Enhanced wash-fastness of cotton fabric dyed with a composite of chitosan-natural dyes extract of *Ceriops tagal*

I Kartini¹,³,⁴, S N Halimah¹, E Rahayuningsih²,³

¹ Functional Coating Materials Research Group, Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Yogyakarta, Indonesia
² Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Yogyakarta, Indonesia
³ Indonesia Natural Dye Institute (INDI), LPPT, Universitas Gadjah Mada, Yogyakarta, Indonesia
⁴ To whom correspondence should be addressed

email: indriana@ugm.ac.id, sitinurh@mail.ugm.ac.id, edia_rahayu@ugm.ac.id

Abstract. Chitosan coating on dyed cotton fabric by the natural dye of Tingi (*Ceriops tagal*) has been done to improve the wash fastness. Hydrophobic coating using HDTMS (hexadecyltrimethoxysilane) was also introduced to obtain multifunctional textiles. Fabric dyeing was done by the dip-coating method in two ways, one-pot (Op) and layer-by-layer (LbL). Specular-reflectance (SR) UV-Vis spectrophotometer was used to access the dyeing quality. An infrared spectrophotometer evaluation was performed to indicate the possible interaction between chitosan and the dye on the dyed cotton fabrics. The leaching degree was determined by using sodium dodecyl sulfate (SDS) and lerak (*Sapindus rarak*) natural surfactant as the leaching agents. The results showed that LbL coating has shown better dye-coverage on the cotton fabrics compared to the Op coating. However, cotton fabric coated by chitosan/tingi (Op) showed better performance than that of the LbL, with a leaching degree of 6.2% on SDS leaching, and 4.1% on lerak’s leaching. While, for LbL coating, the leaching degree was 20.1% on SDS and 13.9% on lerak’s leaching. The hydrophobic coating was stable and not affected by leaching. Different types of molecular interaction between the dye and chitosan from different coating techniques may result in those different performances on leaching.

Keywords: wash fastness, Tingi, natural dye, chitosan composite, *Ceriops tagal*.

1. Introduction
Color is one of the main attractions and is an important criterion for the acceptance of products such as textiles, cosmetics, food, and others [1]. Recently, people put more interest in eco-fashion or also known as sustainable fashion. It is considered as a trend against fast fashion to create a system that can support and counteract the impact of human activities on the environment. Therefore, one consideration in the textile industries is the use of natural dyes for dyeing the fabrics. Natural dyes are revived to reduce the negative effects of synthetic dyes [2,3], thus creating a healthy workplace and living. However, the color of natural dyes suffers from being not sharp and easy to fade. So, efforts to
improve the color intensity and fastness of natural dyes have been the focus of interest to study. Mahlig and Textror [4] have shown the improvement of light and wash fastness properties of dyed cotton fabrics by incorporating the dyes into the sol-gel matrices of silica. The dye sols composition and techniques affected the dyeing performance. Similarly, a nanosol composite of silica and titania has also been proposed to improve the wash fastness of malachite green-dyed cotton fabrics [5]. Enhanced dye absorption was observed at fabrics dyed using dye sols containing more silica than titania. The wash fastness has been improved by 40-95%. The dyed cotton fabrics have also shown antibacterial properties toward both Gram-positive and Gram-negative bacteria leading to multifunctional textiles.

Other efforts are based on the surface properties of the fabrics. Generally, fabrics produced from vegetable fibers, for example, cotton, flax, and linen are less suitable to dye with natural dyes than protein fibers such as silk and wool [6,7]. To obtain the intense color of vegetable fabrics, the dyeing process has been involving cationic agents, such as chitosan [6, 8-9]. Chitosan is a linear polysaccharide composed of a random distribution of β (1-4) connected to D-glucosamine (acetylation unit). It is an N-acetylglucosamine derivate from chitin that can be found abundantly in the shrimp and crab shells as a byproduct of the food-processing industry, so it is renewable and environmentally benign. The chitosan incorporation for textile dyeing has resulted in improved washing and rubbing fastness properties of the dyed fabrics [9] as well as the dye uptake from the dye bath of C.I. Reactive Red and C.I. Reactive Yellow. Complexation with chitosan has also enhanced the light and wash fastness of Curcuma dyed cotton fabrics [10].

In this study, chitosan is introduced to form a composite with natural dye of Tingi (regional name of Ceriops tagal) extract. The dye resource is tree barks of a mangrove family that offer unique and sophisticated brown color for the fabrics. This brown color is commonly used for a traditional cloth called Batik in Indonesia. Two different techniques of dip-coating for fabric’s dyeing are applied and compared. Wash fastness was tested using sodium dodecyl sulfate (SDS) [4] and natural detergent called lerak as the leaching agents. Lerak is a regional name for Sapindus rarak and has been used for centuries in Indonesia to wash Batik’s cloth. Finally, multifunctional coating using hexadecyltrimethoxysilane (HDTMS) was set up to give a hydrophobic surface to the dyed fabrics.

2. Experiments

2.1. Materials

The material used in this study was a commercial extract of Tingi natural dyes (Ceriops tagal) obtained from Gama Indigo Workshop Gallery Yogyakarta. Hexadecyltrimethoxysilane (HDTMS), sodium dodecyl sulfate (SDS), hydrochloric acid (HCl), 96% of ethanol were purchased from Merck. Lerak solution was bought from a local Batik shop. The chitosan flakes (>85% degree of deacetylation) were procured from IPB Bogor and the cotton fabric was from Prima Fabric Shop, Kudus. Distilled water and 2% (v/v) of acetic acid were from local chemical shops.

2.2. Methods

Two grams of chitosan was dissolved in 2% (v/v) acetic acid under vigorous stirring for 2 h at room temperature. The solution was used for fabric coating. The cotton fabric that will be used as Batik material was cut to a size of 5x2 cm. It was washed using a 1% (w/w) commercial detergent solution under sonication for 10 min. Then, the fabric was rinsed using 100 mL distilled water under sonication for 10 min and dried in the oven for 45 min at 80 °C. The fabrics were ready for dyeing.

The method used in fabric dyeing was dip-coating. The fabrics were soaked into the Tingi natural dye solution (10 mL of distilled water and 40 mL of the concentrated dye extract) for 5 min, then removed and drained for another 5 min. The dyeing was repeated 5 times. The fabric was then dried at room temperature for 24 h and heated in an oven for 10 min at 80 °C. The coating of the fabrics with chitosan was carried out in a ratio of 1: 4 (10 mL of chitosan and 40 mL of the concentrated dye extract). The techniques used in this coating process are Op and Lbl. The Op coating technique was a coating technique in which all the solutions were mixed, in this case, 10 mL of 2%
(v/v) chitosan solution was mixed with 40 mL of the concentrated dye extract. Then, the liquid mixture was used to coat the fabric. Similar drying steps were applied to the coated fabrics. While, the Lbl technique was a separate coating technique in which the fabric was pre-coated with chitosan solution, dried in an oven for 30 min at 80 °C followed by a layer coating of 40 mL of the concentrated dye extract. The coated fabrics were then dried similarly as the Op. The dyed fabrics by Op dan LbL were characterized using an SR-UV Vis spectrophotometer to determine the reflectance spectra. The chitosan, dye extract, and chitosan-dye extract powders were analyzed using the FTIR spectrophotometer to identify their functional groups.

Fastness testing was carried out by vigorous washing using sodium dodecyl sulfate (SDS) [4] and lerak as the leaching agents. The SDS was used as much as 1% (w/v). The tested fabrics were soaked for 1 h at room temperature in a closed system. The fastness test using lerak was carried out by immersing the fabrics in 100 mL of the concentrated lerak for 1 h. The fabrics were then dried at room temperature for ± 24 h. The washed cloth was then characterized by an SR-UV Vis spectrophotometer to determine the reflectance of the dye after washing. The degree of leaching was calculated using the formula introduced by Mahltig and Textor [4], 

\[ D = \frac{100(r_A - r_B)}{(100 - r_B)} \]

where \( r_A \) and \( r_B \) were the reflectances after and before leaching, respectively, while \( D \) was the degree of leaching. The values of \( r_A \) and \( r_B \) were taken at the wavelength where the reflection spectra of the dyed fabrics were minimum.

The hydrophobic coating was carried out by dip-coating using a 4% (w/v) HDTMS solution in ethanol. The fabrics were immersed in the HDTMS for 5 min, then slowly removed and drained for 5 min. The coating was repeated 5 times. The fabrics that have been coated with HDTMS were then dried at 110 °C for 10 minutes and followed by measuring the water contact angle to determine hydrophobicity.

Measurement of the water contact angle was carried out by dripping 5 µL of water using a 5 µL micropipette on an HDTMS coated cloth and then photographed using a Canon 1100D camera with 100 mm macro lens. The fabric was placed parallel to the camera used and followed by photographing the water droplets dripped on the cloth. The photo results were then changed to “B&W” mode and processed using image-j [11] software to determine the angle of contact using the LB-ADSA (Low Bond Axisymmetric Drop Shape Analysis) method.

3. Results and Discussion
Chitosan in an acidic solution of acetic acid became polyelectrolytes due to protonation by acetic acid in the -NH2 group as depicted in figure 1[12]. Figure 2 showed the infrared spectra of the powder form of the dye extract of C. tagal, chitosan, and the composite of C. tagal-chitosan. Those three spectra have shown large broad peaks at ~3500 cm⁻¹ indicating the presence of a large number of –O-H groups.

**Figure 1.** Protonation reaction of chitosan in acetic acid solution

**Figure 2.** Infrared spectra of the powder of Tingi natural dye (a), chitosan (b), and Tingi natural dye-chitosan (c)
The natural dye extracted from tree barks of *C. tagal* contains 13-40% of the procyanidin-type condensed tannin group so that staining with the bark gives a reddish-brown color [13]. Condensed tannins are more widely distributed in plants than hydrolyzed tannins [14]. Of about 71%, condensed tannins of procyanidin have been confirmed in the bark tree of *C. tagal* [15]. Figure 2a showed sharp peaks at a wavenumber of 1743 cm\(^{-1}\) which is a C=O vibration from the ester group in tanned materials and a wavenumber of 1612 cm\(^{-1}\) which is a C=C aromatic vibration [15]. Similar peaks have also been detected in figure 2c of the composite powder of *C. tagal*-chitosan. The vibration peak of C=C from the ester group in tanned material shifted to a higher wavenumber (1753 cm\(^{-1}\)), indicating stronger vibration leading to the strong interaction between the dye and chitosan. Related shifting is also observed for the –O-H vibration, from 3417 to 3425 cm\(^{-1}\). Figure 3 illustrates the interaction between –O-H groups of procyanidin representing the condensed tannin in *C. tagal* extract and the chitosan frameworks through the formation of hydrogen bonding. The widening of the broad peak around 3500 cm\(^{-1}\) in figure 2c is an indication of the formation of more hydrogen bonds in the composite powder. It is also observed that there is no peak shift in the N-H vibration at 1597 cm\(^{-1}\) in both figures 2b and 2c, so it can be assumed that the interaction between dye and chitosan does not occur through the N-H cationic group of chitosan.

To evaluate the effect of the coating technique on the dye coloring and wash fastness, fabric dyeing using chitosan and the dye extract was done by using one pot (Op) and layer-by-layer (Lbl) techniques. Table 1 shows the photos of the dyed fabrics with and without chitosan. It can be seen that the fabric’s color using chitosan for Op techniques shows a more intense brown color than fabric dyeing without chitosan. These results are following coloring using chitosan and reactive dyes [9], but a different mechanism.

**Table 1.** Color on dyed cotton fabrics with and without chitosan coating before and after leaching testing

| Fabric sample | Before leaching | After SDS leaching | After lerak leaching |
|---------------|----------------|--------------------|---------------------|
| Dyed with *C. tagal* extract | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) |
| Chitosan-dye (Op) | ![Image](image4.png) | ![Image](image5.png) | ![Image](image6.png) |
| Chitosan-dye (Lbl) | ![Image](image7.png) | ![Image](image8.png) | ![Image](image9.png) |

In the Op technique, chitosan and the dye solution were firstly mixed before use for coating. This process allows the dye to interact with chitosan, as illustrated in figure 3. So, as the coating proceeded, there could be more than one possible interaction by hydrogen bonding between the fabric’s surface and the dye-chitosan solution. Figure 7 (left-hand side) displays those possible interactions. The hydrogen bonding may be resulted from –OH – OH- interaction between the hydroxyl group of chitosan backbone and the –OH surface of the cotton fabrics, or directly from the...
hydroxyl group of tannins molecule with surface hydroxyl groups of the cotton fabrics. Therefore, tannin molecules are bound more tightly on the fabric’s surface resulting in more intense color compared to the dyeing without chitosan. It is also observed in table 1 that the color before and after leaching for Op are similar. Even it is more intense.

In the Lbl technique, before dyeing, the fabrics were coated by chitosan. Then, dyeing was performed by soaking the fabrics in the dye solution. This step is repeated 5 (five) times. It can be seen in table 1, that the color of the fabrics is not as intense as the Op, and almost similar to the dyeing without chitosan. Possible interaction between the dye molecule, chitosan, and the fabric’s surface is shown in figure 7 (right-hand side). The dye molecule is only held by one type of hydrogen bonding from the chitosan molecule, thus resulting in weaker interaction between the dye and the surface of the cellulose of the cotton fabrics. Further evaluation by observing the reflectance spectra of the corresponding dyed fabrics is carried out. The data are shown in figures 4, 5, and 6.

The lower the reflectance, the better the dye absorption in the cotton fabrics [4,5]. It can be seen that the lowest reflectance of the dyed fabrics is observed in figure 5, which is the dyeing using chitosan under Op technique. Spectral data are in line with photographic image data as discussed in table 1. The reflectance of fabrics after leaching is quite high indicating a higher leaching degree for the fabrics dyed without chitosan (figure 4). Figure 5 shows that the reflectance difference between the fabrics after SDS and lerak leaching is not so significant. This is also following the qualitative data...
shown in table 1, namely the color difference for fabrics before and after leaching is not so high. However, the one-pot technique produced a precipitate of a mixture of chitosan and the dye. The precipitate attaches to the fabric at the time of the coating, so that it produced blackish-brown spots on the dyed fabrics. This reduces the aesthetic value of the fabric so that the fabric coating using chitosan/dye extract of *C. tagal* under one pot (Op) is not recommended, except the precipitates were firstly removed before the solution used for dyeing. The quantitative leaching degree of the dyed fabrics is presented in Table 2.

**Table 2.** Leaching degree of dyed fabric samples with *C. tagal* extract

| Fabric sample        | Leaching degree (%) |     |
|----------------------|---------------------|-----|
|                      | SDS leaching        | lera leaching |
| Dyed                 | 21.10               | 19.30 |
| Chitosan-dye (Op)    | 6.24                | 3.66  |
| Chitosan-dye (Lbl)   | 20.03               | 13.89 |

*Figure 7.* Possible interaction between the dye molecule represented by procyanidin and the surface of the cotton fabrics in Op dip-coating (left-hand side) and Lbl dip-coating (right-hand side)

The leaching degree of the dyed fabrics was improved as chitosan introduced into the dye composition. The Op technique offers significant enhancement of the wash fastness as listed in Table 2. The leaching degrees are both below 7% for Op after SDS or lera leaching. Lera leaching has shown softer washing to the dye color than that of SDS. *Lera* (*Sapindus rarak*) contains saponins which are a natural surfactant [16].

**Table 3.** The water contact angle of fabric samples before and after the leaching test

| Fabric sample      | Water contact angle (°) |            |
|--------------------|--------------------------|------------|
|                    | Before leaching          | After lera's leaching |
| Dyed with *C. tagal* extract | 120.10 ± 1.22 | 120.40 ± 2.31 |
| Chitosan-dye (Op)  | 97.97 ± 2.05            | 107.83 ± 2.74 |
| Chitosan-dye (Lbl) | 117.07 ± 2.34           | 116.57 ± 3.07 |
The chitosan/dye coated fabrics in one pot and layer by layer were then coated by HDTMS to result in a multifunctional coating of hydrophobicity. The water contact angles of the dyed fabrics are displayed in Table 3. The leaching test was only carried out using lerak as the leaching agent since it is the soft leaching agent to the natural dyed cotton fabrics. It can be seen that the water contact angle of all dyed fabrics increased after leaching testing. This probably due to the interaction of the HDTMS coated fabric with lerak thus increasing the value of the contact angle of the fabric. By this fact, it is then possible to use lerak as the surface-active agent for inducing hydrophobicity on a glass substrate mimicking the use of dodecylamine to form a composite with titania for superhydrophobic coating [17].

4. Conclusions
The role of chitosan to improve the wash fastness of the natural dye extract of Ceriops tagal on the cotton fabrics has been presented. Chemical interaction between the cotton, the dye, and chitosan determined the degree of the wash fastness. Chitosan supports the dye attachment through the formation of hydrogen bonding. One-pot dyeing technique of dip-coating offers wash fastness enhancement of almost six times. Introducing HDTMS resulted in improved surface hydrophobicity leading to the production of multifunctional textiles.

5. References

[1] Rymbai H, Sharma R R and Srivastav M 2011 Int. J. Pharm. Tech. Res. 3(4) 2228-45
[2] Pipattanamongkol P, Lourith N, Kanlayavattanakul M 2018 Sustain. Chem. Pharm. 8 88–93
[3] Nam C and Xiang C 2019 Int. J. Fash. Des. Technol. Educ. 12(3) 335-345
[4] Mahltig B and Textor T 2006 J. Sol–Gel. Sci. Technol. 39 114
[5] Kartini I, Ilmi I, Kunarti E S and Kamariah 2014 Bull. Mater. Sci. 37(6) 1419–26
[6] Kampeerapappun P, Phattararittigul T, Jitrong S and Kullachodore D 2010 Chiang Mai J. Sci. 38(1) 95-104
[7] Nuryadin S, Erdawati E and Purwanto A 2013 Jurnal Riset Sains dan Kimia Terapan 3(1) 229-238
[8] Suicharit S, Awae F, Sengmama W and Srikulkit K 2011 Chiang Mai J. Sci. 38(3) 473-484
[9] Chatha S A S, Hussain A I, Ali S, Saif M J, Mallhi A I, Sagir M, Naz M Y 2016 J. Chil. Chem. Soc. 61(2) 2895-97
[10] Shukla D and Vankar P S 2018 Fibers Polym. 19 1913–20
[11] Rueden C T, Schindelin J, Hiner M C, DeZonia B E, Walter A E, Arena E T and Eliceiri K W 2017 BMC Bioinformatics 18(1) 529
[12] Rinaudo M, Pavlov G and Desbrieres J 1999 Polym. 40 7029–32
[13] Jansen C H and Borus D J 2006 Dyes and Tannins of Tropical Africa 3rd ed. (Netherlands: PROTA Foundation)
[14] Hon D N and Shiraishi N 2001 Wood and Cellulosic Chemistry 2nd ed. (New York: Marcel Dekker)
[15] Kasmudjiastuti E 2014 J. Leather Rubber Plast. 3 71–8
[16] Fajriaty I, Adnyana K and Fidrianny I 2014 Int. J. Pharm. Pharm. Sci. 6(11) 487-92
[17] Kartini I, Santosa S J, Febriyanti E, Nugroho O R, Yu H and Wang L 2014 J. Nanopart. Res. 16 2514