Potential of Hardwood Kraft Lignin as a Bio-based Dye for Cotton Fabrics

Ji Sun Mun,[a] and Sung Phil Mun [b,*]

The dyeing characteristics of hardwood kraft lignin (KL) were investigated on cotton fabrics, assessing its potential as a sustainable and environmentally friendly dye. Dyeability was evaluated by varying the KL concentrations, temperature, and time. An aqueous solution of Na_2CO_3 (1.0%) as the dye bath and a fabric-to-liquor ratio of 1:50 were used. Cationizing effects were studied using (3-chloro-2-hydroxypropyl) trimethylammonium chloride (CHPTAC), and the mordanting effects of various mordants were also evaluated. Post-mordanting was performed with $FeSO_4$, $FeCl_2$, Fe-lactate (Fe-lac), $MgSO_4$, $CuCl_2$, $CuSO_4$, and $Al_2(SO_4)_3$. A mordant concentration of 1 mM o.w.f. (0.5 mM for $Al_2(SO_4)_3$), with a liquor ratio of 1:30, at 60 °C for 30 min were employed. Suitable dyeing conditions were 2.0% o.w.b., 90 °C, and 90 min, resulting in a brownish color of the cotton fabric. The fabrics exhibited a range of light brown to light grayish brown colors and showed lighter colors than the untreated fabrics when mordanted with $MgSO_4$ and $Al_2(SO_4)_3$. The color difference (ΔE) between cationized and uncationized cotton fabrics was 3.48. From the colorfastness assessment, KL-dyed cotton fabric showed good rubbing and washing fastness for staining, but poor light and washing fastness for fading.

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Keywords: Hardwood kraft lignin; Bio-based dye; Cotton; Dyeing; Mordanting; Cationization

*Contact information: a: Department of Carbon Materials and Fiber Engineering, Jeonbuk National University, 54896, Jeonju, Korea; b: Department of Wood Science and Technology, Jeonbuk National University, 54896, Jeonju, Korea; *Corresponding author: msp@jbnu.ac.kr*

INTRODUCTION

Recently, carbon neutrality has emerged as a solution to environmental issues. In this regard, the interest in the utilization of bioresources, such as lignin, which is the second most abundant organic resource on earth, is growing in the wood-related industry. Approximately 50 million tons of lignin are produced worldwide annually (Demuner *et al.* 2019), and kraft lignin (KL) comprises about 85% of the total quantity (Tejado *et al.* 2007). However, most of the lignins from the pulp and paper industry are incinerated to generate energy and to recover pulping chemicals (Mancera *et al.* 2011), and less than 2% is being utilized for other purposes (Lora and Glasser 2002). Because KL has unique and complex structure depending on the species, and the presence of sulfur derived from Na_2S used for pulping, producing high quality value-added products from KL is challenging (Vishtal and Kraslawski 2011; Demuner *et al.* 2019; Jardim *et al.* 2020). Nonetheless, methods for industrial-scale utilization and value addition of KL have been continuously studied by increasing the reactivity and processibility of KL through various modifications, because KL is readily available and relatively inexpensive.

The textile industry is one of the major contributors to global carbon emissions, accounting for 10% of annual emissions, and if current trends continue, greenhouse gas emissions from the industry will surge more than 50% by 2030 (The World Bank). The environmental impact of the industry's wastewater and waste disposal is also a growing concern, particularly due to the use of synthetic dyes, which pose risks to both the environment and human health (Al-Tohamy *et al*. 2022). While natural dyes are an alternative, commercialization of natural dyes is challenging. The commercialization of bio-based dyes produced from non-edible agricultural or herbal industrial wastes, such as leaves or nutshells, has recently begun (Archroma Inc., USA). Continuous research on natural or bio-based dyes is crucial for compliance with regulatory standards for pollution reduction and to meet consumer demand for environmentally friendly and healthy products.

Previous studies related to dyeing have mainly focused on utilizing KL as a coagulant or flocculent for dye removal in dye wastewater (Kong *et al.* 2015; He *et al.* 2016; Kajihara *et al.* 2018). However, recent studies have attempted to use lignin as a colorant or pigment for surface coating of leather (Pandian *et al.* 2018, 2020, 2021). Although there was a study regarding the application of KL as a dyestuff for fabric dyeing (Agarwal and Pardeshi 2021), the information about the type of KL used or specific dyeing conditions was not fully presented. Furthermore, KL was considered suitable for dyeing cotton fabrics due to its solubility in alkaline conditions, a characteristic that aligns well with the typical alkaline dyeing process of cotton, unlike silk fabric.

In this study, the solubility of KL was increased by dissolving KL in aqueous 1% Na_2CO_3 solution. The potential of KL as a bio-based dye was evaluated by examining the dyeability and mordanting properties on cotton fabrics. In addition, the effect of cationization pretreatment using (3-chloro-2-hydroxypropyl)trimethylammonium chloride (CHPTAC) was evaluated.

EXPERIMENTAL

Materials

The test fabric used was standard cotton fabric (KS K 0905, 115 g/m^2) from Testfabrics (West Pittston, PA, USA).

The KL prepared from mixed hardwoods was kindly provided from Moorim P & P Co., Ltd. (Ulsan, Korea). The *Acacia* spp. from Vietnam and a mixture of *Quercus* spp. and other hardwoods (1:1) from Korea were used for kraft pulping, and the ratio of these wood chips was 50% acacia and 50% mixed hardwood. After kraft pulping, lignin was separated and purified from the black liquor using acid precipitation method with sulfuric acid. Detailed information on pulping conditions, purification process, as well as chemical, structural, and thermal characterization of KL can be found in previous works (Mun *et al*. 2021, 2022; Pe *et al.* 2023). The thoroughly dried KL was stored at ambient temperature and was used as dye material.

The reagents used optionally for cationizing were (3-chloro-2-hydroxypropyl) trimethylammonium chloride (CHPTAC, *ca*. 65% in H_2O) from Tokyo Chemical Industry (Tokyo, Japan) and sodium hydroxide (NaOH, EP, Duksan Pure Chemical, Ansan, Korea). For dyeing sodium carbonate (Na_2CO_3, EP, Yakuri Pure Chemicals, Osaka, Japan) and for mordanting ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, EP, Duksan Pure Chemical, Ansan, Korea), ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$, EP, from Daejung Chemicals & Metals,

Siheung, Korea), ferrous lactate hydrate (Fe-lac, $(CH_3CH(OH)CO_2)Fe{\cdot}nH_2O$, ≥ 98.0%, Sigma-Aldrich, St. Louis, MO, USA), magnesium sulfate anhydrous ($MgSO_4$, GR, Showa Chemical, Tokyo, Japan), copper chloride dihydrate ($CuCl_2{\cdot}2H_2O$, EP, Yakuri Pure Chemicals, Osaka, Japan), copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$, GR, Yakuri Pure Chemicals, Osaka, Japan), and aluminum sulfate ($Al_2(SO_4)_3{\cdot}$16-18 H_2O, EP, Duksan Pharmaceutical, Yongin, Korea) were used. All reagents were used without further purification.

Methods

Cationizing pre-treatment

To cationize cotton fabric, the cationizing agent solution was prepared by diluting (3-chloro-2-hydroxypropyl)trimethylammonium chloride (CHPTAC) to a concentration of 7% in distilled deionized water (DI-water) and then adding NaOH in an amount equal to 30% of CHPTAC. The cotton fabric was placed in a 500-mL beaker containing the cationizing-agent solution (fabric-to-liquor ratio 1:20) and the fabric was treated at 80 °C for 40 min with occasional stirring. After treatment, the excess amount of liquor was removed by suction. Then, the treated cotton fabric was neutralized with 1% acetic acid, fully rinsed with DI-water, and dried at ambient temperature. The cationized cotton fabric was used to compare the dyeability with non-cationized cotton fabric.

Dyeing

The cotton fabrics were dyed in 50-mL beakers at various conditions listed in Table 1. The fabric-to-liquor ratio was fixed at 1:50. The dye bath was prepared with 1% Na_2CO_3 aqueous solution (pH 11.26). The beakers were covered with aluminum foil and were placed on a metal rack in a water bath (OSB-2100, Eyela, Tokyo, Japan). The fabrics were occasionally stirred while dyeing. After dyeing, the fabrics were sufficiently washed with water, and dried at ambient temperature.

Table 1. Dyeing Conditions

Dependent		Fixed
Concentration (%, o.w.b.)	0.5, 1.0, 1.5, 2.0	90 °C, 90 min
Temperature (°C)	50, 70, 90	2.0%, 90 min
Time (min)	30, 60, 90	2.0%, 90 °C

Mordanting

After the cotton fabrics were dyed under suitable conditions of 2.0% (o.w.b.), 90 °C, and 90 min, post-mordanting was conducted in a 30-mL conical beaker. The mordants used were $FeSO_4$, $FeCl_2$, Fe-lac, $MgSO_4$, $CuCl_2$, $CuSO_4$, and $Al_2(SO_4)_3$. The dyed fabrics were mordanted at fixed conditions of 1 mM mordant concentration except for $Al_2(SO_4)_3$ (0.5 mM), 1:30 liquor ratio at 60 °C for 30 min in a shaking water bath (SWB-10, JEIO TECH, Daejeon, Korea). The fabrics were occasionally stirred during mordanting. After mordanting, the fabrics were thoroughly washed with water, and dried at ambient temperature.

Dyeability and surface color

The diffuse reflectance of dyed fabrics was measured under illuminant D65 using the 10° standard observer by Datacolor spectrophotometer (CE7000A, Lawrenceville, NJ, USA) at Korea Dyeing & Finishing Technology Institute (Dyetec, Daegu, Korea). The

color strengths (*K*/*S*) of dyed fabrics were calculated according to Eq. 1 (Kubelka and Munk 1931),

$$K/S = (1 - R)^2/2R \quad (1)$$

where *K* is the absorption coefficient, *S* is the light scattering coefficient, and *R* is the reflectivity.

The surface color (CIE *L*a*b**) and Munsell's hue (*H*), value (*V*), and chroma (*C*)) of the dyed and mordanted cotton fabrics were measured using a spectrophotometer (Color meter, CR-20, Konica Minolta, Tokyo, Japan).

To compare the color difference between the cationized cotton and non-cationized cotton, the Δ*E* value was calculated according to Eq. 2,

$$\Delta E = [(L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2]^{1/2} \quad (2)$$

where L_1^*, a_1^*, b_1^* are the L^*, a^*, and b^* values of cationized cotton fabric, and L_2^*, a_2^*, b_2^* are the L^*, a^*, and b^* values of non-cationized cotton fabric.

Colorfastness

The washing, rubbing, and light fastness of KL dyed cotton fabric were evaluated according to the Standard Test Methods KS K ISO 105-C06 (2010) (A2S), KS K ISO 105-X12 (2016), and KS K ISO 105-B02 (2014) (Exposure cycle A1, method 5), respectively. These assessments were conducted at Dyetec.

RESULTS AND DISCUSSION

Effect of Dyeability on Concentration, Temperature, and Time

A widely adopted approach to assess dyeability is through surface reflectance measurement, a simple, easy, and non-destructive way to evaluate the color change of a substrate after dyeing. Although surface reflectance measurement does not directly measure dye uptake quantitatively, the percentage of dye exhaustion between different fabrics can be compared by analyzing the *K*/*S* values. The ratio of the amount of light absorbed by the dyed fabric to the amount of light incident on the fabric, as represented by the *K*/*S* values, allows for the comparison of the relative dyeing performance of different substrates. The *K*/*S* values are influenced by several factors, including the type of dye or fabric used, as well as the dyeing conditions.

Figure 1 shows the changes in *K*/*S* values of KL-dyed cotton fabrics with respect to dyeing concentration, temperature, and time. The results of dyeing under four different KL concentrations of 0.5%, 1.0%, 1.5%, and 2.0% o.w.b., at the constant dyeing temperature (90 °C) and time (90 min) are shown in Fig. 1(a). The *K*/*S* value of the KL-dyed cotton fabric was 1.3 at a concentration of 0.5% o.w.b., and it increased to 2.4 at a concentration of 1.5% o.w.b. However, the increase in *K*/*S* value slowed down as the concentration approached 1.5% to 2% o.w.b., reaching a dyeing equilibrium at around 2% o.w.b. Thus, a dyeing concentration of 2% o.w.b. was deemed suitable for dyeing cotton fabric with KL. The results of dyeing cotton fabrics under three different temperature conditions (50, 70, and 90 ℃), with a dyeing concentration of 2.0% o.w.b. and a time of 90 min, are shown in Fig. 1(b). As the dyeing temperature increased from 50 to 90 ℃, the *K*/*S* value of the cotton fabric also increased. This phenomenon is attributed to the higher temperature enabling greater swelling of the cotton fibers, which in turn increases the

adsorption of KL on the surface of the fiber. Figure 1(c) shows the results of dyeing the cotton fabric for three different times (30, 60, and 90 min) at a dyeing concentration of 2.0% o.w.b. and a temperature of 90 °C. As the duration of dyeing increased from 30 to 90 min, the *K*/*S* values of the cotton fabrics increased linearly. The outcome suggested that longer dyeing times were more effective in improving the dyeability of cotton fabric with KL than shorter times. However, due to economic reasons, the dyeing temperature and duration were limited to a maximum of 90 °C and 90 min, respectively, resulting in the dyeing equilibrium not being reached under the experimental temperature and time conditions. The highest *K*/*S* value was observed under the dyeing conditions of a concentration of 2.0% o.w.b., at a temperature of 90 °C, and a duration of 90 min, and is therefore considered the most suitable for dyeing cotton fabric with KL.

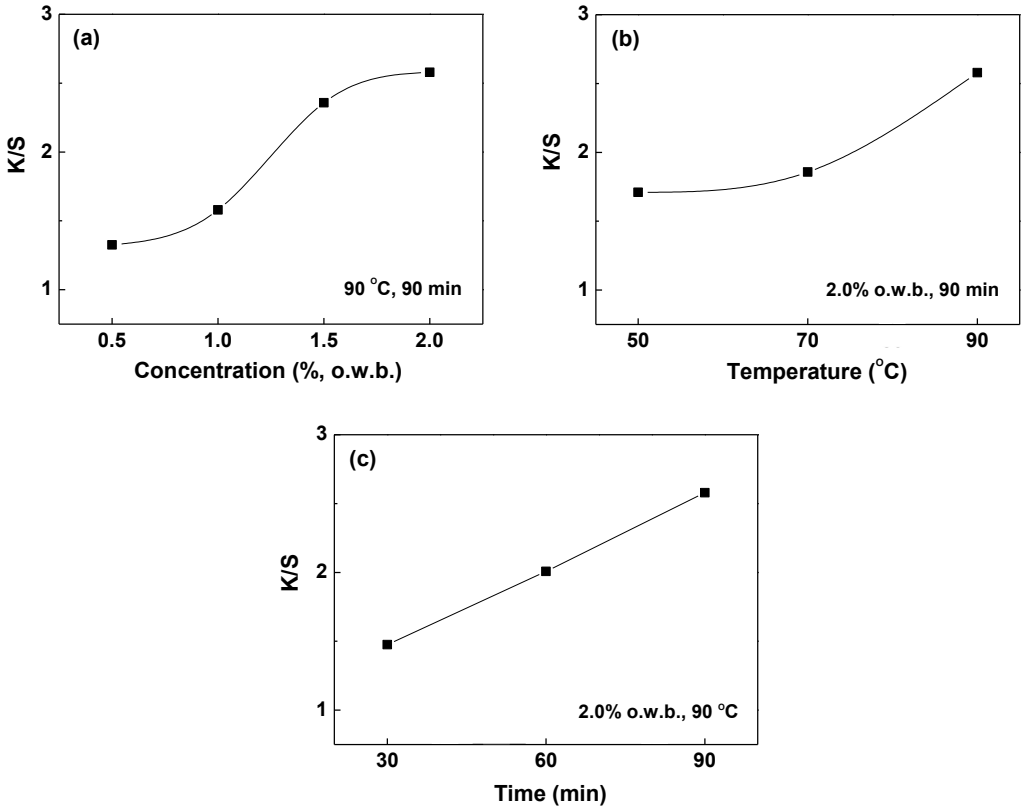

Fig. 1. Effect of dyeing concentration (a), temperature (b), and time (c) on K/S values.

Figure 2 showed the change in KL fixation with KL concentration at a dyeing temperature of 90 °C. The fixation (%) of KL on cotton fabrics, based on weight changes before and after dyeing at KL concentrations of 0.5%, 1%, 1.5%, and 2% o.w.b., resulted in 0.9%, 1.3%, 2.5%, and 2.8%, respectively. Only a small percentage of KL was fixed on the fabric, while the majority remained in the dye bath. One of the reasons for the low fixation was due to the molecular weight of KL. Considering the molecular weight of KL used for dyeing was around 3,000 g/mol (Mun *et al.* 2021), challenges in effective penetration into cotton fiber were anticipated, potentially impacting the overall dyeing process. Smaller molecular weight dyes are generally known to exhibit better dyeability, as they can more easily penetrate the fibers or substrate being dyed. Although the majority of KL remained in the dye bath, the remaining KL can be simply recovered using acid precipitation method and can be repurposed for other applications.

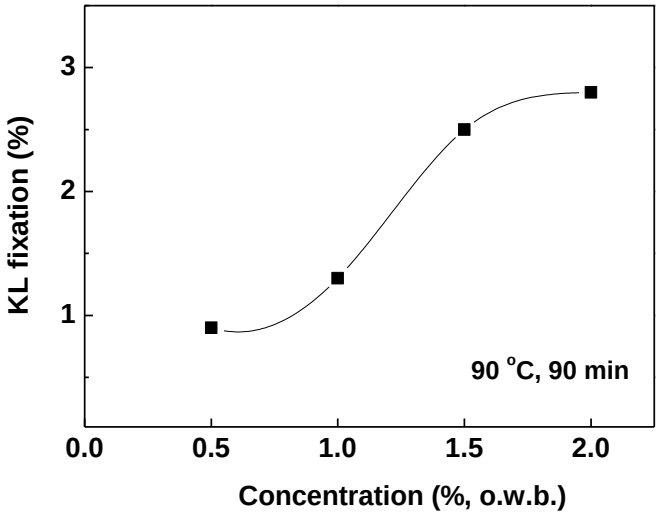

Fig. 2. Changes in KL fixation with concentration

Color Characteristics of Mordanted Fabrics

One of the important processes in natural dyeing is mordanting, because the adsorption, affinity, and color fixation of dyes with fibers can be enhanced by forming a complex between dyes and mordants (Prabhu and Bhute 2012; Singh and Singh 2018). Mordants are commonly divided into natural and synthetic types, and synthetic mordants are largely used to simplify natural dyeing processes (Cho 2010). Depending on the mordant used after mordanting, fabrics dyed with polychromatic dyes can exhibit different color changes. Among mordants, alum, chrome, and tin are known as brightening agents, while iron and copper are known as dulling agents (Singh and Singh 2018). In general, aluminum is also known to have a brightening effect when used as a mordant.

After dyeing with KL, the cotton fabrics were post-mordanted with seven different kinds of mordants. The surface color of the fabrics was assessed in terms of *L*a*b**, *H*, and *V*/*C* values. In Table 2, the *H*, *V*/*C* values, and RGB colors of mordanted cotton fabrics are shown along with non-mordanted ones. The colors were converted from *L*a*b** to RGB values using a color conversion program (E-paint). The color of mordanted cotton fabrics ranged from light brown to light grayish-brown.

Table 2. Colors and Munsell Values of Mordanted-Cotton Fabrics

Anion	Cation	Munsell		Color
		H	V/C	
SO_4^{2-}	Fe^{2+}	8.5 YR	6.1/1.5	
Cl^-		9.0 YR	6.1/2.0	
$C_3H_5O_3^-$		8.7 YR	6.0/1.6	
SO_4^{2-}	Mg^{2+}	6.4 YR	6.4/2.0	
	Cu^{2+}	6.1 YR	6.1/1.7	
Cl^-		6.2 YR	5.9/1.8	
SO_4^{2-}	Al^{3+}	7.0 YR	6.5/2.0	
Non-mordanted		8.4 YR	6.0/2.3	

Mordanting conditions: Post-mordanted with 1 mM concentration o.w.f. (0.5 mM for $Al_2(SO_4)_3$), fabric-to-liquor ratio 1:30, 60 °C, and 30 min

In Fig. 3, the *L**, *a**, *b** values of mordanted cotton fabrics are shown along with non-mordanted ones. The *L** values of cotton fabrics mordanted with $MgSO_4$ and $Al_2(SO_4)_3$ were 66.1 and 66.5, respectively. These values were slightly higher than those of untreated cotton fabric (61.2), which was consistent with the brightening effect mentioned earlier.

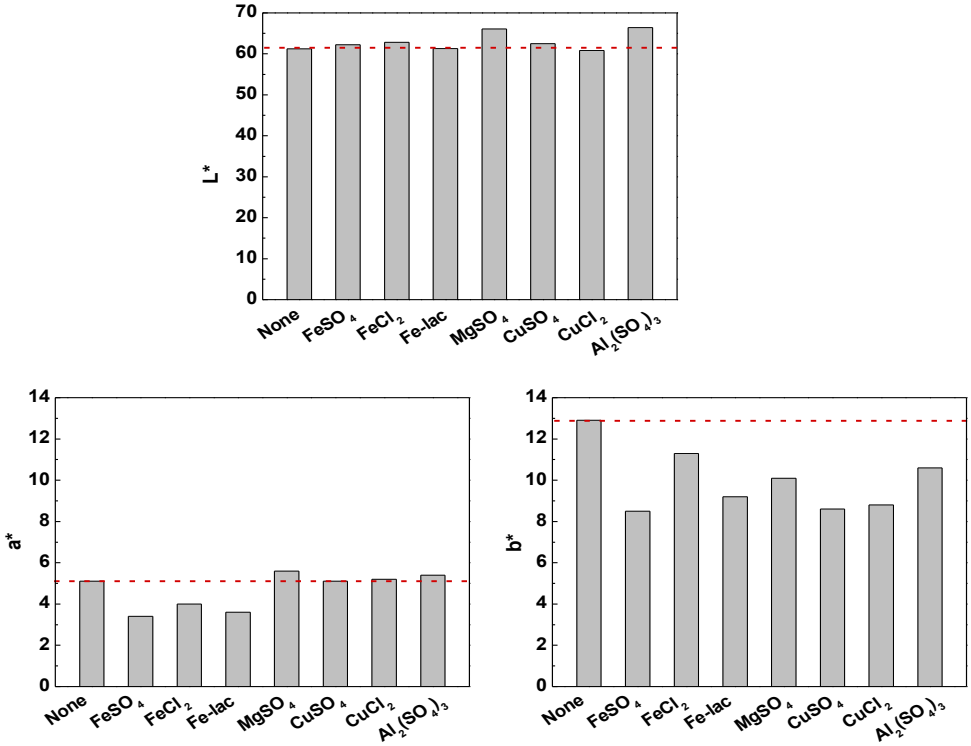

Fig. 3. *L* a* b** values of mordanted-cotton fabrics

However, the *L** values of cotton fabrics mordanted with iron and copper were between 60.8 and 62.8, similar to that of untreated cotton fabric, and showed no distinct dulling effect. The *a** value of iron mordanted fabrics decreased compared to untreated cotton fabric, while the *a** values were similar or slightly increased when the fabrics were mordanted with magnesium, copper, and aluminum. The *b** values of the mordanted fabrics were lower than that of the untreated fabric, regardless of the mordant used. Conversely, the influence of cations on KL dyeing and mordanting of cotton fabric did not show a clear trend.

Cotton fibers are mainly composed of cellulose, making up almost 90% of their composition (Hsieh 2007). Cotton contains many hydroxyl groups, which have the potential to undergo substitution reactions and crosslink with dyes (Cotton Incorporated 2023). The interactions between KL-cotton fiber and KL-mordant-cotton fiber are illustrated in Fig. 4. The mordants containing metallic species play a crucial role in binding fiber and pigment at molecular level during natural dyeing (Prezewozna 2002). Among them, transition metals, such as iron and copper, are known for their ability to easily form complexes and chelates. After mordanting, only a slight color change was observed in mordanted cotton, leading to the assumption that the formation of metal-cotton fiber complexes was challenging. As mentioned earlier, with only a small percentage of KL fixed

on the fabric, the difficulties in effective fixation to cotton fibers were likely due to the high molecular weight of KL. This factor might have contributed to the observed limited color change. In addition, it was inferred that KL shares properties similar to those of monogenetic dyes, which maintain a consistent color even after mordanting.

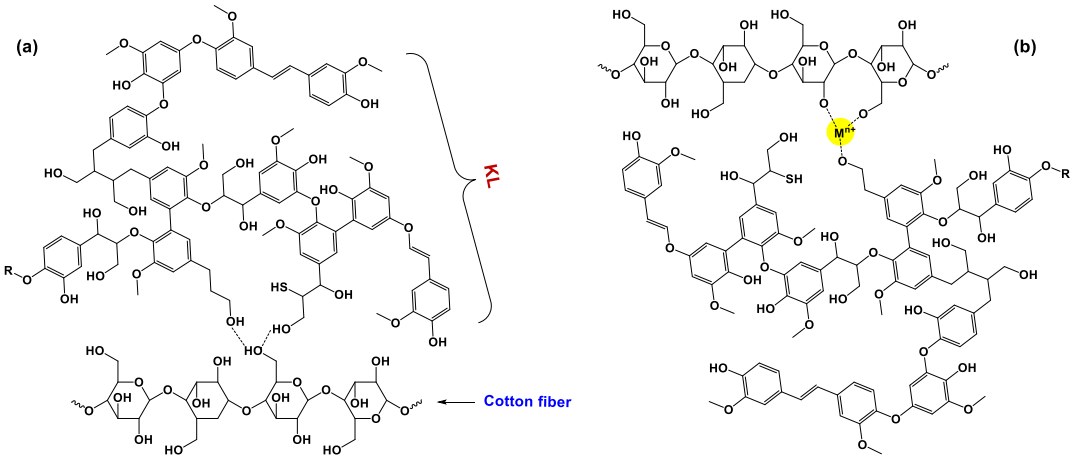

Fig. 4. Possible interactions between KL-cotton fiber (a) and KL-mordant-cotton fiber (b)

Cationizing Effect on Dyeability

Cotton possesses a hydrophilic nature and a porous structure, which enable dye molecules to permeate between the fibrils and into the amorphous regions of the fiber. However, the affinity for dyes is low due to the high crystallinity, typically around 70%, and orientation of cotton fibers, which hinders reagent penetration and subsequent reactions (Zhang *et al*. 1993; Wu *et al*. 2022). In addition, the repulsion stemming from the negative charges of dye molecules and cotton fibers further diminishes affinity and colorfastness (Baek *et al*. 2022; Ji *et al*. 2023). Numerous studies have been conducted to improve the interaction between dye molecules and cotton fibers. The most studied methods fall into two categories: mordanting cotton using metallic salts (Prabhu and Bhute 2012) or bio-alternatives like chitosan (Houshyar and Amirshahi 2002), and pretreatment of cotton through techniques such as mercerization or cationization. Mercerization employs NaOH (Karmakar 1999), whereas the most common approach for cationizing cotton involves incorporating quaternary ammonium salts into cellulose (Choudhury 2014). This introduces cationic groups, altering the anionic behavior of cellulosic fabrics (Correia *et al*. 2021). Among cationizing reagents, CHPTAC is the most commonly used for cationizing cotton. Figure 5 illustrates the reaction mechanism for cationizing process of cotton. Although CHPTAC exhibits low reactivity towards cellulose, it can transform into 2,3-epoxypropyl trimethylammonium chloride (EPTAC) in the presence of NaOH. Because EPTAC is highly reactive, it can form a covalent bond with the anion of cellulose after the conversion (Correia *et al*. 2021).

Cationization pretreatment was conducted on cotton fabric to investigate its colorization effect. Table 3 compares and shows the $L^*a^*b^*$, H, and V/C values, as well as the colors of cationized and untreated cotton fabrics. Following cationization, the L^* value of the cotton fabric decreased, while the a^* and b^* values increased. The b^* value exhibited a notable increase, yielding a more yellowish light brown hue for the cationized cotton fabric compared to the untreated cotton fabric. The color difference (ΔE) between the cationized and untreated cotton fabrics was 3.5, indicating a minor effect of cationization

on the pretreatment of KL dyeing for cotton fabric. After the cationizing pre-treatment, the cotton fabric exhibited a 2.5% increase in weight. In addition, the dye fixation (%) was 4.6% at 2% o.w.b. KL concentration, which showed a slight increase (1.8%) compared to the fixation on untreated cotton fabric.

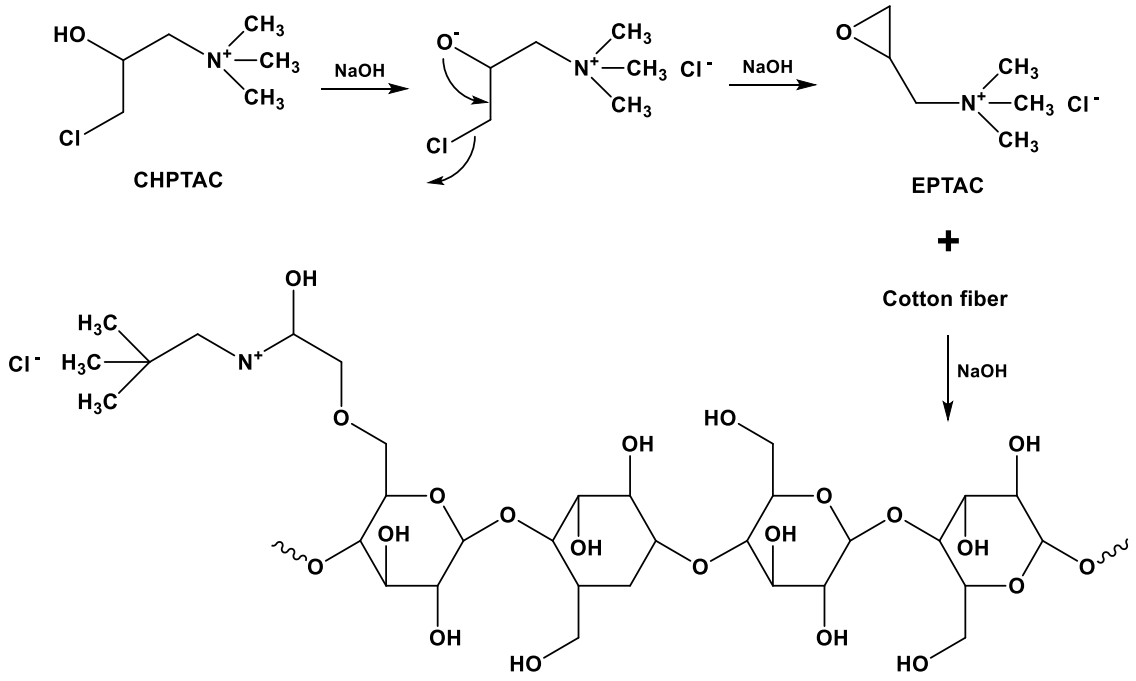

Fig. 5. Cationization of cotton fiber with CHPTAC (Correia *et al.* 2021)

Table 3. Colors and Munsell Values of Mordanted-Cotton Fabrics

Pre-treatment	*L**	*a**	*b**	*H*	*V/C*	Color
Cationized	60.5	6.9	15.8	7.9 YR	5.8/2.9	
Untreated	61.2	5.1	12.9	8.4 YR	6.0/2.3	

Colorfastness

The results of washing, rubbing, and light fastness assessments on KL-dyed cotton fabrics are shown in Table 4. Overall, the colorfastness of the KL-dyed cotton fabrics was very good to excellent, with the exception of light fastness (2) and the fade of washing fastness (2 to 3). Washing fastness assesses the durability of dyed fabrics in terms of color fading and staining. The degree of stain for KL-dyed cotton fabric was evaluated using multifiber fabric. It showed good fastness (3 to 4, 4) for natural fibers silk and cotton, as well as excellent fastness (4 to 5) for semi-synthetic fiber acetate and synthetic fibers nylon, polyester, and acrylic. With regards to rubbing fastness, the KL-dyed cotton fabric exhibited good to excellent rubbing fastness (4, 4 to 5) regardless of whether dry or wet test methods were employed. While KL might have the potential as a light brown dye for low-cost, moderately durable products, enhancing its utilization as bio-based dye might require modifications such as introducing new functional groups or reducing its molecular weight.

Table 4. Washing, Rubbing, and Light Fastness of KL-dyed Cotton Fabric

Washing							Rubbing		Light
Fade	Stain								
	Cotton	Wool	Acetate	Nylon	Polyester	Acrylic	Dry	Wet	
2 to 3	4	3 to 4	4 to 5	4 to 5	4 to 5	4 to 5	4 to 5	4	2

Dyeing conditions: 2.0% o.w.b. KL concentration, 1% Na_2CO_3 (aq), fabric-to-liquor ratio 1:50, 90 °C, and 90 min

CONCLUSIONS

1. Suitable dyeing conditions for cotton fabrics were KL concentration of 2.0% o.w.b., 90 ℃, and 90 min at pH of 11.26 and a fabric-to-liquor ratio of 1:50.
2. The colors of the dyed cotton fabrics were light brown, and post-mordanted fabrics exhibited shades ranging from light brown to light grayish brown.
3. The L^* value of cationized cotton fabrics decreased, while a^* and b^* increased compared to those of untreated cotton. The color of cationized cotton fabric was more yellowish brown than the untreated cotton, resulting in a color difference (ΔE) of 3.5.
4. In the colorfastness assessment for washing, rubbing, and light, the KL-dyed cotton fabric demonstrated good rubbing and washing fastness against staining.

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