clearly showed how PEI enhanced the adsorption of lac dye on cotton fibres. It could also be seen in this figure that isoelectric point (IEP) of PEI-treated cotton fibres shifted to a pH value of approximately 8 with respect to IEP of the natural cotton fibres, a pH value of 2–3 [12].

At optimum pretreatment conditions, the colour of dyed sample was determined by following the method of CIELAB system 1976, whereas, the colorimetric data of cotton fibres pretreated with BSA and PEI are shown in Table 1.

It was found that both the untreated and the BSA-treated cotton fibres offered a light colour, on the other

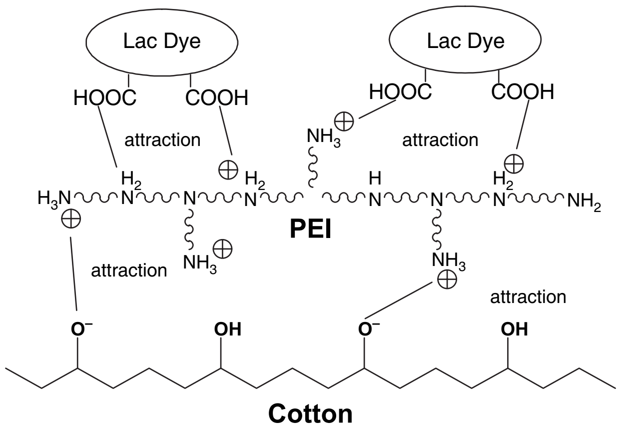

Fig. 6. Schematic diagram of cotton–PEI–lac dye interaction.

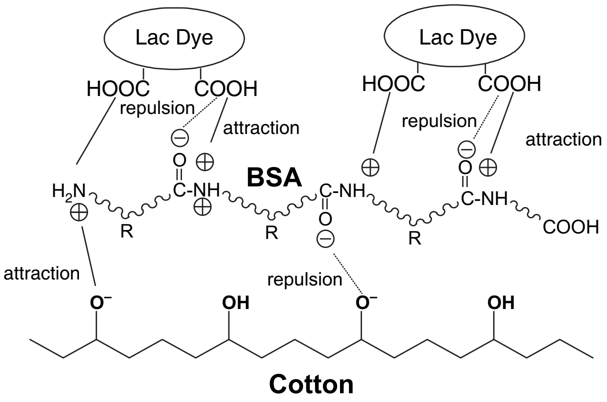

Fig. 7. Schematic diagram of cotton–BSA–lac dye interaction.

hand, the PEI-treated cotton fibres gave a deeper colour due to the decrease in lightness (L^*) and reddish (a^*) values and also a darker shade depth value. The polymer pretreatment for dye adsorption onto cotton fibres might cause the change in colour shade.

The washing fastness of samples was tested and the results are shown in Table 2. In terms of the gray scale assessment, the colour change of the dye adsorbed for the untreated and the treated cotton fibres was the grades between 4 and 5 and the staining on the adjacent fabrics was grade 5. In addition, the light fastness was also tested and found that the change in colour after projecting the light to the sample for 3 days was at grade 3. These results were considered fairly good for natural dye. It could be concluded that the pretreatment of cotton fibres with PEI and also BSA prior to dyeing with lac dye posed no effects on washing and light fastness of samples.

Table 2
Washing and light fastness testing

Testing	Pretreatment conditions		
	Untreated sample	1000 ppm of PEI	200 ppm of BSA
Washing fastness at			
40 °C	4/5	4/5	4
60 °C	4	4	4
Staining at 40 °C			
Wool	5	5	5
Acrylic	5	5	5
Polyester	5	5	5
Nylon	5	5	5
Cotton	4	5	5
Cellulose acetate	5	5	5
Staining at 60 °C			
Wool	5	5	5
Acrylic	5	5	5
Polyester	5	5	5
Nylon	5	5	5
Cotton	4	5	4
Cellulose acetate	5	5	5
Light fastness	3	3	3

4. Conclusion

The zeta potential measurement showed that the surface modification of cotton fibres by pretreatment with PEI enhanced the amount of positive charge on the fibres which was contrast to pretreatment with BSA that exhibited a very similar zeta potential to the corresponding untreated fibres. The adsorption behaviour was in good agreement with the zeta potential results and demonstrated that the modification of cotton fibres with a synthetic polymer (PEI) and also a natural polymer (BSA) enhanced dye adsorption ability. However, the adsorbed amount of lac dye on PEI-treated cotton fibres was higher than that of the cotton fibres pretreated with BSA and did not depend on temperature. Moreover, the zeta potential results and adsorption studies revealed that the uptake of lac dye on the treated cotton fibres might take place by means of an electrostatic attraction between the anions of the dye and the cations on the treated cotton fibre surfaces. The wash fastness and light fastness of lac dye dyeing were largely unaffected by pretreatment.

Table 1
Colorimetric data for pretreatments samples

Pretreatment conditions	L^*	a^*	b^*
Untreated sample	35.55	19.36	0.17
200 ppm of BSA	30.32	18.14	2.04
1000 ppm of PEI	20.39	13.99	2.13

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