

Performance of Cotton Fabric Treated with Chitosan-Based Mordant as Affected by Extraction Time Variations on Tannin Dyes Produced from Cocoa Husk

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Abstract

Natural dyes are substances obtained from animals or plants through extraction. The application of synthetic dyes can affect environmental problems, therefore replacing them with natural dyes is becoming an alternative. Cocoa pod husk is still considered as a waste, whereas it is one of the sources for natural dyes. Cocoa pod husk contains flavonoids, tannins, and β -carotene compounds which generate color. Natural dye is extracted from the husk of the cocoa pod and applied to cotton cloth, and the objective of this research is to evaluate the extraction time to its coloring quality. Extraction of cocoa husk dyes was carried out with distilled water at 60 °C with variations of 1, 2, and 3 hours. The resulting extract contains positive tannins but negative β -carotene. Variations in the extraction time of natural dyes affect the tannin content extracted. The tannin content extracted with variations of 1, 2, and 3 hours was 18.3, 18.7, and 17.9 ppm, respectively. Chitosan-based mordant has a significant effect on the color yield of the fabric. Fabrics with mordant have a darker color than fabrics that are not applied with mordant process. The use of nanochitosan and citric acid crosslinkers can maintain the aging color of the fabric. The fourier transformed infrared spectroscopy (FTIR) results on the fabric showed that color aging occurred due to the presence of ester groups formed between chitosan and dyes. Chitosan-based mordant coating provides better color than without mordant coating. Fabrics coated with chitosan had the best fastness value of 4 (good).

Keywords: Natural dyes, cocoa husk, nanochitosan, mordant, extraction

INTRODUCTION

Cocoa (*Theobroma cacao* L) is an important plantation crop in Indonesia, with an annual production of 200,000 tons (ICCO, 2022). The higher cocoa pods production, the more waste it will create; cocoa husks make up most of the waste by 70–80%. Currently, the cocoa husk is mainly used for making compost, which is then returned

to the plantation soil to meet soil nutrient needs from the decomposition of organic cocoa husk material (Lu *et al.*, 2018). Cocoa husks have the potential to be used as a natural dye since the husk contains a brownish pigment of tannins by 0.84%. Tannin compounds are not easily damaged by temperature compared to other dyes and are resistant to treatment at temperatures of 80–100 °C (Fransiska *et al.*, 2021). Cocoa husks also contain an orange

pigment from β -carotene (Pujilestari, 2015; Dwipayanti *et al.*, 2020).

The pigment in cocoa husk as a dye can be obtained through extraction where pigment extraction can be done simply by soaking it in certain solvents for 24 hours (Visalakshi & Jawaharlal, 2013). However, modifications to the extraction time can be made to optimize the extraction process so that maximum extraction results are obtained (Chairunnisa *et al.*, 2019). An increased extraction time factor will provide contact time with the solvent, thereby increasing the number of broken cells (Wahyuni & Widjarnako, 2015). Haerudin *et al.* (2020) extracted cocoa husk at varying temperatures of 60, 80, and 100 °C and varying times of 1, 2, and 3 hours, which increased the resulting extract. The optimum extraction time and temperature were obtained at 3 hours and 60 °C, which could increase the color intensity value and color difference. However, a too-high increase in extraction temperature and a too-long extraction time can cause the loss of dye compounds in the solution due to oxidation (Haerudin *et al.* 2020; Wahyuni & Wijanarko, 2015).

Natural dyes have several weaknesses, including dull colors, low colorfastness, and the need for repeated coloring processes due to the unstable bond between the dye and the fabric. This problem can be overcome by using mordant substances such as aluminium (Al^{3+}), ferrous sulfate (FeSO_4), and tin (Sn). Mordant or color binder is used in dyeing or coloring fabric by forming molecular bonds between the dye and the tissue on the fabric. The color bound to the tissue will absorb light of a specific wavelength, making the fabric appear colored (Afiani, 2022). However, the use of mordants with these substances can cause long-term environmental and health problems (Visalakshi & Jawaharlal, 2013). As such, there has been an effort to look for

other mordant substances that are more environmentally friendly, one of which is chitosan (Habeish *et al.*, 2013).

Chitosan is widely used as a mordant in the surface modification process of textile materials using natural and synthetic dyes. The role of chitosan as a mordant can be increased by changing the particle size to become nanoparticles. Nanoparticles have a high surface area, thereby increasing cationic groups and reactivity (Habeish *et al.*, 2013). In its nanoparticle form, chitosan is expected to distribute better on the fabric so that the dye binds more strongly to the fabric. Adding cross-linking agents to nano-chitosan can increase the bond strength between chitosan and fabric. Cross-linking agents that can be used in the process of coating fabric with chitosan include silica, dimethylol dihydroxy ethylene urea (DMDHEU), glutaraldehyde, and polycarboxylic acids, including citric acid (Fitri *et al.*, 2022). Cross-linking is the process of connecting two or more polymer chains through covalent or non-covalent bonds. The cross-linking process will link the carboxyl groups in citric acid with the hydroxyl groups in fabric or cellulose with chitosan, while the active amine groups in chitosan will bind the tannin dye from cocoa husk (Lusiana *et al.*, 2021). This research examines the effect of extraction time variations on dyes produced from cocoa husk on cotton fabric treated with chitosan-based mordant with a citric acid cross-linking agent.

MATERIALS AND METHODS

Extraction of dyes from cocoa husks

The study took place in the Post-Harvest Laboratory of the Indonesian Coffee and Cocoa Research Institute. The material used was cocoa

husks from the fully ripe Sulawesi 1 clone harvested in healthy condition from the Kaliwining Experimental Station, Indonesian Coffee and Cocoa Research Institute. The husks were separated from the beans and cut into 5 cm x 3 cm pieces before drying. The husks were dried for 18 hours using an oven at a temperature of 55 °C. The dried husks were ground into powder using a grinder machine and then sieved with a 60-mesh sieve. The powder was extracted using distilled water with a solvent ratio 1:10 (cocoa powder : distilled water). The extraction process was carried out at a temperature of 60 °C with varying times of 1, 2, and 3 hours. The extraction results were filtered to separate the extract from the residue before being put into an evaporator flask to remove the solvent until half the initial volume remained (Pujilestari *et al.*, 2016; Reningtyas *et al.*, 2019).

Preparation of Nanochitosan Solution

A chitosan solution with a concentration of 0.2% (w/v) was made by dissolving 0.2 g of chitosan in 100 mL of 1% (v/v) acetic acid. The solution was stirred constantly with a magnetic stirrer for 24 hours. Sodium tripolyphosphate solution (0.84 g L⁻¹) was added dropwise to the chitosan solution with a ratio of 5 : 2 (v/v) (chitosan : sodium tripolyphosphate). The solution was stirred constantly with a magnetic stirrer for 1 hour and then sonicated for 5 minutes with a stand of 60 seconds every minute. The nanochitosan particle size was measured using a particle size analyzer (PSA) to ensure the formation of nanoparticles in the sample (Nuraeni *et al.*, 2013).

Mordant Solution Coating and Dyeing of Cotton Fabric

We used chitosan as the mordant solution, citric acid cross-linked chitosan, nanochitosan, and citric acid cross-linked nanochitosan.

A cotton cloth measuring 10 cm x 20 cm was soaked in mordant solution. The cross-linking solution used was 5% (w/v) citric acid with a ratio of mordant solution and citric acid solution of 3 : 1. The fabric was soaked in a mordant solution at 50 °C for 30 minutes using a water bath. The fabric was dried at 80 °C for 5 minutes and dried again at a temperature of 120 °C for 2 minutes.

The dyeing process on the fabric was carried out using a dipping system where 10 cm x 20 cm fabric was dipped in 200 mL of natural dye that had been extracted. The fabric dyeing process was carried out 6 times. Dyeing was carried out for ±15 minutes, and then the fabric was drained for 5 minutes before being dyed again. The fabric was dried overnight and soaked in a mordant solution for 30 minutes before drying again.

Characterization of Natural Dye Extracts

Natural dye extracts were characterized using fourier transformed infrared (FTIR), tannin qualitative test, tannin content test, and β-carotene qualitative test. A total of 3 mL of the extract was tested for qualitative tannin by adding 3 drops of 1% FeCl₃ solution. Extracts containing tannin will change color to blackish green. The β-carotene test was carried out using the thin-layer chromatography method. A silica plate was cut to 2 cm x 12 cm, and a top border of 1 cm and a bottom border of 2 cm were made. The mobile phase used was a mixture of 50 mL of n-hexane and acetone (9 : 1), then saturation was carried out. The sample was dropped above the lower border, and the silica plate was inserted into the mobile phase. The process was carried out until the mobile phase was completely eluted. A sample is said to be positive for β-carotene if the retardation factor (R_f) value ranges between 0.9-1 and the spots are orange (Paransa *et al.*, 2014).

Tannin Level Test

The tannin content test began with making a standard solution in which 0.1 g of tannic acid was dissolved in 100 mL of distilled water. The solution was diluted to 20, 40, 60, 80, 100, 120, 140, 160, 180, and 200 ppm. Then, 1 mL of each dilution was added to a 10 mL volumetric flask, 0.5 mL of Folin reagent was added, and 1 mL of Na_2CO_3 solution was added. Distilled water was added following the marks and then left for 60 minutes to obtain standard solutions of 2, 4, 6, 8, 10, 12, 14, 16, 18, and 20 ppm. A standard solution of one concentration was taken to determine the maximum wavelength. The entire concentration of the standard solution was then measured at the maximum wavelength obtained (760 nm) to obtain a standard curve and linear regression equation (Desinta, 2015).

The dried tannin sample was weighed at 0.5 g, and 10 mL of distilled water was added. Then, 1 mL of the sample was placed in a 10 mL measuring flask. The sample was added with 0.5 mL of Folin reagent and left for 3 minutes, and 1 mL of 7.5% Na_2CO_3 solution was added. Distilled water was added until the limit mark and left for 60 minutes. The sample was then measured for absorbance at a wavelength of 760 nm with 2 repetitions. The absorbance value was entered into the standard curve linear regression equation to obtain the tannin content (Desinta, 2015).

Dyed Fabric Characterization

The test was carried out in several ways: the FTIR test, color fastness test, and direction and color difference test using the CIELAB method with a colorimeter.

The $L^*a^*b^*$ values obtained from the CIELAB method were analyzed using a two-factor analysis of variance (ANOVA) using JAMOV software. Directional values and color differences were processed using www.e-paint.co.uk to produce appropriate digital colors.

RESULTS AND DISCUSSION

Nanochitosan Particle Size

Chitosan is used as a mordant in the surface modification process of textile materials, there by minimizing the weaknesses of natural dyes. The role of chitosan can be increased by modifying the particle size to nanoparticle size. Nanochitosan is made using the ionic gelation method with the help of a sodium-tripolyphosphate solution, where the particle size is measured using a particle size analyzer (PSA). The measurement results of synthesized chitosan and nanochitosan in this study can be seen in Table 1.

Figure 1 shows that the average size distribution of nanochitosan particles is 239 nm, which is 80%, so it can be said that most of the samples were nano-sized. The size distribution of chitosan particles is at 1530. This shows that the size of the nanochitosan particles is smaller than the original size of chitosan and is classified in the nanoparticle category. According to Amin (2014), the size distribution of nanoparticles is 100-1000 nm. Reningtyas (2019) obtained a particle size distribution between 279-455 nm, while Agarwal *et al.* (2018) found that the size of nanochitosan was between 162-682 nm with varying concentrations of chitosan and Na-TPP.

Table 1. Chitosan and nanochitosan characterization results

Sample	Particle size diameter (nm)
Chitosan	1530
Nanochitosan	239

The method for making nanochitosan is based on the cross-linking process between the positive amine group (NH_3^+) on chitosan which interacts with the negative phosphate group ($\text{P}_3\text{O}_{10}^{5-}$) from Na-TPP. This interaction will cause chitosan to form a denser structure or pattern, resulting in smaller particle sizes (Xu & Du, 2003). Figure 1 also shows the presence of particles measuring less than 100 nm and more than 1000 nm. The particle size of more than 1000 nm indicates that the cross-linking process between Na-TPP and chitosan is less than optimal, so some particles are still in the chitosan size.

The zeta potential value shows the surface charge of a particle so that it tends to aggregate or repel. The results of the zeta poten-

tial distribution show a peak value of +31.6 mV with a distribution as shown in Figure 2. The zeta potential value of the stable samples was more than +30 mV or less than -30 mV. The zeta potential value is measured based on the surface charge of colloidal or suspension particles, which have positive and negative charges. Particles with a high zeta potential value also have a high surface charge, so the tendency for mutual repulsion between particles of the same charge is higher. A high repulsive tendency will prevent particle aggregation (clumping). The zeta potential results show stable nanochitosan with a positive charge from the protonated amine group (NH_3^+). This shows that the zeta potential value obtained has high nanochitosan stability and low aggregation. The sonication process causes

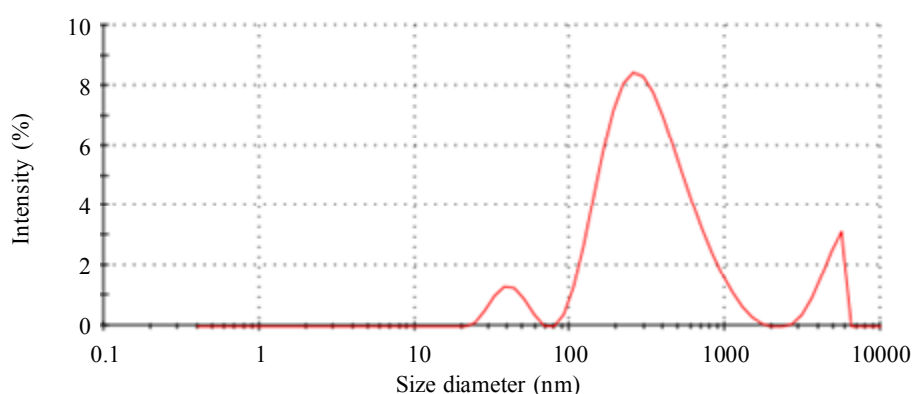


Figure 1. Nanochitosan particle size distribution by intensity

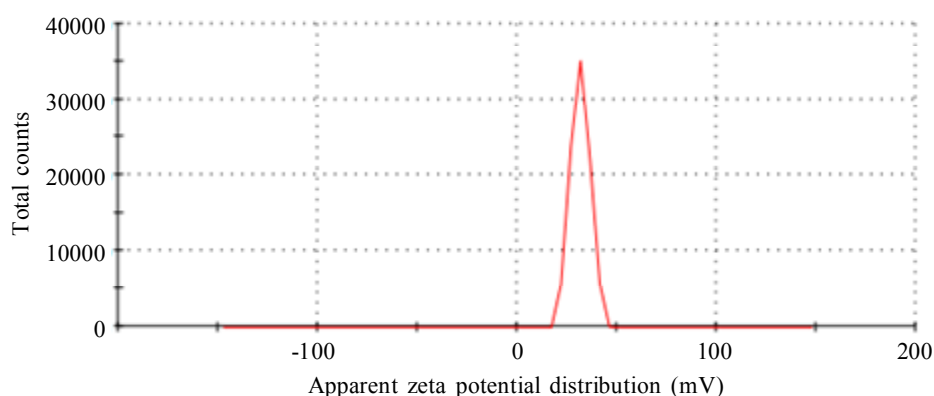


Figure 2. Potential zeta distribution value

high stability of nanochitosan due to sound waves and vibrations, which can separate particle clumps and break them down into smaller sizes.

β -carotene and Tannin Content

The source of dye in cocoa husks can be β -carotene and tannin, but in this study, the desired dye would be tannin, which was free of β -carotene compounds. Testing for the presence of β -carotene in dye extracts was carried out using the thin-layer chromatography method. This method separates samples based on the difference in polarity between the sample and the solvent used, where the closer the polarity between the sample and the mobile phase or eluent, the more the sample will be carried away by the mobile phase. Identification of target compounds is carried out using the retardation factor (R_f), which is the ratio between the distance traveled by the stationary phase and the distance traveled by the mobile phase (Paransa *et al.*, 2014). The results of the β -carotene analysis showed that the dye extract samples were negative for β -carotene at all extraction time variations. This was because there was no movement of the sample, so no yellow stains formed on the silica plate. In research conducted by Paransa *et al.* (2014), there was a yellow stain on the silica plate with the R_f value of pure β -carotene above 0.9 using the same eluent, namely a mixture of n-hexane and acetone. The eluent, acetone, has polar properties, so it will bind to the silica surface, while n-hexane will move with the non-polar sample. Compounds in samples that are polar will remain stationary because they bind to the silica surface, while compounds in samples that are nonpolar will be carried away by n-hexane. The β -carotene compound is non-polar, so it will be carried away by n-hexane, which is indicated by the appearance of an orange stain; however, this stain did not appear in this research.

The β -carotene compound in the extract can be lost during the drying process of the cocoa husks and the extraction process using heating. Heating at high temperatures above 60 °C for a long time can cause the chromophore group to be damaged and β -carotene to become unstable. β -carotene damage can also be observed from physical changes in the cocoa husks as the main ingredient in the extraction process. Cocoa husks change from orange, a color pigment from β -carotene, to brown. This change indicates the loss of β -carotene during the drying process of cocoa husks. In addition, the structure of β -carotene consists of a long hydrocarbon chain with conjugated double bonds. This double bond causes an imbalance in the electron distribution, making it non-polar. This is in contrast to distilled water, which is polar. The extraction principle follows a “Like Dissolve Like” pattern so that β -carotene, which is a non-polar compound, would not be extracted in this research because we used distilled water, which is polar.

The results of the tannin test showed that the sample was positive for containing tannin because the color changed to blue-black, and the results of the FTIR analysis in Figure 4 showed the presence of the tannin phenol group. Desinta (2015) showed positive results for tannin with a color change to blue-black after adding the FeCl_3 compound. The phenol group in tannin acts as an electron pair donor to the iron (III) ion, which acts as an electron pair acceptor. This interaction forms a coordination bond to form an iron (III) phenolate complex. The formation of iron (III) phenolate complexes causes the transfer of electrons to higher orbitals. This transfer causes the complex to absorb light at certain waves in the visible light spectrum, resulting in a blue-black color. The produced blue-black color is a color that is not absorbed or transmitted by complex compounds.

The results of the tannin content test in Figure 3 show that the tannin concentration results at time variations of 1, 2, and 3 hours were 18.32, 18.67, and 17.93 ppm, respectively. Based on the tannin level graph in Figure 3, extraction time influences the concentration of tannin produced. The highest tannin concentration was at an extraction time variation of 2 hours, while the lowest concentration was at an extraction time of 3 hours. Tannin levels increased during 2 hours of extraction but decreased during 3 hours of extraction. At the beginning of the extraction process, contact between the solvent and the extracted substance had not fully occurred, and the tannins had not been completely extracted. This causes the tannin content during 1-hour extraction to be smaller than at 2-hour extraction. Tannin levels began to decrease after 3 hours, possibly because some tannins could no longer withstand high temperatures over a long time. Prolonged time at high temperatures will cause changes in the tannin structure, which can reduce the extract yield (Wahyuni & Widjamako, 2015). Tannins consist of various polyphenolic compounds that form covalent bonds with each other. The covalent bonds between pi orbitals on aromatic carbon will be damaged due to prolonged heating, which can affect the structure of tannins. The tannin

levels in Figure 3 prove that extraction will initially cause the tannin to be extracted until it reaches the optimal point before the tannin level decreases.

FTIR Analysis Results

Figure 4 shows that tannic acid has a strong absorption at a wavenumber around 3275 cm^{-1} , which is the hydroxyl group ($-\text{OH}$). These results align with Wahyono *et al.* (2019), showing that the absorption of the hydroxyl group is in the range of $3600\text{--}3000\text{ cm}^{-1}$. At an absorption of 2741 cm^{-1} , the $-\text{CH}_3$ group was observed in the $2700\text{--}3050\text{ cm}^{-1}$ range. Tannic acid also contains a carbonyl group ($-\text{C}=\text{O}$) located at the wavenumber 1698 cm^{-1} . The carbonyl functional group is found in $1630\text{--}1850\text{ cm}^{-1}$ (Pavia *et al.*, 2009). The wavenumber of 1324 cm^{-1} contains C-O ester in the wavenumber area of $1300\text{--}1100\text{ cm}^{-1}$. The results of the IR spectrum of functional groups extracted at all time variations show that they align with the IR spectrum of tannic acid. This shows that the dye sample contained tannin. In addition, samples with variations in extraction time also showed differences in the percentage values of transmittance of the hydroxyl group ($-\text{OH}$), where the transmittance value of the hydroxyl group ($-\text{OH}$) was the lowest in the 2-hour tannin extraction

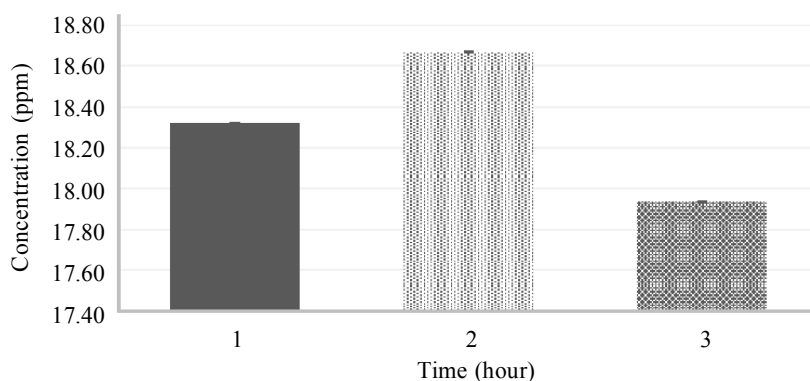


Figure 3. Effect of extraction time on tannin concentration

Notes : Lines above bars indicate standard deviation

time. This can be related to the large number of hydroxyl groups in tannin, where the higher the transmittance value, the more the number of functional groups in the compound decreases because the signal absorption of certain functional groups also decreases. In this study, the hydroxyl groups had the highest number at the extraction time of 2 hours, which was in line with the high levels of tannin obtained. The extraction time of 3 hours has the fewest hydroxyl groups, possibly because some of them have been damaged due to heating, thereby destroying the tannin content. With an extraction time of 1 hour, many hydroxyl groups still have not been detected because they have not been completely extracted.

The IR spectrum of the fabric without mordant treatment is shown in Figure 5a with a black line. The identification results show an absorption of the -OH group at a wavenumber of 3290 cm^{-1} . The wavenumber 2900 cm^{-1} shows the presence of -CH stretching and -CH bending groups. The 1,4 cellulose bond is shown in the wavenumber

of 902 cm^{-1} , while the =C-O ether group is in the area 1362 cm^{-1} . The addition of chitosan/nanochitosan shows a peak at a wavenumber of 3333 cm^{-1} , which is the stretching group -OH and -NH_2 , where there is an overlap between the hydroxyl group from cellulose and the amine group from chitosan due to the adjacent absorption areas. The hydroxyl group is in the wavenumber range of $3600\text{--}3200\text{ cm}^{-1}$, while -NH_2 is in the range of $3520\text{--}3060\text{ cm}^{-1}$. The typical chitosan bond, namely C-N, appears in the range of $1345\text{--}1020\text{ cm}^{-1}$ in all chitosan mordant treatments.

A comparison of the spectral values of fabric without a cross-linking agent with fabric having citric acid as the cross-linking agent is shown in Figure 5b. The addition of chitosan/nanochitosan mordant gave rise to a new peak at a wavenumber 1727 cm^{-1} , which indicates the formation of C=O bonds in the ester group between chitosan and cellulose. The addition of the chitosan/nanochitosan mordant also gave rise to a distinctive new peak at the wave number $1650\text{--}1580\text{ cm}^{-1}$, namely the N-H bending, a typical bond of

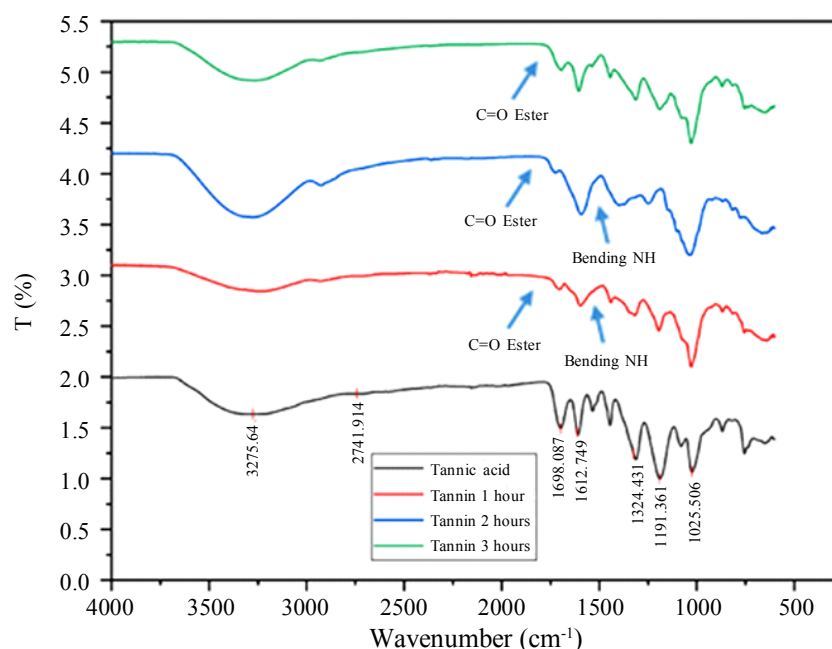


Figure 4. IR spectrum of tannic acid and tannins extracted

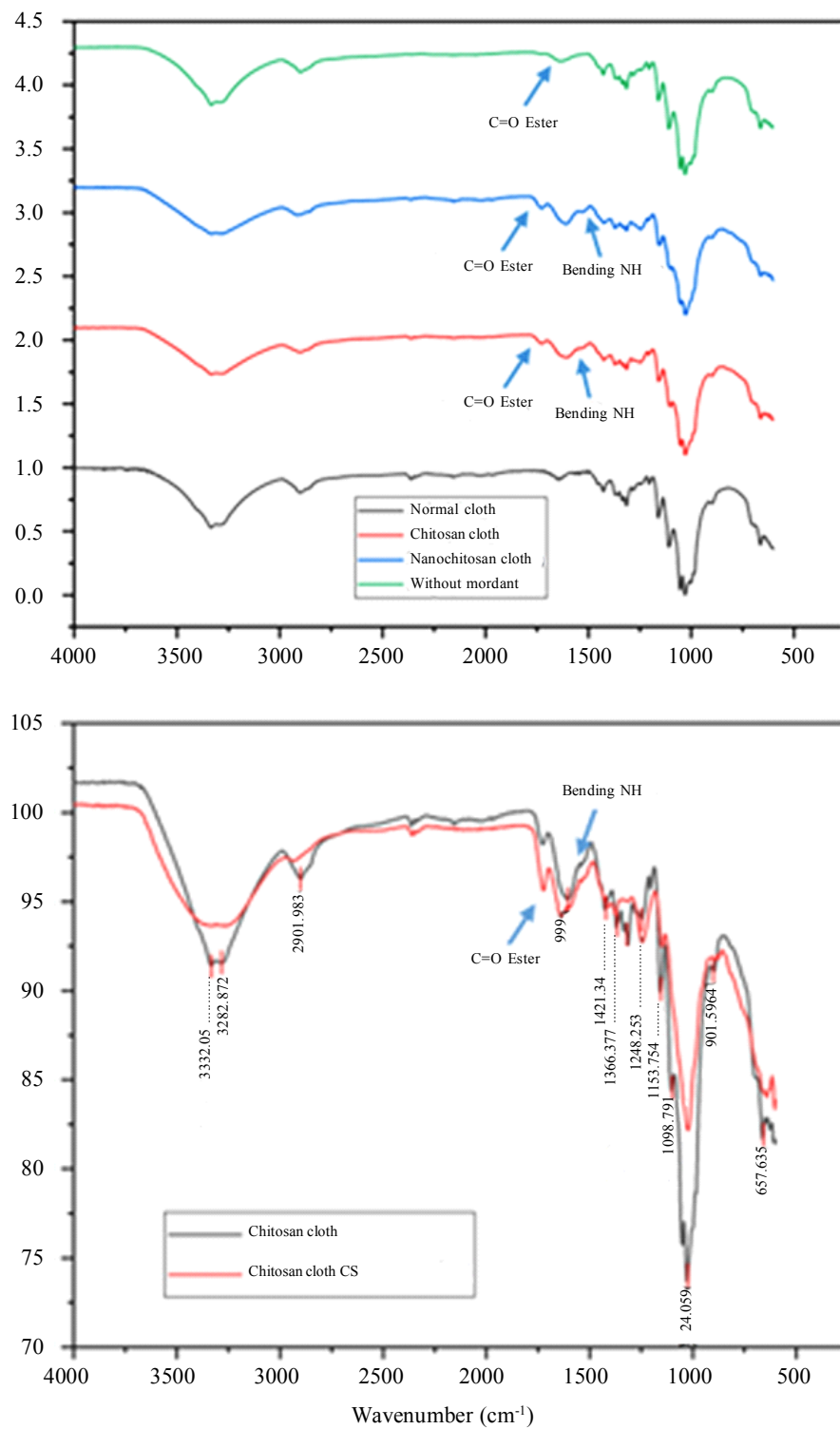


Figure 5. IR spectrum of fabrics of various mordants (a); IR spectrum of fabrics with the addition of citric acid (b)

the amine group in chitosan. The addition of citric acid as a cross-linking agent causes a decrease in the transmittance value at a new peak in the 1727 cm^{-1} area, namely the C=O ester bond. This increase in the number of ester bonds indicates an increase in the formation of ester bonds between cellulose and chitosan due to the addition of citric acid, causing a decrease in the transmittance value.

Directional Test and Fabric Colors

Color is a visual parameter that can provide information about a product. One of the methods that can be used to measure color is $L^*a^*b^*$ according to the Commission Internationale l'Eclairage (CIE) standard (Sinaga, 2019). Measuring color on dyed fabric using a colorimeter can produce $L^*a^*b^*$ values. The results of the direction values and color differences are shown in Table 2.

Table 2 shows that the highest L^* value was found in fabric samples without mordant with dye extraction for 2 hours, at 83.3 ± 0.64 . Fabrics without mordant were not significantly different ($p > 0.05$) based on extraction time variations but were significantly different ($p < 0.05$) from fabrics treated with the addition of other mordant solutions. The highest a^* value was obtained on the 2-hour nanochitosan cross-linked treatment with a

value of 9.72 ± 0.71 , which was significantly different ($p < 0.05$) from the fabric color without adding mordant. The highest b^* value in the color measurement was obtained on the 2-hour chitosan cross-linked treatment at 23.9 ± 0.51 , which was significantly different ($p < 0.05$) from the fabric color without adding mordant. The addition of chitosan and nanochitosan mordant showed no significant color difference. The addition of a cross-linking agent also produces direction values and color differences that are not significant from each other.

In the reaction between fabric, citric acid, chitosan, and dye after dyeing (Fitri *et al.* 2022), the solubility of chitosan in acid causes the amine group (NH_2) in chitosan to be protonated to become an active amine group (NH_3^+), so chitosan becomes polycationic. The addition of citric acid to the chitosan solution will cause the $-\text{OH}$ groups in citric acid and H^+ in chitosan to be released, then O will attack the hydroxyl groups in citric acid to form ester bonds. The same happens when coloring cotton fabric, in which an ester bond occurs between the cotton fabric and citric acid. Adding chitosan/nanochitosan as a mordant also causes the chitosan surface to become cationic so that it can bind natural anionic dyes.

Table 2. Evaluation of tannin coloring on cotton fabric

Sample	L^*	a^*	b^*
Chitosan, 1 hour	65.0 ± 0.97^{bc}	7.23 ± 0.31^{bc}	21.0 ± 0.35^b
Chitosan, 2 hours	59.2 ± 0.57^a	8.46 ± 0.30^c	21.2 ± 0.19^{bc}
Chitosan, 3 hours	59.6 ± 0.62^a	9.09 ± 0.43^c	22.7 ± 0.46^{bc}
Chitosan CS, 1 hour	66.5 ± 1.15^c	7.96 ± 0.27^{bc}	22.3 ± 0.18^{bc}
Chitosan CS, 2 hours	60.2 ± 1.30^{ab}	9.71 ± 0.28^c	23.9 ± 0.51^c
Chitosan CS, 3 hours	64.9 ± 1.22^{bc}	8.96 ± 0.76^c	23.6 ± 1.16^c
Nanochitosan, 1 hour	67.5 ± 1.45^c	7.28 ± 0.71^{bc}	21.5 ± 0.97^{bc}
Nanochitosan, 2 hours	62.9 ± 0.91^b	8.00 ± 0.72^{bc}	22.3 ± 0.95^{bc}
Nanochitosan, 3 hours	66.5 ± 1.32^c	7.80 ± 0.39^{bc}	22.4 ± 0.37^{bc}
Nanochitosan CS, 1 hour	69.2 ± 1.46^c	6.77 ± 0.68^b	20.8 ± 1.47^b
Nanochitosan CS, 2 hours	60.8 ± 1.26^{ab}	9.72 ± 0.71^c	23.8 ± 0.90^c
Nanochitosan CS, 3 hours	65.8 ± 1.22^{bc}	8.39 ± 0.74^c	23.4 ± 0.38^c
Without mordant, 1 hour	83.0 ± 0.62^d	3.76 ± 0.23^a	12.6 ± 0.83^a
Without mordant, 2 hours	83.3 ± 0.64^d	3.41 ± 0.04^a	11.5 ± 0.57^a
Without mordant, 3 hours	81.9 ± 1.37^d	4.30 ± 0.43^a	13.0 ± 1.13^a

Notes : L^* = brightness value; a^* = green-red direction; b^* = blue-yellow direction; CS = cross link; Figures in the same column followed by the same letter are not significantly different at 95% confidence level.

The chitosan-based mordant treatment created a darker color than the nanochitosan-based mordant treatment. This phenomenon does not align with research conducted by Reningtyas (2019), where a particle size of 279–455 nm with a chitosan concentration of 2% can increase the color intensity of fabric compared to a larger particle size. Nanochitosan has a larger surface area, so there are also more active amine groups (NH_3^+). This will increase the adsorption capacity of dyes. The phenomenon of nanochitosan coating resulting in a brighter color could possibly occur because a smaller concentration of chitosan is used to form less nanochitosan, which affects the resulting color. Apart from that, the tannin levels produced can also affect the brightness of the color. Tannin levels at 2 hours of extraction with nanochitosan-based mordant showed a high decrease in brightness levels. This shows that using nanochitosan with dyes at the highest tannin levels can produce darker colors.

The addition of a citric acid cross-linking agent reduced the brightness level of the nanochitosan mordant significantly at an extraction time of two hours. This indicates the influence of citric acid as a cross-linking agent to increase the bond between the mordant in cellulose fibers and chitosan/nanochitosan via ester bonds. However, the addition of the citric acid cross-linking agent produces a brighter color than without the addition of the citric acid cross-linking agent. This may occur because the active amine group of chitosan can also cause citric acid to bind to this group. The active amine group has a lone pair of electrons that can bond with the carboxylate group by forming an amide bond. The hydroxyl group in chitosan is not as effective as the amine group in a reaction so its reactivity is lower than the active amine group. This phenomenon can cause anionic dyes not to be able to bind to the polycationic active groups of chitosan, thereby reducing the resulting color index.

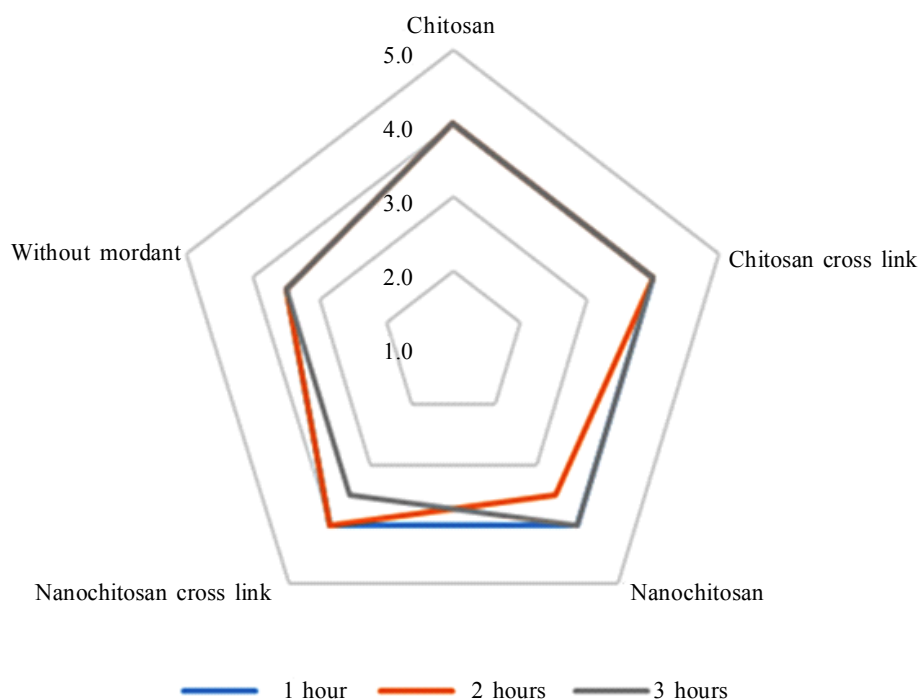


Figure 6. Color fastness test results

Color Fastness

Color fastness measures the strength of color produced, especially by natural dyes. The test results in Figure 6 show the results of different color fastness. Applying mordant to fabric samples affects washing. Chitosan-based and cross-linked chitosan-based mordants provide a fastness score of 4 (good). Nanochitosan-based and cross-linked nanochitosan-based mordants also have a fastness score of 4 (good). However, the 2-hour nanochitosan-based and 3-hour cross-linked nanochitosan-based mordant have a fastness score of 3-4 (fairly good). Fabric without mordant has a fastness score of 3-4 (fairly good). The use of mordant on fabric increases its fastness against washing. This is in line with Sunder (2014), who succeeded in cross-linking fabric and mordant, thereby increasing the stability of fabric and mordant. The use of nanochitosan as a mordant solution did not have a significant effect on the resulting fastness score. This is because the concentration of chitosan used is quite small, so less nanochitosan is formed. The addition of a citric acid cross-linking agent can maintain the color fastness value of the fabric due to the formation of ester bonds, but it is still not good enough. This not-so-good enough color coating is probably caused by the presence of active amine groups, causing the citric acid not to bind to the chitosan's -OH but to the active amine group, causing the dye to be unable to bind to the chitosan. The active amine group of chitosan must be deactivated before adding citric acid to prevent interaction between the amine group and citric acid.

CONCLUSIONS

Variations in extraction time affect the dye produced. Increasing extraction time will increase the tannin levels produced. The highest level of tannin was obtained at an

extraction time of two hours with a level of 18.67 ppm. An extraction time of two hours resulted in the highest color intensity of the fabric. The chitosan-based mordant coating provided a better color to the fabric than the color without mordant coating. The nanochitosan-based mordant coating was unable to increase the color intensity and fastness of the fabric compared to the chitosan-based mordant coating. The fabric with the highest color intensity and fastness was obtained by chitosan-based mordant fabric with a fastness value of 4 (good). The addition of citric acid as a cross-linking agent provides more varied fabric colors. Adding citric acid produces brighter colors than fabrics that do not use cross-linking agents, so it cannot increase color intensity and fastness.

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