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Bifunctional cationic modification of modal fabric for sustainable in textile dyeing with spent coffee grounds

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Abstract

In order to dye cellulose or regenerated cellulose with natural dyes, toxic metal mordants are generally employed. In response to this issue, the novel bifunctional cationic agent was pretreated to modify modal (regenerated cellulose) fabric prior to dyeing to enhance the fiber-dye affinity. The cationization reaction was carried out using a compound containing bicationic sites, *N,N'*-(oxybis (ethane-2,1-diyl))bis(3-chloro-2-hydroxy-*N,N*-dimethylpropan-1-aminium. This unique cationic agent is capable of producing nonvolatile amine and has no odor problem. The successful cationic modification was confirmed through FTIR spectroscopy and zeta potential measurement. The cationized process was optimized at a cationic and sodium hydroxide concentration of 90 and 20 $g\cdot L^{-1}$, respectively, with a duration of 5 h. The modified modal fabric significantly enhanced its dyeability with the extract from spent coffee grounds, resulting in deep brown colors. The cationized sample's color strength was noticeably improved. Cationized samples demonstrated better color fastness to washing than untreated samples. Crock fastness was comparable, except the light fastness at high dye concentrations was slightly lower. By utilizing cationization, it offers a promising and sustainable approach enhancing the dyeing with natural dye for green textile coloration.

1. Introduction

With the rapid growth of the world population, numerous efforts of textile technology were therefore extensively growth in order to meet the demands for various human lifestyles. Research on textiles has been conducted in various areas, including agriculture, construction, clothing and medical textiles. The apparel and footwear industry is vast and dominates the majority of the textile market. It comprises a wide range of product categories, ranging from basic to high-end products. Sustainable processing is a key concern for the textile industry due to its major contribution in pollution, particularly in the dyeing process [1]. The complex effluents comprise various chemicals and dyes that are carcinogenic, mutagenic, and non-biodegradable. In order to encourage environmentally friendly textile dyeing, natural dye was therefore considered the most interesting. Natural colors are derived from a variety of plant, animal, and microbial sources. [2]. Dyeing with natural dyes has several benefits, including non-hazardous reagent release and an environmentally favorable process. This practice is usually associated with the "green concept", which involves the use of ecologically friendly chemicals and processes with minimal environmental impact.

The popularity of natural dyes has been significantly enhanced by their environmental advantages. Nevertheless, the application of toxic heavy metal ions in the various stages of mordanting, including pre-mordanting, meta-mordanting, and post-mordanting, imposes limitations on their application. As a result, contaminants are released into the soil, water, and environment. The primary function of heavy metal ions is to enhance the bond formation between fibers and dye molecules, as well as to improve colorfastness properties. Examples of the prohibited metals include chromium (Cr), copper (Cu), and cobalt (Co). Therefore, several techniques have been academically investigated to avoid the use of toxic heavy metal ions. Several approaches have been developed such as the use of bio-mordants and chemical modification. Chemical modification of the textile substrate with cationic chemicals is considered an attractive technique for natural dyeing due to its high ability to increase dye uptake with acceptable fastness properties [3].

3-Choloro-2-hydroxypropyltrimethylammoniumchloride (CHPTAC) is extensively used as a cationic agent. It eliminates the use of salt in reactive dyeing of cellulosic fiber [4-8]. Nakpathom and coworkers [3] reported the effective dyeing of cationized cellulose with good fastness properties using a natural dye from purple corncob. The main problem with CHPTAC is that it creates volatile, dangerous amines, specifically trimethylamine (TMA), upon the addition of alkali [6]. Its distinctive and unpleasant odor, similar to that of dead fish, readily identifies it.

An alternative bireactive cationic agent was introduced, namely *N,N'*-(oxybis(ethane-2,1-diyl))bis(3-chloro-2-hydroxy-*N,N*-dimethypropan-1-aminium), as depicted in Figure 1. This new chemical was developed by Dow Chemical under the tradename of ECOFAST^{TM} Pure. This chemical offers the benefits of possessing bifunctional reactivity, and non-volatility [9]. The presence of two potential epoxide groups enhances the probability of a reaction with the fiber as well as increasing the number of cationic sites.

Cotton is one of the world's most versatile fibers. Nevertheless, the cultivation has adverse effects for both human health and the environment, including excessive use of fertilizers and the application of numerous persistent pesticides, herbicides, fungicides, and crop-protecting agents. Furthermore, nowadays, customers are becoming more concerned about the harmful substances in textile products. Therefore, the use of eco-friendly textile fibers has gained more attention. Modal is a second generation of regenerated cellulose fiber and a registered trademark of Lensing AG. It is a high-wet-modulus regenerated cellulose fiber whose fibers are derived from renewable forests and manufactured according to viscous-spinning technology. The characteristics of modal fibers are high strength, dimensional stability, and great softness. It is used primarily in high-quality apparel, lingerie, and home textiles.

The use of byproducts from the food and agricultural sectors for ecological textile dyeing is attracting considerable interest owing to their resources, sustainable characteristics, and non-toxic properties. Spent coffee grounds, also known as SCGs, are the major source of agro-industrial wastes produced after brewing roasted coffee. The global coffee consumption in 2022 was approximately 10.7 million tons (International Coffee 2023) and it annually continues to increase. This will produce the massive amounts of SCGs. Generally, SCGs is either discarded in landfills or burned [10]. However, the negative effects on the environment come from their excessive oxygen demand during decomposition and the potential to emit methane, the primary greenhouse gas [11].

SCGs contain a diverse chemical composition of organic compounds, and they are a rich source of hemicellulose [10]. It also includes lignin, oil, cellulose, and bioactive molecules including phenolic compounds and coffee melanoidins. [12-16]. Coffee melanoids have attracted interest in the textile coloration of cellulose, wool, and silk [17-20] due to their dark brown color and functional properties (antioxidant, antimicrobial, and anticancer activity). Coffee melanoids comprise about 16% of SCGs [21]. Additionally, the species and method of infusion preparation typically have an impact on the melanoidin content and bioactive chemicals.

Melanoidins (Figure 2) are generally polymeric complex macromolecules that are thermally generated by the non-enzymatic Maillard reactions of carbohydrates with amino acids [22-25]. Melanoidins are complex compounds whose chemical structures are unidentifed, but their dissociation of carboxylic and phenolic functional groups results in negatively charged molecular structures [26,27]. Thus, the anionic charges of melanoidins would exhibit high affinity for cationized substrates. By employing this strategy, it is possible to eliminate the environmental issues brought about by the use of metallic mordants in natural dyeing.

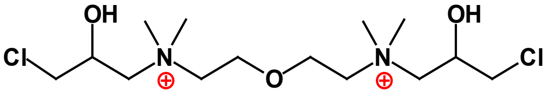

Figure 1. Chemical structure of bireactive cationic agent (ECOFAST^{TM} Pure).

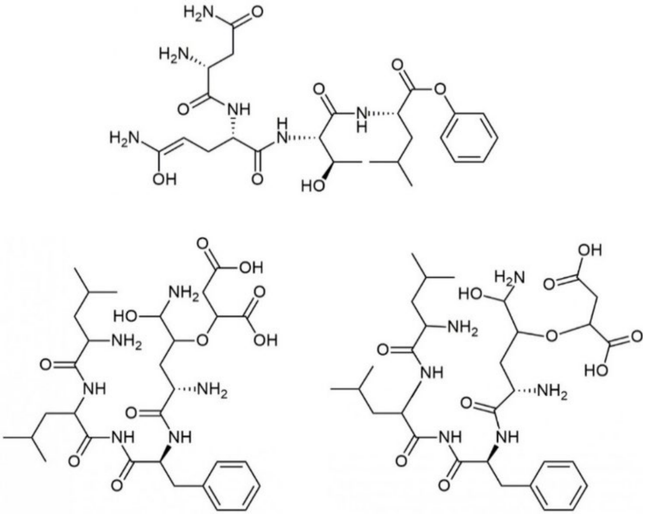

Figure 2. Chemical structure of melanoidins [28].

In this work, the cationization of regenerated cellulose, namely modal, with the bireactive cationic agent to improve the affinity toward the negatively charged SGC extract was investigated using the exhaustion dyeing. The modification was conducted utilizing the uniform application, energy-conserving method known as the cold pad patch (CPB). The cationized samples were analyzed using X-ray diffraction (XRD) analysis, Fourier transform infrared (FTIR) spectroscopy, and zeta potential measurement. The dyed fabrics were assessed the color characteristics, levelness analysis, and color fastness.

2. Experimental methods

2.1 Materials and reagents

Spent coffee sludge was sourced from Starbucks cafe in Bangkok, Thailand. Scoured and bleached modal fabric (plain weave, mass per unit area: 178 g·m^{-2}, warp and weft densities: 96 ends/inch and 97 picks/inch) was purchased from 863 Textile (Bangkok, Thailand). Bireactive cationic agent used was ECOFAST^{TM} Pure solution (*N,N'*-(oxybis(ethane-2,1-diyl))bis(3-chloro-2-hydroxy-*N,N*-dimethylpropan-1-aminium)), supplied from Dow Chemical Thailand Ltd. Sodium hydroxide (NaOH, 50% w/w) was obtained from Merck, Ltd. All other chemical reagents were of reagent grade.

2.2 Methods

2.2.1 Optimization of cationic modification

Modal fabrics were cationized using cold pad batch application at 100% wet pick-up. Alkali and cationic agent were combined just before application to reduce cationic agent hydrolysis. After padding, the treated fabrics were kept at room temperature in a plastic bag to prevent air exposure. After modification, the samples were rinsed multiple times with water to eliminate any residue chemicals, such as alkali and hydrolyzed cationic agents. The samples were then neutralized with diluted acetic acid (1 $g \cdot L^{-1}$) for 30 min in order to achieve the final pH range of 6 to 7 and then dried.

Three parameters were adjusted in order to optimize the cationic pretreatment. These include the following: cationic concentration (10, 20, 40, 50, 80, 100, 120, and 150 $g \cdot L^{-1}$); alkali concentration (5, 10, 15, 20, 30, 40, and 50 $g \cdot L^{-1}$); and reaction time (0.5, 1, 2, 3, 4, 5, and 6 h). After modification with the bireactive agent, the samples were dyed with extract at 50 $g \cdot L^{-1}$ without pH adjustment using an infrared dyeing machine (Starlet 3-DLS800, DaeLim Co., Korea). The dyeing was set at 100°C (1$°C \cdot min^{-1}$) for 1 h with a fabric to extract ratio of 1:20. Excess and surface dyes were then removed from the samples by soaping with detergent (2 $g \cdot L^{-1}$) at 60°C for 20 min. Color strength was then measured; a higher color strength value indirectly indicates a stronger presence of cationic content in the treated fabrics.

2.2.2 Dyeing optimization of cationized samples

After obtaining the optimal cationic modification, further study was investigated to optimize the dyeing conditions of the cationized samples. The following four parameters were studied, including time (10, 20, 40, 60, 80, and 100 min), pH (2, 3, 4, 5, 7, 9, 11, and 12), temperature (40, 50, 60, 70, 80, 90, and 100°C) and dye concentration (5, 25, 50, 75, and 100 $g \cdot L^{-1}$). A ratio of fabric to extract at 1:20 and a heating rate of 1$°C \cdot min^{-1}$ were kept constant for all dyeing experiments. After dyeing, the dyed samples were soaped and washed, as previously described.

2.3 Analyses and testing

2.3.1 Color and levelness analysis

The reflectance spectra of the dyed samples were examined using a spectrophotometer (GretagMacbeth LLC, Switzerland) at three different locations. The CIE (*L*, a*, b**), chroma (*C**), and hue angle (*h*°) were measured using the following instrument configurations (illuminant D65, 10° standard observer). The color strength (*K/S*) was determined via the Kubelka-Munk equation (Equation (1)) by using the wavelength of maximum absorption (λ_{max}).

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \tag{1}$$

where R is the reflectance, K is the absorption coefficient, and S is the scattering coefficient.

The evaluation of dyed fabric uniformity was conducted utilizing the Relative Unlevelness Index (*RUI*), as defined by Equation (4). Reflectance value was measured from 400 nm and 700 nm at with a 10 nm interval. Five random assessments were made for each sample. The *RUI* values were utilized to evaluate the dyeing's uniformity or levelness, as follows: $RUI < 0.20$ indicates excellent uniformity, 0.20 to 0.49 indicates good uniformity, 0.50 to 1.00 indicates poor uniformity, and > 1.00 indicates bad uniformity.

$$RUI = \sum_{\lambda=400}^{700} \frac{S_\lambda}{R_\lambda} V_\lambda \tag{2}$$

Where R_λ is the average reflectance values of each wavelength, S_λ is the standard deviation of reflectance values, and V_λ is the photopic relative luminous efficiency function [29,30].

2.3.2 Color fastness tests

Color fastness to washing was tested following ISO 105-C06 Test No.A1S:2010. The multifiber adjacent fabric was sewn with the test specimen at one of the shorter edges. After that, the test specimen was washed in a gyroWash machine (Model 415/12, James H. Heal, UK) for 30 min at 40°C with standard soap (4 $g \cdot L^{-1}$) and 150 mL of wash liquor. Grayscale was used for assessing changes in color and staining.

Color fastness to rubbing was evaluated following ISO 105-X12: 2016. The test specimen was fastened to the baseboard of the apparatus. For dry rubbing, place a cotton rubbing cloth flat over the finger and rub to and fro 20 times (10 forward, 10 backward) along a track with a 9 N downward force. To perform wet rubbing, the cloth was saturated with distilled water in order to achieve a pick-up rate of 95% to 100%. Next, proceed with the previously mentioned dry rubbing process. Grayscale was used for assessing staining in both cases.

Color fastness to light was performed in accordance with ISO 105-B02:2014. Both the specimen and the blue wool standards (No. 1-8) with the same size were mounted on the paper and exposed to the xenon-arc test chamber. The light fastness was assessed based on the blue wool scale obtained by comparison with blue wool references.

2.3.3 Zeta potential measurement

The surface zeta potential of fabrics was measured with a particle size analyzer (Dynamic Light Scattering Method, Model: ZetaSizer Nano ZS, Malvern Instruments Ltd., UK). The fabric sample was cut into a rectangular piece (7 mm × 4 mm) and then attached to the sample holder using adhesive. The cuvette was filled with deionized water, and the cell containing the sample holder was carefully inserted into the cuvette until the sample holder was fully immersed in the medium. The zeta potential measurements were conducted at 25°C.

2.3.4 FTIR spectroscopy

FTIR spectra in attenuated total reflection (ATR) mode were obtained using a Nicolet iS50 (Thermo Scientific, USA). The samples were then placed directly onto the diamond ATR crystal, ensuring optimum contact with the crystal surface. Transmittance spectra were recorded from 400 cm^{-1} to 4000 cm^{-1} at a resolution of 4 cm^{-1} and a total of three scans. The collected spectra were subsequently processed for noise reduction, baseline correction, and normalization to ensure accurate analysis.

2.3.5 X-ray diffraction (XRD) evaluation

X-ray diffraction was performed using X-ray diffractometer (Bruker AXS Model D8 Advance, Germany; Bragg-Brentano, monochromated

Cu K_α radiation λ= 1.5406 Å). The instrument was operated at an applied voltage of 40 kV and a current of 40 mA. Scans were performed at room temperature, covering a 2θ range from 5° to 60°, with a step size of 0.02° and an acquisition time of 0.2 sec per step.

2.3.6 Scanning electron microscopy (SEM)

A scanning electron microscope (JEOL-JSM5410LV) was used to examine the surface morphology of samples. The samples were mounted on the SEM brass stubs and coated with a thin layer of gold prior to analysis. The examination was carried out using an accelerating voltage of 10 kV, a working distance of 20 mm, and a magnification of 1500×.

3. Results and discussion

3.1 FTIR analysis

The cationization of modal fabric has been confirmed by FTIR-ATR spectroscopy. The FTIR spectra of uncationized and cationized samples are compared in Figure 3. Both samples exhibited the characteristic absorption bands of cellulose. The bands observed at 3600 cm^{-1} to 3000 cm^{-1} are characteristic of hydrogen-bonded OH stretching of cellulose [31]. The peak observed at 2890 cm^{-1} corresponds to C-H stretching. The peak at 1645 cm^{-1} corresponds to the bending of adsorbed H_2O. Additionally, the peaks at 1415, 1365, and 1312 cm^{-1} represent CH wagging (in-plane bending), CH bending (deformation stretching), and OH in-plane bending, respectively. The observed peak at 1056 cm^{-1} indicates the asymmetrical in-plane ring stretching, whereas the peak at 1020 cm^{-1} indicates the stretching of the C-O.

In addition to the characteristic peaks of cellulose functional groups, the cationized sample exhibited a new distinct band in the spectrum at 1510 cm^{-1} in the spectrum. This band was attributed to quaternary ammonium groups ($-N^+-(CH_3)_3$) [32], confirming that cationized modal was successfully produced.

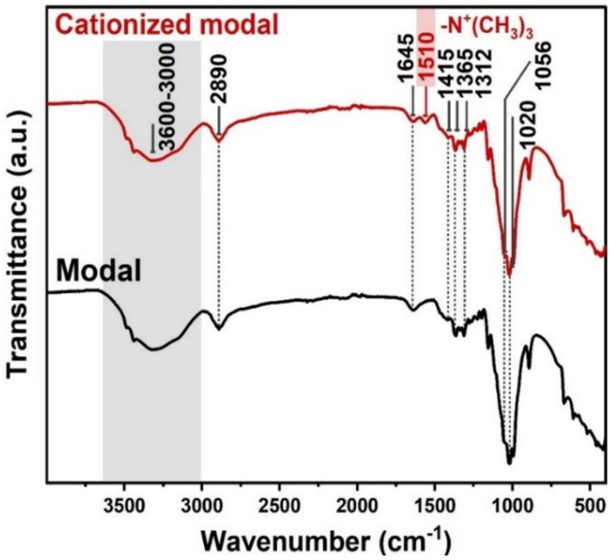

Figure 3. FTIR-ATR spectra of uncationized and cationized modal fabric.

3.2 XRD analysis

The influence of cationization on the crystal structure was investigated using X-ray diffraction. The XRD patterns of the two samples (Figure 4) are similar and exhibit the diffraction pattern of the cellulose II crystalline structure. The 2θ angles of the diffraction peaks are 12.3°, 20.1°,22.0°, and 34.7°, corresponding to the crystal structures (1–10), (110), (020), and (004) planes, respectively. These four characteristic peaks are typical of regenerated cellulose. This suggests that cationization primarily occurred at the fiber's surface and did not alter the crystal structure.

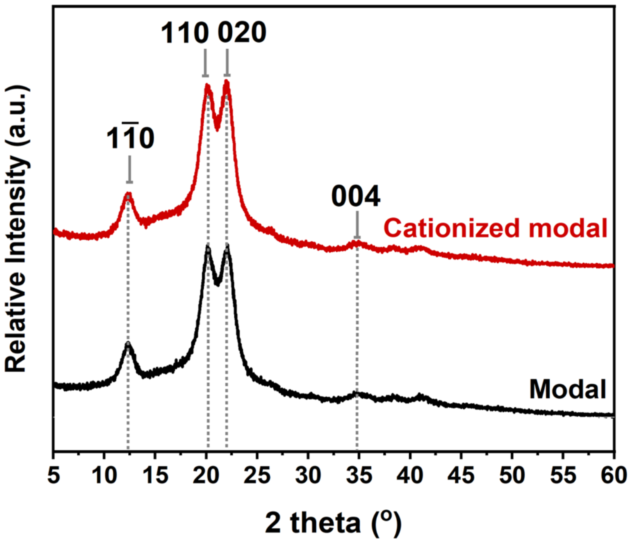

Figure 4. XRD spectra of uncationized and cationized modal.

3.3 Zeta potential measurement

Cationic modification of the fabric can be effectively characterized through the measurement of zeta potential. The surface zeta potential of materials exhibits a direct correlation with the number of cationic charges present. The higher the value, the more cationic charges are present in the material. As shown in Figure 5, untreated modal fabric

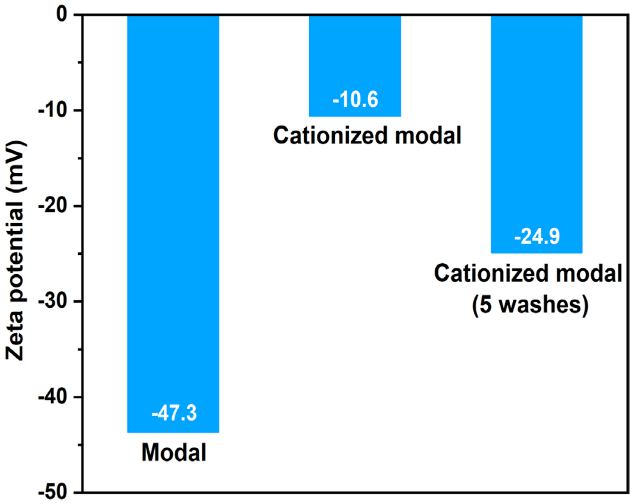

Figure 5. Zeta potential analysis of spectra of uncationized and cationized modal.

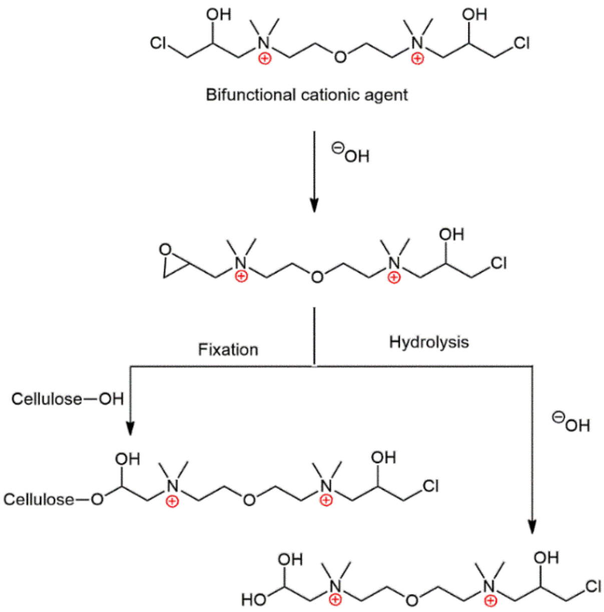

Figure 6. Reaction of cellulose with bifunctional cationic agent.

exhibited a zeta potential of –47.3, whereas cationic modal fiber displayed a zeta potential of –10.6. Therefore, the increase in zeta potential also proved a successful cationization reaction in modal fabric. The cationization mechanism (Figure 6) of this bifunctional cationic agent displays similarities to that of CHPTAC. Initially, it reacts with alkali to produce active epoxide. This epoxide then covalently reacts with cellulose under alkali condition to form cationized cellulose. However, under alkali condition, an undesirable side reaction can occur, leading to the hydrolysis of the cationic agent into an inactive compound. After subjecting to 5 washes of laundry test, the zeta potential of the cationized modal turned to –24.9. This was probably due to the hydrolysis of the cationic moiety under alkali conditions during washing.

3.4 Optimization of the cationization process of modal fabric

Figure 7 demonstrates that cationization parameters, including cationic concentration, reaction time, and alkali concentration, are critical to the final dyeability of dyed fabrics. Figure 7(a) depicts the influence of cationic concentrations ranging from 10 $g \cdot L^{-1}$ to 150 $g \cdot L^{-1}$ on *K/S* under the conditions of 20 $g \cdot L^{-1}$ of NaOH and 6 h of reaction time. The *K/S* increased considerably with increasing cationizing agent concentrations up to 90 $g \cdot L^{-1}$ (*K/S* = 8.55) before decreasing slightly. The treated fabric's color strength was approximately 18 times greater than that of the untreated sample, whose *K/S* was 0.47. This finding indicated that this bifunctional cationic agent significantly increased the number of cationized sites within the regenerated cellulose and electrostatically attracted anionic melanoidin dye molecules, resulting in a significantly increased *K/S* value.

Cationization duration is also a significant factor, as illustrated in Figure 7(b). In this study, cationic and NaOH concentrations were held constant at 100 $g \cdot L^{-1}$ and 20 $g \cdot L^{-1}$, respectively. As the treatment time increased, color strength also increased and reached its maximum at 5 h. A further increase in reaction time showed a minor increase in color strength. A steady color strength after 5 h was due to the complete reaction of cationic agents and fiber.

Figure 7(c) depicts the alkali concentration as the final variable under investigation. This experiment used a cationic concentration of 100 $g \cdot L^{-1}$ and a reaction time of 5 h. It was found that initially, increasing the alkali content from 0 $g \cdot L^{-1}$ to 10 $g \cdot L^{-1}$ did not significantly improve color strength. This is because alkali was first used to convert the cationic agent into its epoxy-active form and to change cellulose into its more powerful nucleophilic cellulosate anion. However, when the alkali concentration exceeded 10 $g \cdot L^{-1}$, the color strength rapidly increased and reached a maximum value of 20 $g \cdot L^{-1}$. This stage involved the reaction between the cationic agent and fiber. This reaction led to the formation of covalent bonds and cationic sites inside the fiber. As a result, enabling the dye molecules to diffuse into the fiber. Under alkaline condition, regenerated cellulose swells more to open up its structure, thereby enhancing its reactivity to cationic agents. However, a decrease in the color strength of cationized fabrics at higher concentrations of alkali was observed. This was due to the hydrolysis of a cationic agent with a hydroxide ion. The hydrolyzed cationic agent is no longer capable of reacting with the fiber. Therefore, a cationic agent concentration of 90 $g \cdot L^{-1}$ and NaOH of 20 $g \cdot L^{-1}$ with a reaction time of 5 h were the most suitable conditions for cationic modification of modal fibers. Figure 8 shows photographic images of untreated and cationized samples under various cationization conditions.

Analysis of variance (ANOVA) was used to evaluate of each variable in the optimization of the cationization conditions of the fabric. The results show that all three factors including cationic concentration, reaction time, and alkali concentration are statistically significant, with the p-value less than 0.05. This indicateds statistical significance at a 95% confident level.

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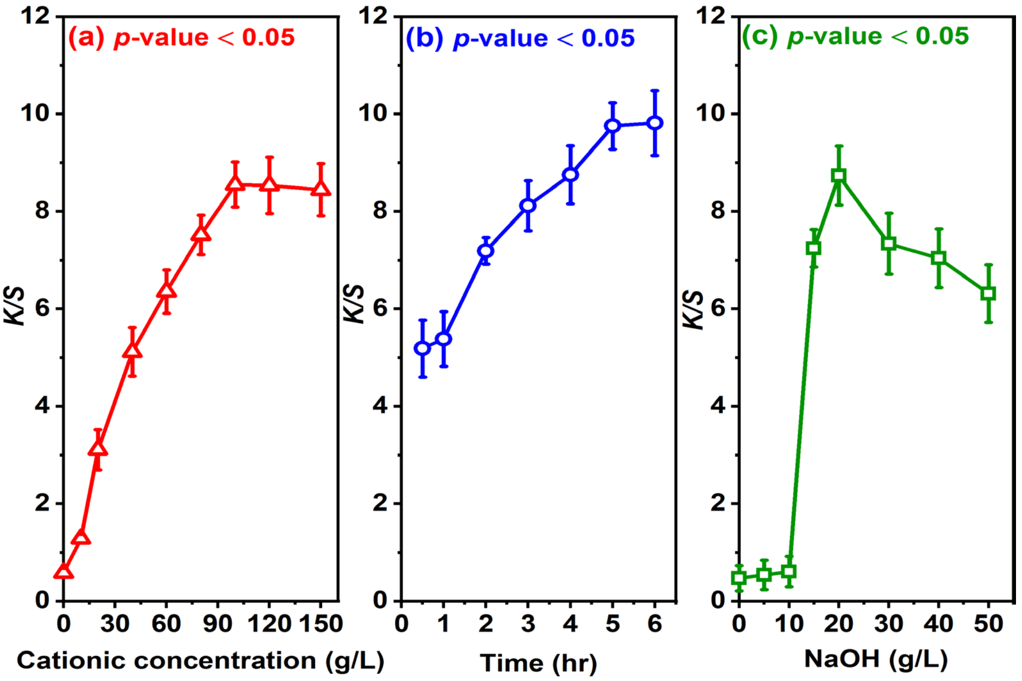

Figure 7. Effect of cationization parameters on *K/S* of dyed samples with coffee grounds (a) cationic concentration (20 g·L^{-1} of NaOH, 6 h, 50 g·L^{-1} of extract), (b) reaction time (20 g·L^{-1} of NaOH, 100 g·L^{-1} of cationic agent, 50 g·L^{-1} of extract), and (c) alkali concentration (100 g·L^{-1} of cationic agent, 5 h, 50 g·L^{-1} of extract).

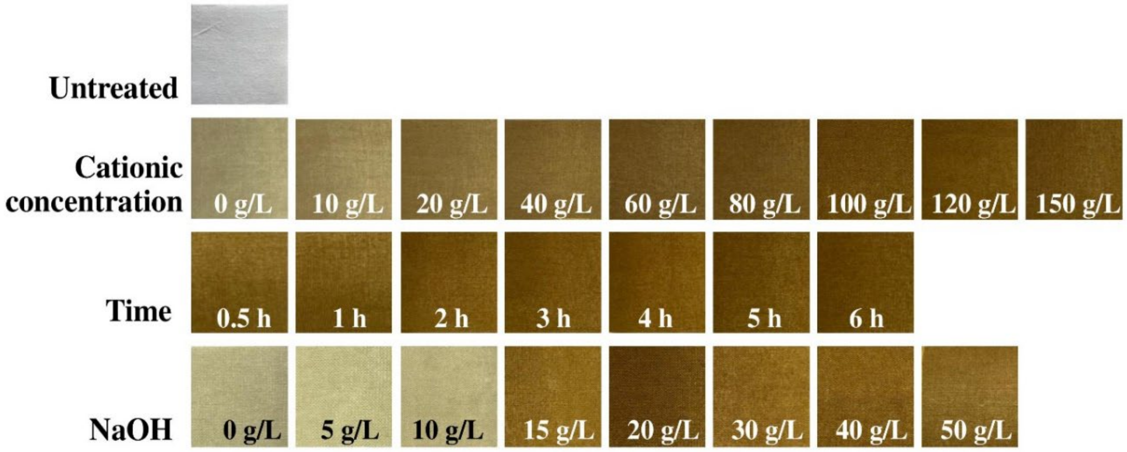

Figure 8. Images of untreated and cationized samples dyed with spent coffee grounds under various cationization conditions.

3.5 Optimization of the dyeing process on cationized modal

After determining the optimal conditions for cationization (20 g·L^{-1} of NaOH and 100 g·L^{-1} of cationic agent for 5 h), we prepared the cationized samples to study the impact of dyeing conditions using exhaustion dyeing. The effect of time, dyebath pH, dyeing temperature, and dye concentration on color intensity of cationized modal fabrics was illustrated in Figure 9. As shown in Figure 9(a), the dyeing conditions are at 100°C, pH = 4.5 (the original pH of the extract), and SCGs = 50 g·L^{-1}. Due to the presence of the cationic moiety, the cationized samples exhibit rapid dyeing within 10 min ($K/S \approx 12$). In order to facilitate the effective diffusion and migration of the dye molecule inside the modal fiber, a duration of 30 min was chosen for the next experiment. In Figure 9(b), the dyeing conditions are at 100°C, 30 min, and SCGs = 50 g·L^{-1}. This demonstrated the strong correlation between pH and color strength. It indicated that the pH significantly impacts the dye uptake of cationized dyed fabric. The color strength rapidly increased from pH 2 to 5 and slightly decreased afterwards. The observed variation in color intensity as a function of pH can be attributed to the interaction between melanoidin natural dyes and the textile substrate. When the pH was below 2.5, coffee melanoidins displayed a slight positive charge, which corresponds to their isoelectric point [33]. As a result, below this pH, melanoidins repelled positive charges from the cationized samples throughout the dyeing. At pH greater than 2.5, melanoidins acquire a greater negative charge, leading to significantly enhanced adsorption onto cationized fabrics. However, the isoelectric point of the cationized sample was approximately 8 [34]. Above this point, the cationized samples also exhibited negatively charged behavior. This will decrease the interaction between dye molecules and the cationized samples, resulting in lower dye uptake.

Figure 9(c) illustrates the relationship between color strength and dyeing temperature, with the dyeing conditions being pH 5, 30 min, and SCGs = 50 g·L^{-1}. The cationized fabrics show an increase in color strength as the temperature rises. Elevated temperatures accelerate the molecular mobility of the dye molecules, thereby enhancing the fabric's dye uptake. Figure 9(d) indicates that cationized samples had excellent build-up properties, as evidenced by the steady increase in color strength as the dye concentration increased. Images of cationized samples under various dyeing conditions are presented in Figure 10. Figure 11 illustrates the proposed electrostatic interaction between cationized regenerated cellulose and SCG dyes. The cationic dye sites on the modal fabric attract the anionic melanoidin colorants of the SGG extract, allowing dyeing without the use of metal mordants, which are typically required to fix natural dyes through coordination bonds.

3.6 Statistical analysis

Analysis of variance (ANOVA) was used to evaluate the significant variables affecting the process. For the optimization of the cationization conditions on the color strength of the modal fabric, the results show that all three factors studied in the work, including cationic concentration, reaction time, and alkali concentration, are statistically significant, with the *p*-value less than 0.05. This demonstrates statistical significance at a 95% confidence level. In studying the effect of the dyeing process on the color intensity of dyed samples, three out of four factors were found to significantly affect color strength, which are dyebath pH, dyeing temperature, and SCG concentration, as their *p*-values were less than 0.05.

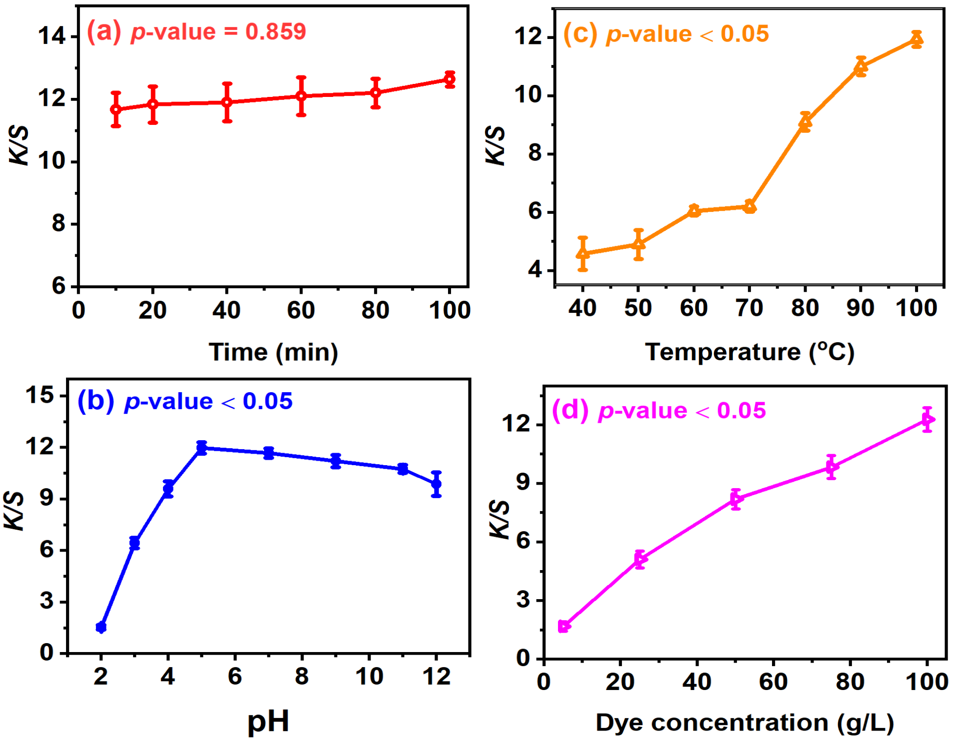

Figure 9. Effect of dyeing process on color intensity of dyed samples with coffee grounds (a) dyeing time (100°C, pH = 4.5 (original pH of SCGs), 50 g·L^{-1} of extract), (b) pH of dyebath (100°C, 30 min, 50 g·L^{-1} of extract), (c) temperature (30 min, pH = 5, 50 g·L^{-1} of extract), and (d) dye concentration (100°C, 30 min, pH = 5).

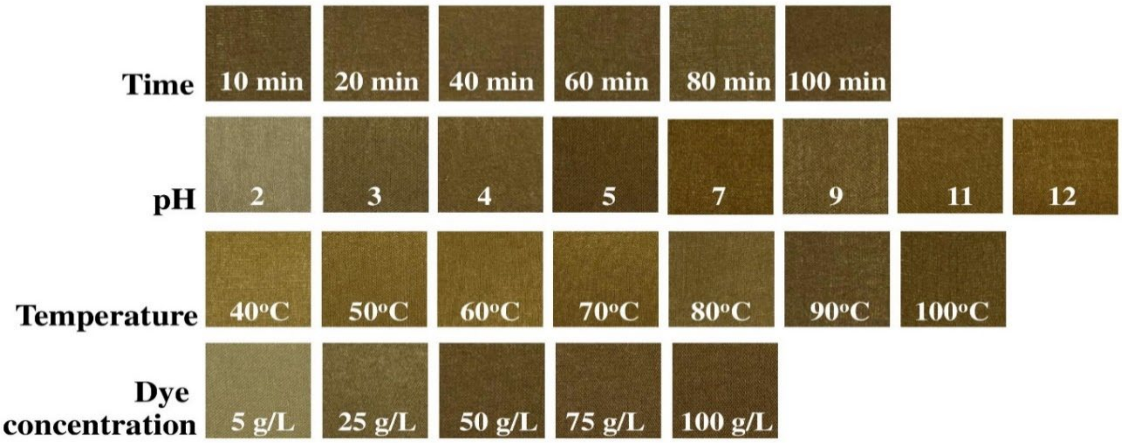

Figure 10. Images of cationized samples under various dyeing conditions.

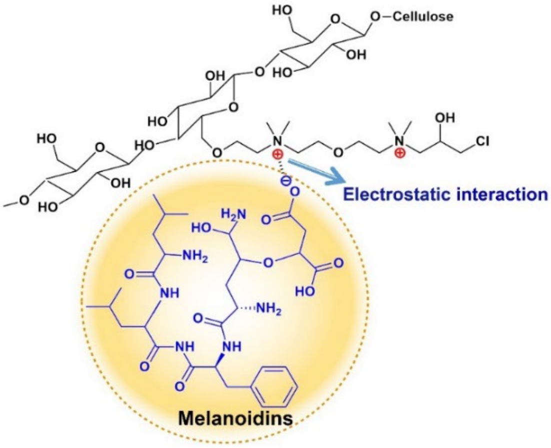

Figure 11. Interaction of cationic modal and melanoidin of extract from spent coffee grounds.

3.7 Colorimetric parameters and *RUI*

The cationized samples were dyed with SCGs extract at different concentrations ranging from 5 g·L^{-1} to 100 g·L^{-1}. The colorimetric values (L^*, a^*, b^*, C^*, h^o), and *RUI*, presented in Table 1. In *CIELAB* color space, the lightness of the sample is represented by L^*, ranging from 0 for black to 100 for white. Colors designated with $a^* > 0$ are considered red, while those with $a^* < 0$ are considered green, those with $b^* > 0$ are considered yellow, and those with $b^* < 0$ are labeled blue. Chroma (C^*) = 0 represents a true achromatic color, while $C^* > 0$ indicates all other colors. The hue angle (h^o) expressed color purity on the scale of 0° to 360°, with 0°/360° = red, 60° = yellow, 120° = green, and 240° = blue.

The L^* result (where a lower L^* indicates a darker hue) suggests that cationized samples can be deep-dyed as the dye concentration increases, as can be seen from a^*, b^*, and h^o values moved in the direction of redness and yellowness. The fabric treated with 100 g·L^{-1} of the extract displayed the highest C^*, indicating the highest color saturation. Compared to the untreated sample, it is clear that the cationized modal had a deeper brown coloration. The application of cationization in dyeing with natural dye has the benefit of maintaining the original color of SCGs while also providing extra dye sites to enhance the color intensity. Considering the degree of levelness, each of the cationized dyed fabrics showed *RUI* less than 0.20, demonstrating excellent uniform dyeing. This high color levelness was also observed even when the dye concentration reached 100 g·L^{-1} of the extract.

3.8 Color fastness properties

The results of color fastness tests obtained with uncationized and cationized dyed samples have been determined for two depths of shade: 25 g·L^{-1} of SCGs represented a pale shade sample, while 100 g·L^{-1} of extract represented a deep shade. Table 2 shows the result of wash fastness. Color staining to multifiber fabric and color change of dyed materials were used to evaluate wash fastness. The cationized samples dyed with SCGs in pale and deep shades exhibited a higher wash fastness rating (Grade 4-5) than those dyed with uncationized samples (Grade 3). Figure 12 displays cross-sectional analysis of cationized samples before and after wash fastness testing. The deep dyeing and uniform distribution of dyes throughout both samples demonstrate the high color fastness of cationized samples. This can be attributed to increased substantivity of the melanoidin pigments in cationized samples via couloumbic interaction, whereas the affinity in uncationized samples was mainly due to Van der Waals forces. In terms of color staining on multifiber, both cationized samples showed a better result than uncationized samples.

Considering the crock fastness of cationized dyed fabrics in Table 3, the rating of dry crock fastness was good to very good (grades 4 and 4-5). This indicates that the dyeing was not on the fiber surface. When performed in wet condition, the crock fastness performance slightly decreased. The high crock fastness observed in cationized samples indicates effective diffusion and penetration of dye molecules throughout the fiber. The uncationized samples also showed good to very good (grades 4 and 4-5) due to their relatively low *K/S*, which resulted in less dye loss during testing.

In terms of light fastness, both samples were at a good level (grade 4), except for the cationized samples dyed with SCG at 100 g·L^{-1}, whose rating was fair to good (grade 3-4). Overall color fastness of the cationized dyed sample was found to be satisfactory, indicating that modifying modal fabric with bicationic agent is an effective technique for natural dyeing without the need for metal mordanting.

Table 1. Color measurement and ***RUI*** of cationic fabrics at different extract concentrations.

SCGs (g·L^{-1})	L*	a*	b*	C*	h°	RUI
5	67.46	4.11	16.66	17.16	76.13	0.14 (excellent levelness)
25	53.44	6.46	20.19	21.20	72.27	0.19 (excellent levelness)
50	47.50	7.95	21.82	23.23	69.98	0.19 (excellent levelness)
75	44.75	8.72	22.25	23.90	68.59	0.05 (excellent levelness)
100	41.87	9.51	22.50	24.43	67.09	0.16 (excellent levelness)

Table 2. Wash fastness of uncationized and cationized fabrics.

Sample	Dye concentration	Wash fastness						
	(g·L^{-1})	Color change	Color stain					
			Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
Uncationized	25	3	3-4	3-4	3-4	3-4	3-4	3-4
	100	3	3-4	3-4	3-4	3-4	3-4	3-4
Cationized	25	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	100	4-5	4-5	4-5	4-5	4-5	4-5	4-5

Table 3. Crock fastness and light fastness of uncationized and cationized fabrics.

Sample	Dye concentration	Crock fastness Crock fastness		Light fastness
	$(g{\cdot}L^{-1})$	Dry	Wet	
Uncationized	25	4-5	4	4
	100	4-5	4	4
Cationized	25	4-5	4	4
	100	4-5	4	3-4

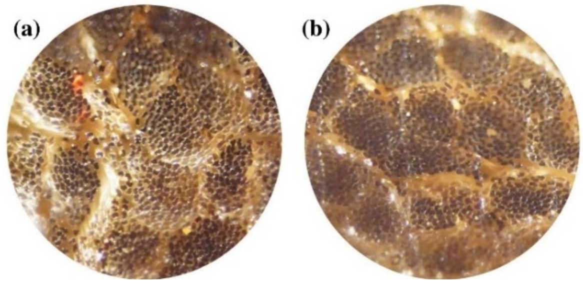

Figure 12. Cross-sectional images of fabric dyed with 100 $g{\cdot}L^{-1}$ spent coffee grounds (a) before, and (b) after the wash fastness test.

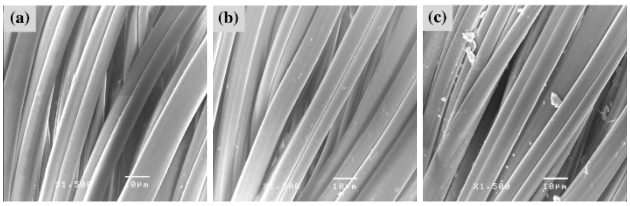

Figure 13. SEM images of modal fabrics (a) uncationized, (b) cationized, and (c) cationized and dyed with 100 $g{\cdot}L^{-1}$ spent coffee grounds.

3.9 SEM

The impact of cationization of modal on surface morphology was characterized by SEM. The untreated modal's surface morphology (Figure 13(a)) was relatively smooth and uniform, with longitudinal grooves, which are typical of regenerated cellulose fibers. The cationized sample (Figure 13(b)) showed no significant change in morphology. This shows that the modification of fabric through cationization has no impact on the fiber's structure. The dyed sample of cationized fabric showed a few agglomerations on the fiber surface (Figure 13(c)). This could be caused by the residue of SCGs particles in the extract, which may deposit on the fiber surface during dyeing.

4. Conclusions

This study employed a bifunctional cationic agent to cationize modal fabric through the cold-pad batch method, utilizing spent coffee grounds as a natural dye. This bifunctional cationic agent offers several advantages, including its non-volatile nature, bifunctional reactivity, and the presence of bicationic sites. This environmentally friendly dyeing process can be effectively used for the dyeing of modal fabric with natural dye without using any toxic metal mordant. FTIR and zeta potential analysis demonstrated the successful cationic modification. The optimization of the cationized process was achieved using a cationic concentration of 90 $g{\cdot}L^{-1}$ and sodium hydroxide concentration of 20 $g{\cdot}L^{-1}$, with a duration of 5 h. To obtain deep dyeing, it was recommended to carry out dyeing at pH 5, 100°C, and 30 min of dyeing time. Compared to the untreated fabric, the cationized samples had a deeper natural brownish color and significantly enhanced color strength, as well as excellent color uniformity. This is due to the strong attraction between negatively charged melanoidin dyes and cationized modal fabrics. Cationized samples exhibited superior characteristics with regard to wash fastness. Color fastness to crocking was comparable, except the light fastness at high dye concentrations was found to be slightly lower due to the higher K/S. Due to the higher cost of this bireactive cationic agent (approximately 20 USD per kg) compared to traditional mordants like $FeSO_4$ or $AlKSO_4$, cationization of cellulose may not be economically advantageous. However, from a sustainability perspective, this approach eliminates the need for harmful metal mordants and maintains the original hue of the melanoidin dye with high color strength. Therefore, the use of cationization in natural dyeing has the potential to produce sustainable textiles.

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