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Enhancing the efficiency of hemp fiber dyeing with natural dyes: Indigo and lac

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Abstract

Hemp fibers dyed with natural dyes are environmentally sustainable, but it is typically difficult to achieve an intense shade and washing durability. In this study, mercerization and cationization using polyelectrolyte, Poly-diallyldimethylammonium chloride (polyDADMAC), were chosen to enhance the dyeing efficiency and mechanical properties. Indigo and lac were chosen as natural dyes due to their widespread use. SEM demonstrated that untreated fibers contained the non-cellulose boundary layer on the surfaces, but after mercerization, the surfaces were smoother, making them suitable for absorbing natural dyes. In agreement with the FT-IR, the spectra of non-cellulose disappeared after mercerizing. Following cationization, the FT-IR spectra confirmed the consequences of using poly-DADMAC. Tensile testing demonstrated that mercerized hemp yarns were 34.1% stronger compared to untreated hemp yarns due to the decrease in non-cellulose content and that the intermolecular attraction of cellulose was not disturbed. The color strength and fastness properties were described by the K/S value. Mercerization considerably affected the K/S of indigo dyeing, while cationization affected lac dyeing significantly. Besides that, both treatments improved fastness properties as well.

1. Introduction

Vegetable fibers are among the natural fibers that humans have recognized and utilized for centuries. The products from vegetable fiber are widely used due to their outstanding features: lightweight, good heat-insulating, comfortable to wear, safe from chemicals, biodegradability, and distinct appeal [1-3]. Vegetable fibers that possess properties suitable for various applications are currently being developed to increase their value and customer demand. Hemp (*Cannabis sativa L. subsp. sativa*) is one of the most versatile plants that was cultivated in China around 2300 B.C. and became known in East Asia. It was later propagated to the Mediterranean, Europe, and America as a substitute for flax or linen, which were scarce then. Hemp grows well in warm to hot climates, so it can be grown almost anywhere [4,5]. Hemp can be utilized in multiple applications; oil extracted from seeds is used as a food component, cosmetic, and personal care product [6-8]; and cannabidiol CBD extracted from panicle leaves is used for medicine and diet supplements [9,10]. Hemp fibers are high-quality fibers extracted from bast, appearing dark brown and difficult to bleach. The fibers have a low density of approximately 1.25 $g{\cdot}cm^{-1}$ [11] and less shrinkage but are strong with a strength of 210-750 MPa [12]. Hemp fibers can be used as a raw material for manufacturing a wide range of products, including composite materials [13-15], and textiles [16-18], which will be the focus of this research.

In the global textile market, hemp fabrics continue to be widely popular with consumers. In 2019, the market value was USD 4.5 billion, and it is anticipated that by 2027, it will reach USD 43.8 billion [19]. Thus, there is competition for the development of hemp products in order to obtain market share. Dyeing is one of the processes that enhances the value of a fabric. The quality of the dyeing process leads to better staining performance, and many researchers are currently studying the procedure for natural fiber dyeing to achieve high-quality coloring [20-22].

In accordance with current environmental campaigns related to climate change and the reduction of CO_2 emissions, this research aims to study the dyeing of hemp fibers with natural dyes, which are an environmentally friendly alternative and harmless for the user. Therefore, the product will have a distinction regarding its naturalness that will appeal to consumers concerned with this issue. On the other hand, almost all synthetic dyes contain aromatic compounds that extremely affect the environment, most of which originate from wastewater discharged from the textile industry [23]. Some synthetic dyes contain heavy metal such as arsenic, cadmium, chromium, cobalt, etc., which causes carcinogens [24]. Besides natural dyes being safe for consumers, the other materials used in the dyeing process are

readily available locally, preserving people's culture and traditional knowledge. Therefore, this research investigates the dyeing of hemp fiber with natural dyes that respond to environmental issues, minimize toxicity, and maintain indigenous knowledge. Two natural dyes, indigo and lac, which produce blue and red, respectively, were chosen to represent the natural dyes as their primary colors and widespread use [25,26].

Natural indigo is extracted from fresh indigo leaves in the form of a precursor called indican or indoxyl-B-D-glucoside [27]. The indigo-blue pigment, which is water-insoluble and cannot be absorbed on fibers, will be reduced in an alkali solution into a water-soluble leuco-indigo form. After that, the leuco-indigo absorbed on cellulosic fibers will be subsequently oxidized into an indigo-blue form bonded to fibers [28]. In Southeast Asia, indigo-dyed fabrics are well-known and in considerable demand due to their uniqueness, which can create various patterns. Nevertheless, good-quality indigo fabrics are still in short supply, whereas poor-quality are available in abundance [29].

Lac is a natural quinone dye obtained from the insect species kerria lacca. It grows in a rain tree (*Samanea saman*) and releases a resinous cocoon to encapsulate itself, giving a scarlet pigment [30]. The primary substance of lac is laccaic acid, which is water-soluble and can be extracted using common solvents, i.e., methanol, ethanol, or water [31]. Currently, lac is used in various applications, including the food industry [32], pharmaceuticals [33], and cosmetics [34]. In textile applications, the process of lac dyeing with cellulosic fibers is simple. However, it is challenging to maintain dye on the fibers since it easily fades when exposed to sunlight or washing [35].

The main disadvantage of natural dyeing is that it is difficult to obtain the same color repeatedly since the ingredients are derived from nature, so the dyeing efficiency is uncertain. Additionally, without synthetic mordants, it is challenging to achieve an intense shade, and it usually fades after being washed [21,22,36]. There are many factors that influence natural dyeing, including the preparation of fibers prior to dyeing, the dyeing procedure, the additives used, the compatibility or interaction between fibers and natural dyes, etc., all of which affect dyeability.

Nowadays, several studies have attempted to improve the efficiency of natural fiber dyeing with both natural dyes and synthetic dyes. Since hemp fibers comprise ~75% cellulose, the remaining non-cellulose components are ~4% pectin, ~4% hemicellulose, and ~2% lignin [37,38], which hinder dye absorption on fiber surfaces. There are several methods to improve the fiber surfaces before dyeing: for example, using scouring agents such as nonionic surfactants for the initial removal of fat, dust, and other impurities; applying enzymatic treatments to remove pectin, which has a high content in hemp [18]; and employing alkali treatment, which is a low-cost and highly effective method to remove non-cellulose from the fiber surfaces before dyeing [39-41], especially excellent at removing hemicellulose due to its high hydrophilicity [42]. Besides that, the mercerization enriches the fiber's luster as well. Furthermore, the tension applied during the mercerization causes the structure to be re-oriented and enhances the fibers' mechanical properties [43]. Additionally, some studies have proved that mercerized fibers improve the interfacial adhesive with polymer matrix in composite materials, providing increased strength dramatically [42,44].

Moreover, the modification of natural fiber with cationic polyelectrolytes is one of the most efficient methods for enhancing dye uptake, such as using 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC) [45-47], poly acrylamide-co-diallyldimethylammonium chloride (PAcD) [45], poly[bis(2-chloroethyl) ether-alt-1,3-bis[3-(dimethylamino)propyl]urea]quaternized (P42) [46], and poly-DADMAC [45,48] which is expected to improve the fiber dyeing efficiency with indigo and lac in this research. The latter one, PolyDADMAC, proven to be effective as an additive in dyeing processes with synthetic dyes [49], is a water-soluble cationic polyelectrolyte chosen for cationization treatment to enhance the dyeing efficiency of natural dyes due to its large electrostatic attractive force [50].

In this research, studies on hemp fibers were conducted in the form of single yarns, and then the dyeing efficiency was investigated with two natural dyes, indigo and lac. The effects of yarn treatments, mercerization, and cationization were studied. The tensile strength of treated hemp yarns was measured to determine their mechanical properties. The surface morphology of obtained hemp fibers was examined using scanning electron microscopy. For analyzing their surface chemical structures, fourier transform infrared spectroscopy was employed. Dye absorption efficiency was evaluated using a spectrophotometer, and then the results were identified as color strength (K/S) and CIE L*a*b*. To compare the color strength of dyed hemp fibers before and after washing with standard detergent, K/S was also used to indicate fastness properties.

2. Experimental

2.1 Materials

Hemp yarns, with an average liner density of 158.8 tex, were kindly supplied by Hemp Saithong's community enterprises, Chiang Mai, Thailand. Sodium hydroxide (NaOH), used for preparing an alkali solution in the mercerization treatment, was purchased from RCI Labscan, Thailand. Sodium ethylhexyl sulfate as a wetting agent was purchased from StarTech Chemical, Thailand. Poly-diallyldimethylammonium chloride (polyDADMAC), used as a cationic agent, was purchased from Sigma-Aldrich, USA. Thiourea dioxide (TDO), used as a reducing agent for the indigo dying process, was purchased from Sigma-Aldrich, USA. Hydrogen peroxide (H_2O_2), used as an oxidizing agent, and acetic acid, used as a neutralizing agent, were purchased from RCI Labscan, Thailand. SDC standard soap (SDCE Type 1), used as the non-fluorescent brightening detergent for fastness testing, was purchased from SDC Enterprises Limited, UK. Natural dyes, indigo was kindly supplied by Surin's community enterprise, Thailand, and lac powder was purchased from Chao-Krom-Poe Dispensary Pharmacy, Thailand.

2.2 Mercerization and cationization post-treatment

Raw hemp yarns (HR) were dried at 80°C for 24 h, then held on a spring bar. Consequently, the yarns would be stretched during mercerization. The yarns were soaked in 300 $g{\cdot}L^{-1}$ of NaOH solution and 5 $g{\cdot}L^{-1}$ of 50% sodium ethylhexyl sulfate at 30°C for 10 min before being neutralized by 10 $g{\cdot}L^{-1}$ of acetic acid and rinsed with deionized (DI) water. The mercerized hemp yarns (HM) were done.

In the instance of the cationized-mercerized hemp yarns (HMC), the HM yarns were soaked in 10 $g{\cdot}L^{-1}$ of 20% polyDADMAC solution at 50°C for 15 min, then dried without rinsing.

2.3 Dyeing

Indigo dyeing was performed in a solution containing 200 g of indigo, 60 $g{\cdot}L^{-1}$ of TDO, and 2 $g{\cdot}L^{-1}$ of NaOH. In this process, indigo blue was reduced to leuco-indigo, where the mixture's color changed from blue to greenish yellow. Subsequently, the yarns were soaked in the solution at 30°C for 30 min. The mass ratio of hemp yarns to the solution is 1:30. Whereupon, the yarns were strained out of the solution and then added to 50 $g{\cdot}L^{-1}$ of 50% H_2O_2. During this process, leuco-indigo was oxidized, which reverted to its original indigo form, causing the mixture to change from greenish yellow to blue. After that, dyed yarns were rinsed with ID water and then dried.

For lac dyeing, 200 g of lac powder was boiled in 1 L of ID water for 30 min. The mixture was filtered by the vacuum filter, and then the yarns were added to the solution before being heated to 90°C for 30 min. The mass ratio of hemp yarns to the solution is 1:30. The dyed yarns were rinsed with ID water and then dried. The recipes and processing conditions of all samples are displayed in Table 1.

2.4 Characterization

The functional groups of hemp fibers were evaluated by the fourier transform infrared (FT-IR) spectroscopy using Invenio S (Bruker, USA) in the attenuated total reflectance (ATR) mode, in the range 4000 cm^{-1} to 450 cm^{-1} with a resolution of 4 cm^{-1} and 64 scans at room temperature.

The surface morphology of both treated and untreated hemp fibers was investigated by the scanning electron microscopy (SEM) using the JSM-5410LV (JEOL, Japan) at 15 kV at room temperature. The samples were dried at 80°C for 2 h, and then coated with gold before the operation.

The mechanical properties of the hemp yarns were determined by tensile properties based on ASTM D3822-07 using the universal testing machine, the Autograph AGS-X (Shimazu, Japan). Ten from each sample were operated at a 500 $mm{\cdot}min^{-1}$ crosshead speed and 500 mm gauge length at room temperature. Testing results were reported as tenacity and elongation at break. The linear density of the hemp yarns was determined using the dried weights of 10 m of yarn samples taken from different bundles [51].

The color strength (K/S) and CIE L*a* b* of dyed yarns was determined using the spectrophotometer, the Color Quest XE (Hunter Lab, USA), with the illuminant D65, 10° observer function. The L* value represents lightness; the a* value refers to the greenness-magentas opponent colors; and the b* is relative to the blueness-yellowness opponents [52]. K/S was calculated by Equation (1), the Kubelka-Munk Equation:

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

where R corresponds to the reflectance of dyed substance, K corresponds to the absorption coefficient, and S corresponds to the scattering coefficient.

The fastness testing was conducted in accordance with ISO 105 C06 A2S (2010) using the launder-o meter (GyroWash, UK). The dyed yarns were carded and sewn onto a 40 mm × 100 mm multifiber adjacent fabric, and then introduced to the stainless-steel container with 10 steel balls with a diameter of 6 mm in a solution containing 5 $g{\cdot}L^{-1}$ ECE detergent. The mass ratio of hemp yarns to the detergent solution was 1:50. The launder ran at 40°C for 30 min, then rinsed with ID water and dried at room temperature. The color strength of washed yarns was measured by the spectrophotometer, and then K/S and CIE L* a* b* were used as an indicator for evaluating the color intensity before and after washing.

3. Results and discussion

3.1 FT-IR analysis

FT-IR spectra of the HR, HM, and HMC fibers are shown in Figure 1. The observed peaks at 2900 cm^{-1} and 2849 cm^{-1} of untreated fibers (HR) correspond to the C-H symmetrical stretching of the alkyl and methylene groups of hemicellulose, which are removed after applying NaOH during the mercerization treatment [53,54]. In addition, the weak signal at 1720 cm^{-1} corresponding to the stretching vibration of the carboxylic ester (C=O) of pectin and hemicellulose [54] displays a notable reduction. Also, a small peak at around 1247 cm^{-1} is assigned to the C-O stretching peak of lignin [40], which shows

Table 1. Sample code of untreated and treated hemp yarns.

Sample code	Mercerization	Cationization	Indigo dyeing	Lac dyeing
HR	-	-	-	-
HI	-	-	✓	-
HL	-	-	-	✓
HM	✓	-	-	-
HMI	✓	-	✓	-
HML	✓	-	-	✓
HMC	✓	✓	-	-
HMCI	✓	✓	✓	-
HMCL	✓	✓	-	✓

H = hemp; R = raw; I = indigo, L = lac; M = mercerized; C = cationized.

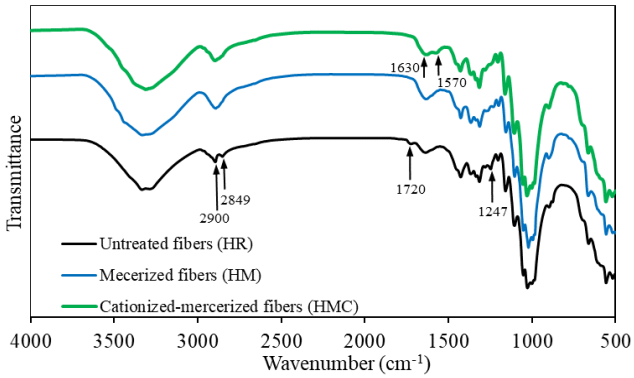


Figure 1. FT-IR spectra of untreated and tread hemp fibers.

a significant decrease after mercerization. The intensity of the peak of the hydroxyl group stretching vibration between 3000 cm^{-1} to 3500 cm^{-1} of mercerized fibers (HM) is slightly greater than that of untreated fibers. This phenomenon implied that the mercerization treatment had increased the amount of cellulosic proportion in the fibers' structures [39]. The presence of 1570 cm^{-1} of cationized-mercerized fiber (HMC) might be attributed to the N-H symmetric deformations resulting from the cationization treatment [45] that implied the association of polyDADMAC with the cellulose unit. Further note that the absorption around 1630 cm^{-1} is typically assigned to the O-H bending of absorbed water [54], which might overlap with the N-H asymmetric deformation band at 1627 cm^{-1} [45], which is also associated with the use of polyDADMAC.

3.2 Surface morphology of fibers

The surface morphology of untreated and treated fibers was revealed by SEM. There were clearly observable surface morphological differences between those fibers. Figure 2(a-c) illustrates that all samples have similar fiber sizes of approximately 25 µm. Figure 2(a) shows that the untreated fibers (HR) contain surface impurities and tend to bind together. In contrast, the mercerized fibers (HM) (Figure 2(b)) and cationized-mercerized fibers (HMC) (Figure 2(c)), which were both treated with NaOH solutions, are relatively neat and clearly separated. These indicate the efficacy of alkali treatment using NaOH solution in reducing non-cellulose entities that affect the fiber's surface appearance. Figure 1(d) shows that HR fibers have irregular surfaces due to the boundary layer of substances such as wax and oils. Figure 1(e) shows that HM fibers exhibit smoother surfaces, confirming that using NaOH effectively removed the impurities, including the non-cellulose component, from the surfaces. The HMC fibers (Figure 2(f)) exhibit similar morphological characteristics to HM fibers, suggesting that cationization treatment did not significantly affect the surface morphology

3.3 Mechanical properties

The mechanical properties testing of the hemp fibers was conducted in the form of single yarns. Table 2 shows that mercerized yarns (HM) have a noticeable increase in tenacity compared to untreated yarns (HR), from 13.5 $cN{\cdot}tex^{-1}$ to 18.1 $cN{\cdot}tex^{-1}$. This was possibly due to the decrease of non-cellulose components (e.g., pectin, lignin, wax, and hemicellulose), as confirmed by FT-IR spectra. Lyu *et al.* [53] have proved that good mechanical properties are related to the removal of those non-cellulose components, resulting in increased hydrogen bonding between cellulose chains, which would be expected to improve the tensile properties. At the same time, the HM yarns were stretched during the mercerization process, causing the fiber's micro- and macro-structures to orientate with the applied tension, which additionally contributed to the yarns being stronger [55,56]. However, both mercerized yarns and cationized-mercerized yarns were more brittle, as indicated by the decrease in elongation.

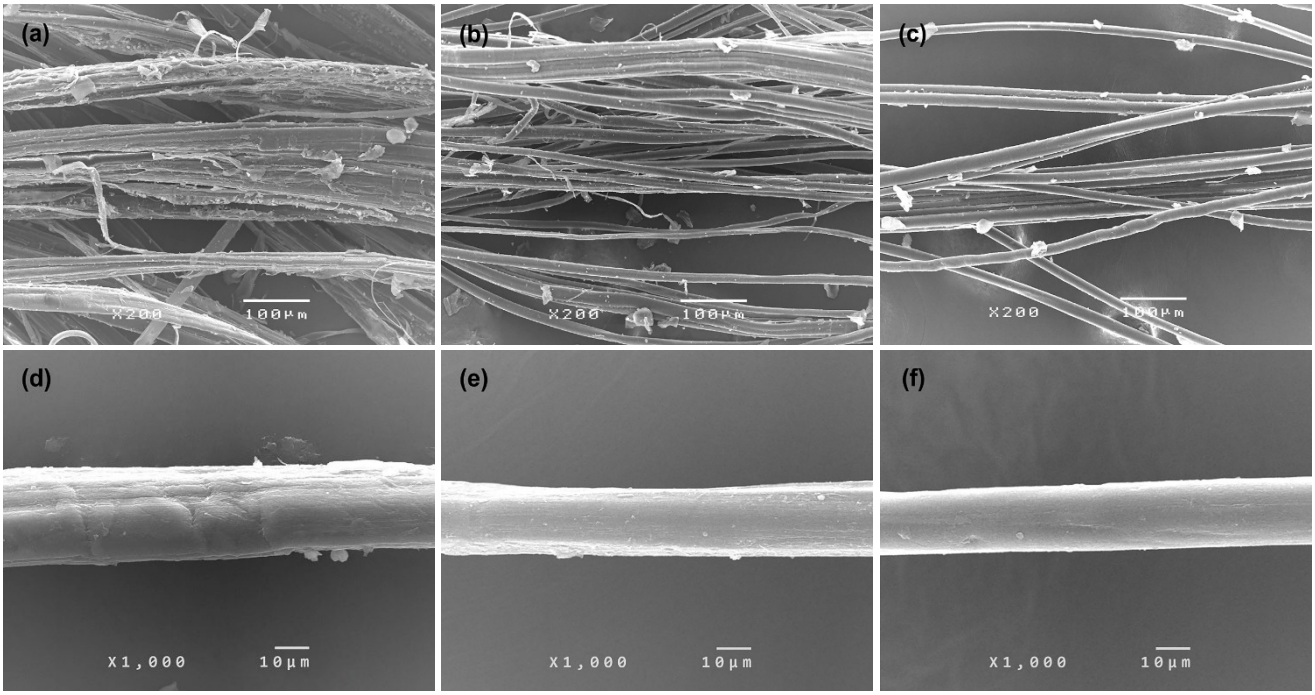


Figure 2. The surface morphology of untreated fibers (HR) (2a,2d)), mercerized fibers (HM) (2b,2e)), and cationized-mercerized fibers (HMC) (2c,2f)).

Table 2. The mechanical properties of hemp yarns.

Sample code	Linear density (tex)	Tenacity (cN·tex^{-1})	Elongation (%)
HR	158.8 ± 12.0	13.5 ± 1.4	8.3 ± 0.5
HI	157.7 ± 9.9	13.1 ± 1.8	9.1 ± 1.1
HL	158.1 ± 11.1	12.7 ± 1.7	8.8 ± 1.3
HM	134.5 ± 8.6	18.1 ± 2.6	5.2 ± 0.7
HMI	133.3 ± 9.2	17.7 ± 1.8	4.8 ± 0.9
HML	134.8 ± 9.3	18.2 ± 2.2	5.7 ± 0.6
HMC	132.9 ± 10.7	17.2 ± 2.1	5.9 ± 1.2
HMCI	132.3 ± 9.4	16.7 ± 1.9	5.3 ± 0.5
HMCL	132.0 ± 8.8	17.4 ± 1.3	4.5 ± 0.8

H = hemp; R = raw; I = indigo, L = lac; M = mercerized; C = cationized.

Table 3. Color strength of indigo-dyed and lac-dyed yarns.

Dye	Sample	K/S	L*	a*	b*
Undyed	HR	-	61.5	3.1	14.3
	HM	-	59.8	4.0	14.9
	HMC	-	60.3	3.3	14.1
Indigo-dyed	HI	13.3	28.6	-2.7	-13.7
	HMI	21.8	24.2	-1.6	-16.3
	HMCI	23.8	19.6	1.0	-18.4
	HI*	10.8	33.1	-3.4	-12.7
	HMI*	19.7	26.4	-1.9	-15.6
	HMCI*	21.7	23.8	-0.9	-15.7
Lac-dyed	HL	10.8	29.2	15.4	0.5
	HML	14.9	24.9	16.0	2.0
	HMCL	21.1	20.3	19.9	2.7
	HL*	2.0	51.9	13.8	3.9
	HML*	4.2	34.5	14.2	2.6
	HMCL*	8.9	25.9	13.4	-1.3

H = hemp; R = raw; I = indigo, L = lac; M = mercerized; C = cationized
*washed yarns

Slight decreases in mechanical properties were observed after cationization treatment of HMC yarns, which is 17.2 cN·tex^{-1}. It might be caused by the cationic association, as displayed in FT-IR spectra, that interferes with the H-bonds between cellulose molecules. These phenomena were similar to the dyeing process. The dyed yarns, i.e., HMI, HML, HMCI, and HMCL, show a slight decrease in strength. It might be attributed to the added dyes, which were foreign substances that could affect the fiber's structures. However, it was found that the tenacity of yarns was unaffected by the type of natural dye used, both indigo and lac.

3.4 Color strength

Hemp yarns dyed with indigo and lac were measured for reflectance before being calculated to K/S, as displayed in Table 3. The appearances of the yarns are shown in Figure 3. The measurements of color strength revealed that the undyed yarns (HR, HM, HMC) showed an insignificant difference in the L* a* b* values. For dyed yarns, it was obvious that the mercerization directly affected the K/S as it removed non-cellulose, especially lignin and pectin, which had a very high content in hemp fibers compared to other natural fibers. Thus, the increasing cellulose proportion gave the fiber a better ability for dye absorption.

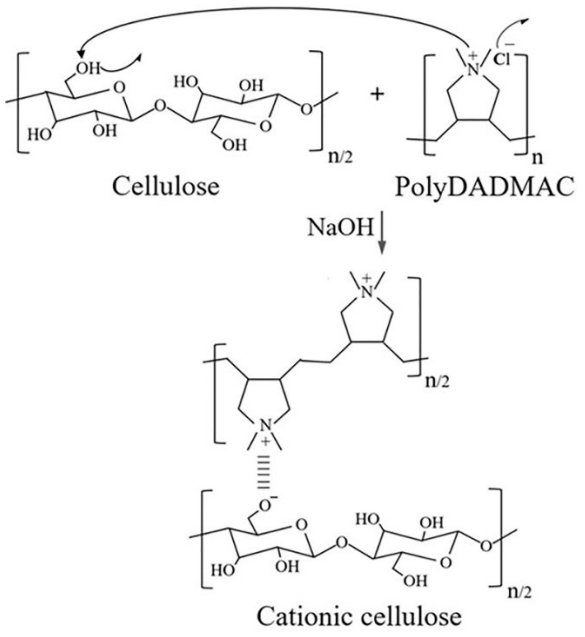
Figure 3. The undyed, indigo-dyed, and lac-dyed hemp yarns.

Table 3 also demonstrates that the indigo-dyed mercerized yarns (HMI) give K/S of 21.8, which is 63.9% higher than untreated yarns (HI), consistent with the decrease of the b* value referred to the higher degree of blue, as shown in Figure 3. Similarly, the mercerization

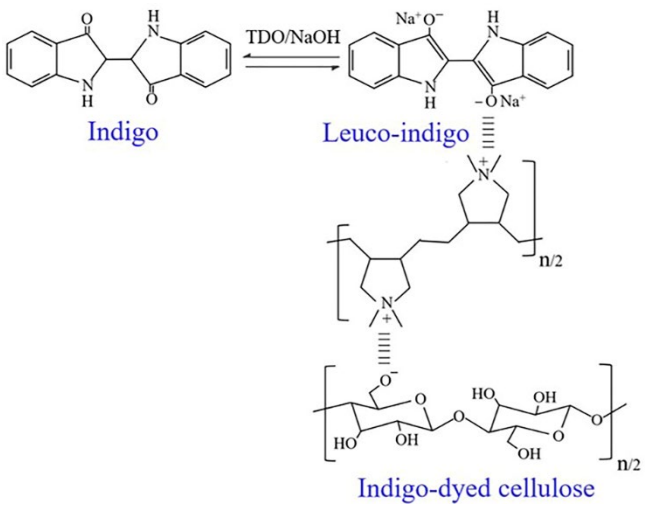
raises the K/S of lac-dye yarns (HML) by 37.9% compared to untreated yarns (HL), and the increase of the a* value referred to a higher degree of red. It could be concluded that the mercerization greatly affected the dyeing efficiency, especially indigo dyeing, due to the decrease of non-cellulose, as evident in the FT-IR spectra, which might result in the hydroxy group on cellulose structure interacting well with indigo.

The cationized-mercerized yarns exhibit high dyeing efficiency. According to Correia *et al*. [45] and Aguado *et al*. [48] studies, once the hemp fibers undergo the cationization treatment, there will be ionic bonding between the primary hydroxy group on cellulose and polyelectrolyte, as shown in Scheme 1. Furthermore, Young *et al*. [57] reported that by using TDO as a reducing agent, indigo would be transformed into leuco-indigo form, as shown in Scheme 2. Consistent with our results, indigo dyeing with cationized-mercerized yarns (HMCI) gives the K/S of 23.8, an increase of 9.2% compared to mercerized yarns (HMI).

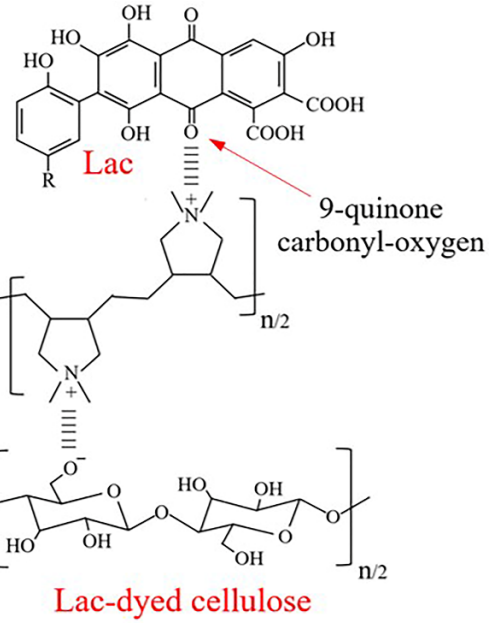
When lac dying with cationized-mercerized yarns (HMCL), K/S is 21.1, which is 41.6% higher than for mercerized yarns (HML) and 95.4% higher than those yarns without treatments (HL). From such results, cellulose might have got positive charges from the cationic agent polyDADMAC, as shown in Scheme 1. These charges might affect the interaction between lac and cellulose, as shown in Scheme 3. As confirmed by Chairat *et al*. [35], their study reported that the 9-quinone carbonyl-oxygen group in the lac molecule structure exhibits a significantly high negative potential compared to other loci. There could be electrostatic ion-dipole forces with a positive charge on the cationic cellulose. Further, there might even be H-bonds with the primary cellulosic hydroxyl groups on the cellulose molecule, as shown in Scheme 4 proposed by Dulo *et al*. [31].



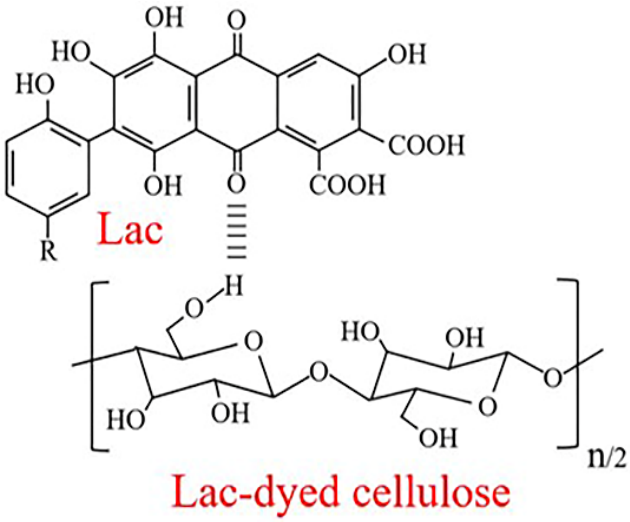
Scheme 1. The cationization of cellulose with polyDADMAC, proposed by Correia *et al.* [45].



Scheme 2. The possible interaction between cationic cellulose and leuco-indigo.



Scheme 3. The possible interaction between cationic cellulose and lac.



Scheme 4. The interaction between cellulose and lac without cationization, proposed by Dulo *et al*. [31].

Table 4. Color fastness to washing (staining, ISO 105 C06 A2S:2010).

Sample	Color change	Color staining					
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
HI	4-5	3-4	3	3	4-5	4-5	4-5
HMI	4-5	3-4	4	3-4	4-5	4	4-5
HMCI	5	5	5	4-5	5	5	5
HL	1	4-5	4	4	4	4	4
HML	2	4-5	4-5	4-5	4-5	4	4-5
HMCL	4	5	4-5	4-5	4-5	4-5	4-5

H = hemp; R = raw; I = indigo, L = lac; M = mercerized; C = cationized

3.4 Fastness properties

The fastness testing employed the K/S as an indicator for evaluating the color strength before and after washing. In the context of indigo dyeing, Table 3 illustrates that the indigo-dyed-untreated yarns faded considerably after washing (HI*), as indicated by the 18.8% decrease in K/S compared to un-washed yearns (HI). In contrast, mercerization substantially enhanced fastness properties as K/S decreased by only 9.6% (HMI*) compared to un-washed yearns (HMI). It can be seen that the removal of non-cellulose on the fiber surface has a significant effect on indigo absorption. In addition, indigo did not readily wash off, which might be attributed to the dyeing process; the insoluble indigo was reduced to water-soluble leuco-indigo, which was able to be absorbed by the fibers before being oxidized to be insoluble again so that indigo could not be easily washed off compared to other natural dyes. Further, it was found that washed-mercerized yarns (HMI*) had a percentage change of 9.6 compared to un-washed yarns (HMI), while washed-cationized-mercerized yarns (HMCI*) were 8.8 compared to un-washed yarns (HMCI). It can be seen that utilizing cationization made only a 0.8% difference, which implied that this treatment slightly affected the fastness properties of indigo-dyed yarns.

Meanwhile, washing of lac-dyed yarns results in a K/S decrease of up to 81.5% (HL*) compared to un-washed yarns (HL) since lac is a water-soluble dye and is naturally based. Therefore, it is difficult to maintain dyes in fibers, leading to poor fastness properties. Nevertheless, when those fiber surfaces were modified by mercerizing, there was an observed improvement in fastness, resulting in a decrease of 71.8% in the K/S (HML*) compared to un-washed yarns (HMI). By the way, cationization caused a more significant effect on fastness as K/S decreased by 57.8% (HMCL*) compared to un-washed yarns (HMCL). Evidently, cationization had more effect on fastness than mercerization, which might be attributed to the influence of the negative potential at the 9-quinone carbonyl-oxygen, which attracted a positive charge on polyDADMAC.

For evaluating the color fastness to washing, Table 4 shows the color changes and staining of the multifiber adjacent fabric. It was found that indigo-dyed yarns (HI) exhibited color change within the range of 4 to 5, or “good” to “excellent.” The staining observed on nylon and cotton was at a rate of 3, or “fair.” But when the yarns were mercerized (HMI), it would improve its color staining significantly within the range of 3 to 4. Obviously, indigo dying with cationized-mercerized yarns (HMCI) exhibited a higher washing fastness than HMI, with a rate of 5. In the case of lac-dyed yarns (HL), the color change was within the range of 1 to 2, or “very poor” to "poor," while the color staining was in the range of 4 to 5, and there was no difference in staining on each component of the multifiber. Nevertheless, after mercerized-cationization treatment, the lac-dyed yarns (HMCL) exhibited dramatically improved color change at a rate of 4.

4. Conclusions

From this research, it can be concluded that dyeing hemp fibers with natural dyes, indigo, and lac, without treatments, tends to be less intense and have poor fastness, particularly lac-dyed fibers, which exhibited dramatic faded colors after washing that it was challenging to obtain various shades due to its natural base and high water-soluble. According to FT-IR and SEM analysis, it was clearly observable that the mercerization treatment removed the non-cellulose, including hemicellulose, pectin, and lignin. These made the hemp surfaces suitable for dye absorption and improved the fastness properties, particularly indigo, where color strength was obviously increased along with the washing durability. In addition, mercerization could also increase the fibers' strength by applying tension, which contributed to orienting the micro- and macro-structures. Furthermore, cationization using the polyelectrolyte poly-DADMAC, would also enhance dye take up as it would improve the interaction between hemp fibers and dyes, which was evident in lac dyeing and fastness but slightly insignificantly affected strength. However, improving the efficiency of hemp fiber dyeing with other natural dyes with various polyelectrolytes should be further investigated.

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References

[1] A. K. Jakubowska, E. Bogacz, and M. Zimniewska, “Review of natural fibers: part 1-vegetable fibers,” *Journal of Natural Fibers*, vol. 9, pp. 150-167, 2012.

[2] H. R. Kymalainen, and A. M. Sjoberg, “Flax and hemp fibres as raw materials for thermal insulations,” *Building and Environment*, vol. 43, pp. 1261-1269, 2008.

[3] F. Ahmed, and I. H. Mondal, “Introduction to natural fibres and textiles,” In *Fundamentals of Natural Fibres and Textiles*, I. H. Mondal Ed.: Woodhead Publishing, 2021, pp. 1-30.

[4] J. Ampruk, *Forensic analyses natural and synthetic fibers using FT-IR spectroscopy*. Nakhon Pathom: Silpakorn University, 2012.

[5] R. Zah, R. Hischier, A. L. Leao, and I. Braun, "Curaua´ fibers in the automobile industry-a sustainability assessment," *Journal of Cleaner Production*, vol. 15, pp. 1032-1040, 2007.

[6] C. Lopez, B. Novales, H. Rabesona, M. Weber, T. Chardot, and M. Anton, "Deciphering the properties of hemp seed oil bodies for food applications: lipid composition, microstructure, surface properties and physical stability," *Food Research International Journal*, vol. 150, p. 110759, 2021.

[7] M. Kowalska, M. Ziomek, and A. Zbikowska, "Stability of cosmetic emulsion containing different amount of hemp oil," *International Journal of Cosmetic Science,* vol. 37, pp. 408-416, 2013.

[8] R. Paul, R. Williams, V. Hodson, and C. Peake, "Detection of cannabinoids in hair after cosmetic application of hemp oil," *Scientific Reports*, vol. 9, p. 2582, 2019.

[9] T. Morenoa, F. Montanes, S. J. Tallona, T. Fentona, and J. W. King, "Extraction of cannabinoids from hemp (*cannabis sativa l.*) using high pressure solvents: an overview of different processing options," *Journal of Supercritical Fluids*, vol. 161, p. 104850, 2020.

[10] R. L. Hilderbrand, "Hemp & Cannabidiol: what is a medicine?," *Missouri Medicine*, vol. 115, pp. 306-309, 2018.

[11] N. Lu, and S. Oza, "Thermal stability and thermo-mechanical properties of hemp-high density polyethylene composites: effect of two different chemical modifications," *Composites Part B: Engineering*, vol. 44, pp. 484-490, 2013.

[12] L. Y. Mwaikambo, and M. P. Ansell, "Mechanical properties of alkali treated plant fibres and their potential as reinforcement materials. I. hemp fibres," *Journal of Materials Science*, vol. 41, pp. 2483-2496, 2006.

[13] M. J. Al-Kheetan, "Performance improvement of hemp-shiv cementitious composites through hot water and steam treatment," *Construction and Building Materials*, vol. 367, p. 130315, 2023.

[14] G. A. Sivasankar, P. A. Karthick, C. Boopathi, S, Brindha, R. J. T. Nirmalraj, A. Benham, "Evaluation and comparison on mechanical properties of abaca and hemp fiber reinforced hybrid epoxy resin composites," *Materials Today: Proceedings*, article in press, 2023.

[15] A. C. Santos, and P. Archbold, "Suitability of surface-treated flax and hemp fibers for concrete reinforcement," *Fibers*, vol. 10, p. 101, 2020.

[16] K. Vandepitte, S. Vasile, S. Vermeire, M. Vanderhoeven, W. V. Borght, J. Latr´e, A. D. Raeve, and V. Troch, "Hemp (*cannabis sativa l.*) for high-value textile applications: the effective long fiber yield and quality of different hemp varieties, processed using industrial flax equipment," *Industrial Crops and Products*, vol. 158, p. 112969, 2020.

[17] G. Gedik, and O. Avinc, "Hemp usage in textile industry," In *Revolutionizing the Potential of Hemp and Its Products in Changing the Global Economy*, T. Belwal and N. C. Belwal Eds.: Springer, 2022, pp. 69-55.

[18] K. Palanikumar, E. Natarajan, K. Markandan, C. K. Ang, and G.Franz, "Targeted pre-treatment of hemp fibers and the effect on mechanical properties of polymer composites," *Fibers*, vol. 11, p. 43, 2023.

[19] M. Zimniewska, "Hemp fibre properties and processing target textile: a review," *Materials*, vol. 15, p. 1901, 2022.

[20] S. Balakrishnan, D. Wickramasinghe, and S. Wijayapala, "Study on dyeing behavior of banana fiber with reactive dyes," *Journal of Engineered Fibers and Fabrics*, vol. 14, pp. 1-12, 2019.

[21] X. Yan, L. Hong, S. Pei, A. Hamilton, H. Sun, R. Yang, A. Liu, and L. Yang, "A natural yellow colorant from *buddleja officinalis* for dyeing hemp fabric," *Industrial Crops and Products*, vol. 171, p.113968, 2021.

[22] D. Grifoni, L. Bacci, G. Zipoli, G. Carreras, S. Baronti, and F. Sabatini, "Laboratory and outdoor assessment of uv protection offered by flax and hemp fabrics dyed with natural dyes," *Photochemistry and Photobiology*, vol. 85, pp. 313-320, 2009.

[23] M. A. Ahmed, and A. A. Mohamed, "A systematic review of layered double hydroxide-based materials for environmental remediation of heavy metals and dye pollutants," *Inorganic Chemistry Communications*, vol. 148, p. 110325, 2023.

[24] T. B. Tafesse, A. K. Yetemegne, and S. Kumar, "Analysis of copper, chromium & lead in hawassa and arba minch textile effluents," *Journal of Chemistry and Chemical Sciences*, vol. 5, pp. 153-168, 2015.

[25] A. P. Manian, S. Mueller, T. Bechtold, and T. Pham, "Quantification of indigo on denim textiles as basis for jeans recycling," *Dyes and Pigments*, vol. 216, p. 111327, 2023.

[26] R. Santos, J. Hallett, M. C. Oliveira, M. M. Sousa, J. Sarraguça, M. S. J. Simmonds, and M. Nesbitt, "HPLC-DAD-MS analysis of colorant and resinous components of lac-dye: a comparison between *kerria* and *paratachardina* genera," *Dyes and Pigments*, vol. 118, pp. 129-136, 2015.

[27] K. G. Gilbert, H. G. Maule, B. Rudolph, M. Lewis, H. Vandenburg, E. Sales, S. Tozzi, and D. T. Cooke, "Quantitative analysis of indigo and indigo precursors in leaves of *isatis spp.* and *polygonum tinctorium*," *Biotechnology Progress*, vol. 20, pp. 1289-1292, 2004.

[28] K. Luepong, P. Punyacharoennon, and W. Yimklib, *Printing on cotton and polyester by lac dye without mordanting for the small enterprise*. Bangkok: Rajamangala University of Technology Phra Nakhon, 2018.

[29] T. Teerakulchaikit, *The study and development of outdoor relax furniture from indigo dyed cotton cloth*. Nakhon Pathom: Silpakorn University, 2014.

[30] A. Adhikari, S. Mukherjee, A. K. Chakraborty, S. Biswas, A. Basu, C. Chakraborty, S. Chattopadhyay, D. Das, and D. Chattopadhyay, "Lac-extract doped polyaniline nano-ribbons as fluorescence sensor and molecular switch for detection of aqueous AsO_4^{3-} and Fe^{3+} contaminants," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 431, p. 114000, 2022.

[31] B. Dulo, K. Phan, J. Githaiga, K. Raes, and S. D. Meester, "Natural quinone dyes: A review on structure, extraction techniques, analysis and application potential," *Waste and Biomass Valorization*, vol. 12, pp. 6339-6374, 2021.

[32] S. Yamada, N. Noda, E. Mikami, J. Hayakawa, and M. Yamada, "Analysis of natural coloring matters in food: III. application of methylation with diazomethane for the detection of lac color," *Journal of the Association of Official Analytical Chemists*, vol. 72, pp. 48-51, 1989.

[33] P. Dagur, and M. Ghosh, "Evaluation of antiproliferative activity of lac dye fractions against mda-mb-231 and siha cell lines," *Anti-Cancer Agents in Medicinal Chemistry*, vol. 22, pp. 2577-2585, 2022.

[34] H. Oka, Y. Ito, S. Yamasa, T. Kagami, J. Hayakawa, K. I. Harada, E. Atsumi, M. Suzuki, M. Suzuki, H. Odani, S. Akahori, K. Maeda, H. Nakazawa, and Y. Ito, "Separation of lac dye components by high-speed countercurrent chromatography," *Journal of Chromatography A*, vol. 813, p. 71, 1998.

[35] M. Chairata, S. Rattanaphania, J. B. Bremnerb, and V. Rattanaphania, "An adsorption and kinetic study of lac dyeing on silk," *Dyes and Pigments*, vol. 64, pp. 231-241, 2005.

[36] A. P. Periyasamy, "Natural dyeing of cellulose fibers using *syzygium cumini* fruit extracts and a bio-mordant: a step toward sustainable dyeing," *Sustainable Materials and Technologies*, vol. 33, p. e00472, 2022.

[37] D. Cronier, B. Monties, and B. Chabbert, "Structure and chemical composition of bast fibers isolated from developing hemp stem," *Journal of Agricultural and Food Chemistry,* vol. 53, pp. 8279-8289, 2005.

[38] H. M. G. Werf, J. E. H. Veen, A. T. M. Bouma, and M. Cate, "Quality of hemp (*cannabis sativa l.*) stems as a raw material for paper," *Industrial Crops and Products*, vol. 2, pp. 219-227, 1994.

[39] K. B. Hamou, H. Kaddami, F. Elisabete, and F. Erchiqui, "Synergistic association of wood/hemp fibers reinforcements on mechanical, physical and thermal properties of polypropylene-based hybrid composites," *Industrial Crops and Products*, vol. 192, p. 116052, 2023.

[40] Z. Maa, G. Panb, H. Xua, Y. Huanga, and Y. Yang, "Cellulosic fibers with high aspect ratio from cornhusks via controlled swelling and alkaline penetration," *Carbohydrate Polymers*, vol. 124, pp. 50-56, 2015.

[41] C. Tezara, J. P. Siregar, H. Y. Lim, F. A. Fauzi, M. H. Yazdi, L. K. Moey, and J. W. Lim, "Factors that affect the mechanical properties of kenaf fiber reinforced polymer: a review," *Journal of Mechanical Engineering Science*, vol. 10, pp. 2159-2175, 2016.

[42] D. Bishnoi, G. P. Singh, and M. S. Shekhawat, "The effect of mercerization on the physical, mechanical, morphological, and chemical properties of aerva tomentosa fiber and fiber-reinforced urea-formaldehyde composites," *Materials Today: Proceedings*, article in press, 2023.

[43] I. Jordanov, B. Mangovska, and P. F. Tavčer, "Mechanical and structural properties of mercerized cotton yarns, bio-scoured with pectinases," *Tekstil,* vol. 59, pp. 439-446, 2010.

[44] N. Lu, R. H. Swan, and I. Ferguson, "Composition, structure, and mechanical properties of hemp fiber reinforced composite with recycled high-density polyethylene matrix," *Journal of Composite Materials,* vol. 46, pp. 1915-1924, 2011.

[45] J. Correia, F. R. Oliveira, R. C. S. C. Valle, and J. A. B. Valle, "Preparation of cationic cotton through reaction with different polyelectrolytes," *Cellulose,* vol. 28, pp. 11679-11700, 2021.

[46] J. Correia, K. Mathur, M. Bourham, F. R. Oliveira, R. D. S. C. Valle, J. A. B. Valle, and A. M. Seyam, "Surface functionalization of greige cotton knitted fabric through plasma and cationization for dyeing with reactive and acid dyes," *Cellulose*, vol. 28, pp. 9971-9990, 2021.

[47] T. Zhang, S. Zhang, W. Qian, J. He, and X. Dong, "Reactive dyeing of cationized cotton fabric: the effect of cationization level," *ACS Sustainable Chemistry & Engineering*, vol. 9, pp. 12355-12364, 2021.

[48] R. Aguado, Q. Tarr´es, P. Mutj´, M. A. P`elach, M. Delgado-Aguilar, "Non-covalently cationized nanocellulose from hemp: kinetics, key properties, and paper strengthening," *Industrial Crops and Products*, vol. 188, p. 115582, 2022.

[49] C. Sampl, J. Schaubeder, U. Hirn, and S. Spirk, "Interplay of electrolyte concentration and molecular weight of polydadmac on cellulose surface adsorption," *International Journal of Biological Macromolecules*, vol. 239, p. 124286, 2023.

[50] I. W. Mwangi, J. C. Ngila, P. Ndungu, and T. Msagati, "Preconcentration and spectrophotometric determination of polydadmac in treated water by in situ co-precipitation with naphthalene," *Physics and Chemistry of the Earth*, vol. 72-75, pp. 54-60, 2014.

[51] H. Ma, Y. Li, Y. Shen, L. Xie, and D. Wang, "Effect of linear density and yarn structure on the mechanical properties of ramie fiber yarn reinforced composites," *Composites Part A: Applied Science and Manufacturing*, vol. 87, pp. 98-108, 2016.

[52] T. B. Elmaaty, E. A. El-Aziz, J. Ma, F. El-Taweel, and S. Okubayashi, "Eco-friendly disperse dyeing and functional finishing of nylon 6 using supercritical carbon dioxide," *Fibers*, vol. 3, pp. 309-322, 2015.

[53] P. Lyu, L. Xia, X. Jiang, X. Liu, W. Xu, C. Hurren, and X. Wang, "Efficient extraction of technical fibers from hemp in an ethanol-water mixture," *Industrial Crops and Products*, vol. 178, p. 114620, 2022.

[54] D. Dai, and M. Fan, "Characteristic and performance of elementary hemp fibre," *Materials Sciences and Applications*, vol. 1, pp. 336-342, 2010.

[55] M. N. Islam, *Apparel Fibers.* Dhaka: Popular Color & Printing, 2006.

[56] G. F. S. Hussain, K. R. K. Iyer, and N. B. Patil, "Influence of mercerization and crosslinking on the dynamic and static moduli of cotton yarns," *Textile Research Journal*, vol. 52, pp. 663-665, 1982.

[57] Y. A. Sona, J. P. Honga, and T. K. Kim, "An approach to the dyeing of polyester fiber using indigo and its extended wash fastness properties," *Dyes and Pigments*, vol. 61, pp. 263-272, 2004.