

Enhancement of lac dye adsorption on cotton fibres by poly(ethyleneimine)

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Abstract

The effect of poly(ethyleneimine) (PEI) on the adsorption and desorption of lac dye (Natural dye 25; CI 75450) on cotton fibres is reported. We show that PEI increases the dye adsorption and decreases any subsequent desorption of lac dye from the cotton fibres. At equilibrium, the ratio of the number of molecules of lac dye per ethyleneimine repeat unit is ~ 1 in solution but it is close to 3.5 when the PEI adsorbed to the cotton. This suggests that the building is electrostatic in character. The effect of NaCl on the adsorption and desorption of lac dye on cotton fibres has therefore been investigated. It is found that the amount of lac dye adsorbed on fibres increases when NaCl is present in the lac dye solution, but the amount that may be desorbed also increases.

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1. Introduction

Cotton is the most common textile fibre in the world. A natural cellulosic fibre, cotton possesses many useful characteristics such as comfort, it is soft to the hand, has good absorbency, color retention, good strength, is machine-washable, and in today's society is easy to handle and sew. Cellulose is a polymer consisting of anhydroglucose units

connected with 1,4 oxygen bridges in the beta position. The hydroxyl groups on the cellulose units enable hydrogen bonding between two adjacent polymer chains. The degree of polymerization of cotton is 9000–15,000. Raw cotton consists of about 96% cellulose and 4% waxes, pectin, and other proteinaceous and plant materials. These minor constituents must be removed in the scouring and bleaching process to leave the soft, clean, white, absorbent fibre that is satisfactory for the nonwovens industry, at least after the application of an appropriate finishing oil. Cotton swells in a high humidity environment and in

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concentrated solutions of certain acids, salts and bases. The diameter of cotton fibres is $\sim 20\text{ }\mu\text{m}$ whilst the length is $\sim 18\text{ mm}$.

Natural cellulose fibres are negatively charged ($\zeta_{\text{plateau}} = -11\text{ mV}$) due to the presence of carboxyl and hydroxyl-groups [1]. In the case of raw (untreated) material these groups are covered by noncellulose compounds present in the primary wall of the natural fibre. The textile purification processes are applied in order to degrade, remove or complex these compounds. After such purification the zeta potential decreases, further explained by the improved accessibility of anionic groups. Cotton can be easily dyed but the cellulose–dye bond is not very strong. The pretreatment of cotton to enhance its dye adsorption using commercial cationic agents such as Matexil FC-PN, Matexil FC-ER, and Solfix E has been explored; it was found that such pretreatment increased the color strength of the dyeing and improved wash fastness [2].

Natural dyes are known for their beautiful and multi-hued shades. Lac dye (Natural dye 25; CI 75450) is a natural dye extracted from a secretion of the insect *Coccus laccae* (*Laccifer lacca* Kerr) and is widely used for coloring food and dyeing textile such as silk, cotton, and wool. It may also be used for oil painting, in varnishes and possibly in watercolors. It is identified to be two groups of substances: four closely related laccaic acids A, B, C, and E, all of which are water-soluble pigments producing a red color and erythrolaccin which dissolves in alcohol producing pale-yellow color [3–5].

However, this natural dye has a limited usefulness in cotton dyeing as it does not readily adsorb to (dye) cotton. Therefore, natural dyes require a mordant to fix to the fabric, and prevent the color from either fading after exposure to light or washing out. Mordants promote the binding of dyes to fabric by forming a chemical bridge from dye to fibre, improving the staining ability of a dye along with increasing its fastness properties. Mordants form insoluble compounds of the dye within the fibre [6]. Currently, most dyeing processes use metallic mordants. The presence of certain functional groups in suitable positions in the dye molecule causes its coordination to the

metal ion. Unfortunately, many of the metallic mordants are toxic, and have serious detrimental effect on the environment. Clearly, a new type of mordant is required.

Courtaulds and Clariant have developed the Sandene process using “Sandene 8425” in which the cellulosic fibres are modified with a cationic polymer under basic conditions for acid and reactive dyes. Similarly, Hercules have produced “Hercosette 125”, a cationic polymer based on a polyamide and epichlorohydrin but this still possesses low light fastness and brightness [7].

Poly(ethyleneimine) (PEI)—a highly branched aliphatic polyamine—is characterized by the repeating chemical unit denoted as $-(\text{CH}_2-\text{CH}_2-\text{NH})-$. PEI is manufactured by the acid-catalyzed ring opening homopolymerization of ethyleneimine (or aziridine) monomer. The amine groups in PEI exist in primary, secondary and tertiary forms in the approximate ratio of 1:2:1 [8] with a branching site every 3–3.5 nitrogen atoms along any given chain segment. PEIs function as weak Lewis bases in aqueous environments. As the molecular weight of PEI increases, the polymer coils in solution assume a Gaussian conformation. This implies that there are charged nitrogen groups both on the surface and in the sterically protected interior of the molecule. It has been demonstrated in empirical studies that the attachment of the highly charged PEI molecule to anionic surfaces results in a near monolayer of polymer at the interface. In aqueous solution PEI exhibits a strong affinity to anionic materials such as polyanions and negatively charged organic and inorganic solids. PEIs are highly soluble in most polar materials including water, alcohols, glycols and certain organic solvents. The most prominent feature of PEI is its extremely high cationic charge density [9]. Therefore, PEI is widely used, for example, as an excellent brightener and retention aid for low-toxicity for paper [10], dispersant for toner compositions [11], densifying agents which improves H-bonding ability of fibre [12], cationic coagulant for heavy metal sequestering from effluent stream [13], adhesion promoters for pretreatment of nonwoven cellulosic fibres for improved wet strength [14], corrosion inhibitor for acid cleaning of metal [15] and a retention aid for inorganic

pigments (clay, calcium carbonate, titanium dioxide) on cellulosic paper fibres.

Accordingly, the fact that PEI promotes adhesion between similar and dissimilar materials, enhances surface characteristics such as wettability, bondability, is toxicologically benign, and of opposite charge to the lac dye, makes PEI a suitable candidate for a mordant.

2. Experimental

2.1. Materials

2.1.1. Cotton fibres

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

Aldrich Mw ~2000(LS) 50 wt.% solution in water: used as received.

2.2. Instrumentation

Dyeing experiments were carried out in a custom-built reactor designed for this study. Temperature control was achieved via a simple hot plate and circulating bath in conjunction with a magnetic stirrer. At appropriate times, aliquots of the solution were removed and the amount of lac dye remaining in solution (i.e. not adsorbed) was quantified using an UV–VIS spectrophotometer (Lambda 20, Perkin Elmer).

2.3. Methods

2.3.1. Adsorption isotherm of lac dye onto cotton fibres

Adsorption isotherms were determined by measuring the lac dye concentration in a dye/cotton mixture as a function of time, lac dye and cotton concentrations, temperature and salt concentration. On a scale of 4 g of cotton fibres to 80 ml of lac dye solution, the fibres were dyed with a range of lac dye concentrations 20–180 mg/ml at 2, 23, 40, and 60 °C. After removing the cotton, an aliquot of the residual lac dye solution was buffered and the concentration measured using UV–VIS spectrophotometer at 495 nm; the amount of lac dye adsorbed onto cotton fibres was calculated by subtraction. The absorbance of lac dye solution for each dyeing time was monitored until constant. The equilibrium residual concentrations of the lac dye in the bath were calculated, from which the adsorbed dye could be quantified from the known initial dye concentration.

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

The cotton fibres were dyed in lac dye solution with 1.0 M NaCl. Subsequently, samples were immersed in fresh water to study the desorption.

2.3.3. Adsorption isotherm of PEI onto cotton fibres

The cotton fibres were immersed in a range of PEI solutions at various temperatures on the scale of 4 g of cotton fibres to 80 ml of PEI solution. Aliquots of the PEI solution were removed at various times and complexed with 0.50% w/v of copper sulphate. The absorbance of the PEI/Cu complex was quantified using UV–VIS spectrophotometer and hence the amount of residual PEI was determined.

2.3.4. Adsorption isotherm of lac dye onto cotton fibres after pretreatment using PEI

PEI-treated cotton was dyed in 75 mg/ml of lac dye concentration. The residual lac dye at various dyeing times was quantified as described previously.

2.3.5. Desorption studied of lac dye on cotton fibres before and after pretreatment using PEI

Dyed samples were immersed in fresh water after drying at 70 °C. The absorbance of lac dye solution was measured using UV–VIS spectrophotometer to monitor the amount of lac dye that desorbed from the fibres.

2.3.6. Determination of the amount of lac dye reacted with PEI

Lac dye was prepared in 75 ml of 0.50 mg/ml PEI solution at various pH 9, 8, 7, 6.5, 6, 5.5. The mixtures were left overnight to flocculate and the residual lac dye in solution was measured using UV–VIS spectrophotometer. The amount of flocculated lac dye per ethyleneimine monomer unit was calculated.

3. Results and discussion

The adsorption isotherm of lac dye to cotton can be measured simply via UV–VIS spectrophotometer. In Fig. 1, the adsorbed amount of lac dye on cotton fibres per gram of fibre is plotted as a function of the equilibrium concentration of lac dye (mg/ml) at various ratios of cotton fibres to lac dye solution. As can be seen, the adsorption of lac dye onto cotton fibres shows a reasonably high affinity isotherm.

It is found that the saturation level of lac dye on cotton fibres increases with decreasing amount of cotton in the same concentration of lac dye

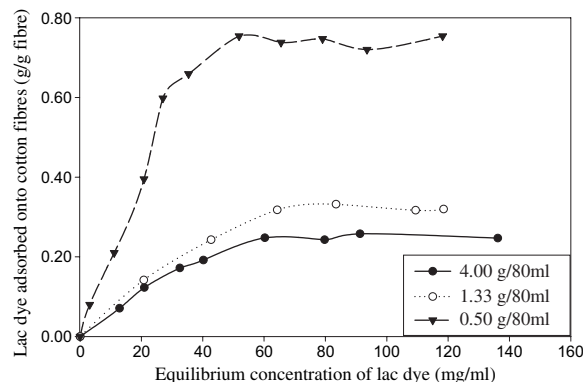


Fig. 1. Adsorption isotherm of lac dye adsorbed onto cotton fibres as a function of the mass of fibres present at 23 °C.

solution. This suggests that the dye is behaving in a manner that is more complex than a simple adsorbate, e.g. being affecting the pH or ionic strength of the medium, or there may be some other cooperations in the adsorption mechanism. This illustrates the importance of a coherent study. Therefore, in all studies presented here the cotton concentration was held constant at 4 g of cotton fibres to 80 ml of lac dye solution. Given the potential of an electrostatic character to this binding, the effect of NaCl on the adsorption and desorption was first studied and these results are shown in Fig. 2. It was found that the amount of lac dye adsorbed on cotton fibres increases when NaCl is present in the lac dye solution.

The problem of dyeing cotton without a mordant is also illustrated in Fig. 2. At the highlighted times, the dye bath is replaced with pure water and the ensuing desorption followed. The final amount of lac dye adsorbed to the cotton is comparable for the two cases, and four times lower than the maximum adsorption. It shows that NaCl can increase the adsorption ability of lac dye onto fibres, but the lac dye can also be desorbed easily from fibres. The increase in electrolyte concentration increases the dye adsorbed by the fibres, due to both diminishing the effects of the electronegative potential that cellulosic fibres acquire when immersed in water solutions [16] and the repulsion between adjacent adsorption sites.

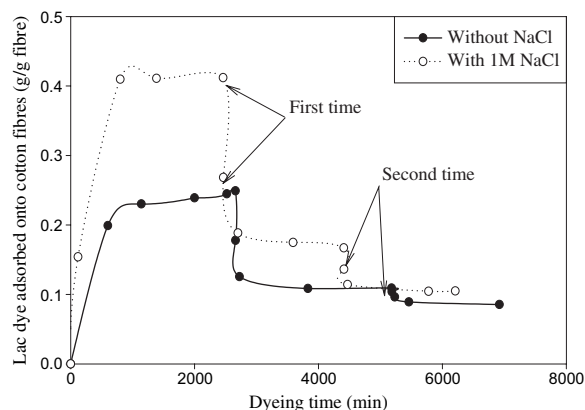


Fig. 2. Effect of NaCl on adsorption–desorption of lac dye onto cotton fibres. At the times marked with arrows, the dye bath is replaced with pure water to explore the desorption process.

To describe the thermodynamics of adsorption, adsorption isotherms were recorded over a wide range of temperatures. In Fig. 3, it may be seen that an increase in lac dye concentration results in an increase in the dye adsorbed to the fibres. This follows a Langmuir-type isotherm at low concentration and low temperature. An increase in temperature leads to a reduction of the adsorbed amount. However, it is also observed that at high temperatures, the plateau adsorbed amount is attained more rapidly than at low temperatures.

The aim of this work is to develop non-metal based mordants and candidate for such a mordant is PEI. The adsorption of lac dye to PEI-treated cotton was therefore examined. First, however, the adsorption of PEI to the cotton was explored. Table 1 shows the amount of PEI at equilibrium on cotton fibres. Temperature has a negligible effect on the adsorption unlike the simple dye behaviour and the PEI adsorbed amount is independent of substrate concentration.

In Fig. 4, the adsorption isotherms of lac dye onto PEI-treated cotton are presented. By comparison with Fig. 3, it can be seen that the PEI significantly increases the adsorbed amount of lac dye. Unlike Fig. 3, the PEI pretreated cotton/dye adsorption process shows an insignificant temperature dependence, the largest dye adsorbed amount is attained at 23 °C. The temperature dependence is presented in Fig. 5.

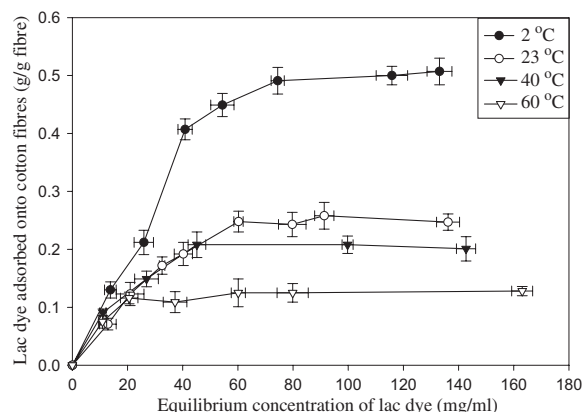


Fig. 3. Adsorption isotherm of dyeing lac dye onto cotton fibres as a function of temperature, cotton fibres 4 g per 80 ml of lac dye solution.

Table 1

Amount of PEI adsorbed on cotton fibres at equilibrium (mg/g fibre)

Temperature (°C)	PEI adsorbed on cotton fibres at equilibrium (mg/g fibre)
23	4.73 (± 0.07)
40	4.23 (± 0.09)
60	4.30 (± 0.03)

Of key importance here is to understand the mechanism by which PEI promotes adsorption to the cotton. Therefore, it is necessary to quantify how the PEI–lac dye binding is perturbed when the PEI is bound to the cotton.

The former interaction is relatively easy to quantify—the PEI becomes insoluble when a stoichiometric amount of lac dye (an acid) is present. A simple titration was therefore performed to measure the lac dye per ethyleneimine monomer unit ratio as a function of pH (Fig. 6). At high pH, where the PEI is uncharged, there is no binding of lac dye to the PEI. On decreasing pH, the PEI becomes increasingly cationic, and the amount of lac dye bound per ethyleneimine monomer unit increases. A limiting value of unity is attained, understandable in terms of a simple acid–base reaction.

Cotton fibres are negatively charged ($\zeta_{\text{plateau}} = -11$ mV) due to the presence of carboxyl and hydroxyl-groups [1], whereas the lac dye has hydroxyl-groups and carboxylic group in molecule and therefore also presents a negative charge [3].

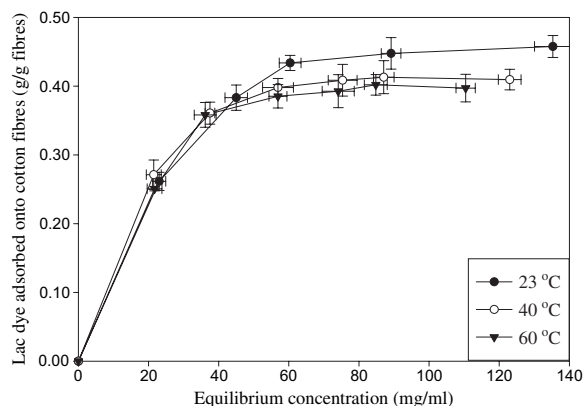


Fig. 4. Adsorption isotherm for lac dye adsorbed onto cotton pretreated with 1000 ppm of PEI.

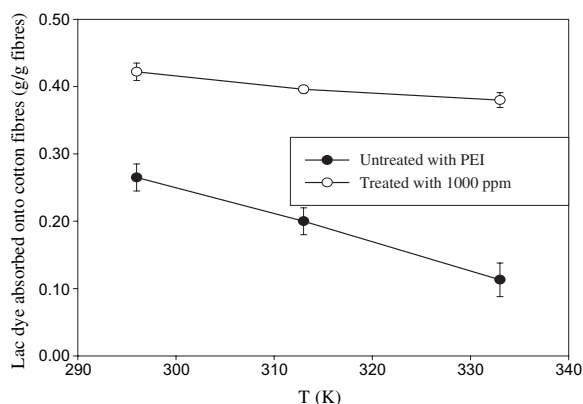


Fig. 5. Effect of temperature on the amount of lac dye adsorbed onto cotton fibres.

Hence, the binding of the negatively charged dye molecules to the fibres is not favoured electrostatically, attempts to improve the surface of cotton fibres were undertaken. PEI significantly increases the adsorption of lac dye on fibres and also decreases the desorption of dye from cotton fibres. Improved adsorption ability of dye on fibre is proposed to be a result of the high cationic character of PEI [11] which interacts with negative charge on cotton fibres and lac dye molecules.

Based on the adsorption isotherms (Fig. 4 and Table 1), the amount of PEI and lac dye bound to the cotton fibres are known. In solution, this ratio has a limiting value of unity. In the presence of 1000 ppm of PEI, the amount of lac dye adsorbed increases, and this ratio has a value of ~ 3.5 , Table 2.

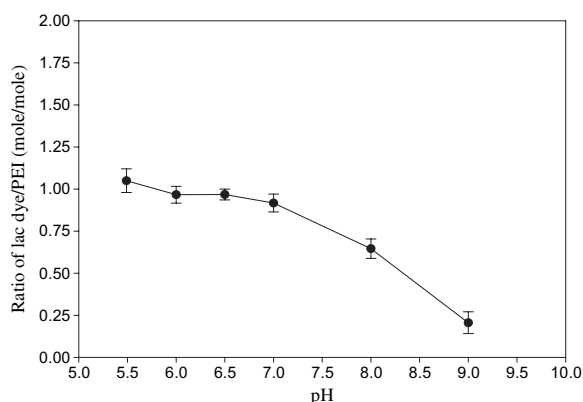


Fig. 6. Ratio of lac dye to react with PEI at various pH.

Table 2

Amount of lac dye in different conditions at room temperature

Condition	Amount of lac dye
Lac dye adsorbed on cotton (i.e. not treated); g/g of fibres	0.249 (± 0.0064)
Lac dye adsorbed on PEI-treated cotton (1000 ppm); g/g of fibres	0.446 (± 0.012)
Enhancement in the amount of lac dye (before and after treatment with PEI) bound to the cotton fibres; g/g of fibres	0.197 (± 0.0184)
PEI adsorbed on cotton (1000 ppm); g/g of fibres	0.00473 (± 0.00007)
Ratio of lac dye molecule per ethyleneimine unit; mole/mole	1
Expected amount of lac dye adsorbed on cotton; g/g fibres	0.0568
Ratio of lac dye molecules per ethyleneimine unit when PEI adsorbed on cotton; mole/mole	3.47

A schematic diagram of the interaction is shown in Fig. 7. The situation is rather more complex than the simple representation as laccaic acid A, one of the principal components of the lac dye, has one $-\text{NH}-$, one $-\text{COOH}$ rather than two acid groups. This $-\text{NH}-$ group could bind a second molecule of acid.

4. Conclusion

The effect of poly(ethyleneimine) (PEI) on cotton dyeing with lac dye was studied. It was found that PEI enhances dye adsorption of cotton fibres and also decreases the dye desorption from

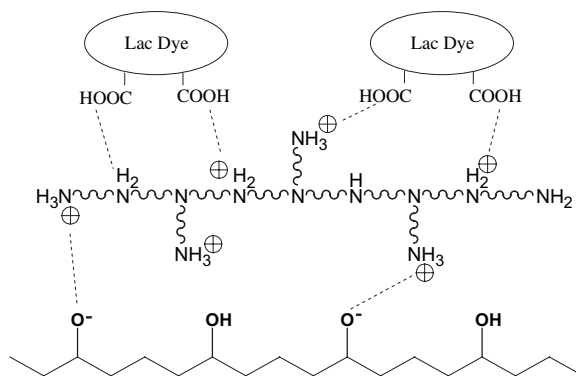


Fig. 7. Schematic diagram of cotton–PEI–lac dye interaction.

fibres. The adsorption isotherm of lac dye on cotton fibres after treatment with PEI solution can be seen to be of Langmuir-type at low temperature. The effect of NaCl on adsorption and desorption of lac dye on cotton fibres are also studied. It is shown that NaCl increases the adsorption ability of lac dye on cotton fibres. However, the dye still shows a high desorption from cotton fibres. In addition, the ratio of lac dye reacted with PEI are determined. It was found that the ratio of mole of lac dye to mole of ethyleneimine is quite constant around 1 at pH lower than 7. But increases to ~ 3.5 when the PEI is bound to the cotton.

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