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EFFECTS OF CHITOSAN AS BIO-MORDANT ON COTTON FABRIC DYEING WITH VARIOUS NATURAL DYES

Efek Kitosan sebagai Bio-Mordant pada Pewarnaan Kain Katun dengan Berbagai Pewarna Alami

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ABSTRACT

Natural dyes are alternatives to synthetic dyes as batik dyes. However, color results produced by natural dyes were not as good as synthetic dyes, hence mordant compounds were required. As a substitute for metal mordant, it was essential to have another alternative mordant, such as chitosan. This research was intended to analyze the color produced by various sources of natural dyes, betel nut; spurred mangrove (tingi) bark; baheda (jolawe) peel; mangrove bark; mahogany bark; and copperpod (jambal) bark, quantitatively by testing the value of color differences (ΔE) on variations of the chitosan concentration and fabric dyeing. In conclusion, the use of chitosan could enhance the absorption of dye into the fabric. In a chitosan concentration of 10 g/L, betel nut reached an ΔE value at 15.40; spurred mangrove 16.26; baheda peel 18.97; mangrove 10.87; mahogany 14.01; and copperpod 19.33. Furthermore, the test of fastness to sunlight with greyscale showed the value in range of 4-5 (good).

ABSTRAK

Pewarna alami adalah alternatif untuk pewarna sintetis sebagai pewarna batik. Namun, hasil warna yang dihasilkan oleh pewarna alami tidak sebaik pewarna sintetis, maka diperlukan senyawa mordan. Sebagai pengganti mordan logam, penting untuk memiliki mordan alternatif lain, seperti kitosan. Penelitian ini dimaksudkan untuk menganalisis warna yang dihasilkan oleh berbagai sumber pewarna alami: pinang; kulit kayu tengar (tingi); kulit buah jaha (jolawe); kulit kayu bakau; kulit kayu mahoni; dan kulit kayu soga (jambal), secara kuantitatif dengan menguji nilai perbedaan warna (ΔE) pada variasi konsentrasi kitosan dan pewarnaan kain. Kesimpulannya, penggunaan kitosan dapat meningkatkan penyerapan pewarna ke dalam kain. Pada konsentrasi kitosan 10 g/L, pinang mencapai nilai ΔE pada 15,40; kulit kayu tengar 16,26; kulit buah jaha 18,97; kulit kayu bakau 10,87; kulit kayu mahoni 14,01; dan kulit kayu soga 19,33. Selanjutnya uji tahan luntur terhadap sinar matahari dengan skala abu-abu menunjukkan nilai pada kisaran 4-5 (baik).

INTRODUCTION

In the past, batik artisans dyed batik fabric with various kind of natural dyes from barks, fruits, or leaves (Parmono, 2016). The advantage of natural dyeing process was it's being environmentally sustainable. (Kumalasari, 2016; Lestari and Satria, 2017). These days, synthetic dyes are frequently used in the batik dyeing process, because they emerge more vibrant color. However, its waste is non-biodegradable since it contains heavy metals and certain azo dyes. Dissolved oxygen depletion and water pollution which causes the death of aquatic biota are some environmental damage arise as an impact of synthetic dye waste. Besides, liquid waste will harden soil by clogging its pores, leads the soil into productivity decreases (Amalia & Akhtamimi, 2016).

Natural dyes are alternatives to synthetic dyes as batik dyes. As a country rich in floral diversity, Indonesia has a great potential for developing natural dyes. Their natural components, have a relatively low pollution value, biodegradable and non-toxic (Habib, Adeel, Ali, Amin, & Khan, 2021).

However, coloring result produced by natural dyes inferior to synthetic dyes. The color result of using natural dyes is duller. Besides, it fades faster when washing and drying in the sun (Vankar, 2017). To improve the result of dyeing with natural dyes, the fabric must be pretreated with mordant substances. Mordant is an addition compound used to increase the affinity of dye absorption into fabric so that a better color result and fastness can be obtained (Mussak & Bechtold, 2009).

Metal compounds are commonly used as mordant substances. Aluminum, chromium, iron, copper, and lead are types of metal salt used oftentimes. Those metal compounds can harm the environment, especially lead and chromium, so their usage is prohibited (Cunningham *et al.*, 2011). The most frequent mordant substances used by batik artisans are *Tunjung* ($FeSO_4$), *Alum* ($KAl(SO_4)_3$), and Lime (CaO). The remaining metal mordant solution, however, does not go through the waste treatment process (Indrayani, 2018). Thus, it can pollute the water source of nearby environment.

As a substitute for metal mordant, it is essential to acquire alternative mordant such as chitosan. Chitosan is a natural cation polymer obtained from the deacetylation of chitin gained from the outer shell of shrimp, crabs, and other crustaceans. It is generally used to increase anti-microbiological characteristic of fabric. In textiles, however, chitosan also increases the absorption of dyes into the fabric (Enescu, 2008). Several research are done by doing pretreatment on cotton fabric dyed with anthocyanins and phenoxazine, showed that pretreatment of fabric with chitosan increased the absorption of dye into the fabric and the value of color strength (K/S) significantly (Dessie, Ashenafi, Berhane, Gashawbeza, & Tesfaye, 2020; Evitasari & Rahayuningsih, 2020; Evitasari, Rahayuningsih & Mindaryani, 2020). The value of color strength will rise along with the chitosan concentration.

This research was intended to study the chitosan role as cotton fabric pre-mordant material in the dyeing process by various sources of natural dyes, including betel nut (*pinang*) (*Areca catechu*), spurred mangrove (*tingi*) (*Ceriops tagal*), baheda (*jalawe*) (*Terminalia bellirica*), mangrove (*Rhizophora apiculata*), mahogany (*Swietenia mahagoni*), and copperpod (*jambal*) (*Peltophorum*

pterocarpum) as shown in Figure 1, quantitatively for dyeing batik fabric. In addition, to determine the effect of chitosan concentration as well as variations in dipping cycle to the result of batik fabric dyeing.

Figure 1. The natural dyes used in the research, (a) Betel nut (pinang); (b) baheda (jalawe); (c) mangrove; (d) mahogany; and (e) copperpod (jambal)

RESEARCH METHODS

Materials

Primissima cotton fabric obtained in Yogyakarta. Chitosan (with deacetylation degree of 90%) was brought from ChemMix Yogyakarta. Natural dyes, spurred mangrove, baheda, and copperpod obtained from Ngasem Market Yogyakarta; betel nut from Bengkulu; and mangrove from East Nusa Tenggara. The last material is Merck acetic acid glacial.

Procedure and Analysis

Mordanting and dyeing process

The cotton fabric treatment was done by dipping the fabric into 5% NaOH solution. Chitosan dissolved into a 2.5% v/v acetic acid solution with chitosan concentration variation of 0-7.5 g/L. In the pretreatment process, the fabric dipped into the chitosan solution for 60 minutes at 60^0 C and dried. The modified fabric then dipped into a natural dye solution.

Analysis of Color Difference Value

This analysis was to determine changes in color based on CIELab parameters (L*, a*, and b*). The color difference was calculated between the untreated dyed fabric as control and the chitosan treated dyed cotton fabric. Equation 1 calculated the value of the color difference (ΔE). The dyed fabric later tested for light fastness according to SNI 08-0289-1989 in the parameter of gray scale.

$$\Delta E = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right]^{1/2} \quad (1)$$

RESULTS AND DISCUSSIONS

Dyeing Results

Natural dyes contained in betel nut, spurred mangrove, baheda, mangrove, mahogany, and copperpod were dominated by tannins. Tannins are compounds contained within natural dyes that produce brown color, with variations in red, yellow, and green. The content of tannins in natural dyes used in this research is presented in Table 1.

Table 1. Content of Tannins in Natural Dyes

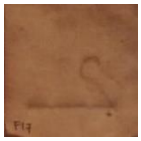
Natural Dyes	Tannin Concentration (%)
Betel nut	11.32
Spurred mangrove	38.59
Baheda	30.18
Mangrove	34.81
Mahogany	42.47
Copperpod	28.43

In this study, the dyeing result of a fabric that underwent chitosan pre-mordanting process and untreated fabric were compared. The differences are shown in Table 2.

Table 2 shows the results of natural coloring dyes for betel nut, spurred mangrove bark, baheda peel, mangrove bark, mahogany bark, and copperpod bark on a cotton fabric without and with chitosan mordanting. The betel nut produce cream color; the spurred mangrove bark bring out dark orange; baheda peel result brownish green; mangrove bark result in light brown color raise; mahogany bark bring out the brick red color; and copperpod bark produce pink color.

The chitosan, which brought the effect of anti-static and anti-wrinkle, would intensify stiffness and rigidness of the fabric texture. In addition, the results of dyeing fabric with chitosan mordant in Table 2 showed that the colors produced were darker than those without mordanting. It is indicated that chitosan could increase the absorption of natural dyes into the cotton fabric.

Table 2. Comparison of the results of dyeing fabric with various natural dyes

Natural Dyes	Chitosan Mordanting	
	Untreated	Treated
Betel nut		
Spurred mangrove		
Baheda		
Mangrove		
Mahogany		
Copperpod		

Shin (2010) pre-treated chitosan on the cotton fabric dyed with anthocyanins. In the result, his research also showed that the fabric pretreatment with chitosan enhanced the absorption of dye into the fabric and the value of color strength (K/S) significantly (Shin, Min, & Dong, 2010). Therefore, by using greater amount of chitosan concentration the color strength value will be increased.

Effects of Chitosan Concentration and Dyeing Cycles

The color difference value (ΔE) on chitosan-modified cotton fabric colored with various natural dyes is presented in Figure 2–7. It can be seen that higher ΔE value can be obtained by increasing the concentration of dyes. Likewise, the amount of dyeing was related to the characteristics of tannin compounds as natural dyes. Tannin was a vessel compound dye. Thus, multiplying the dyeing process can result darker color.

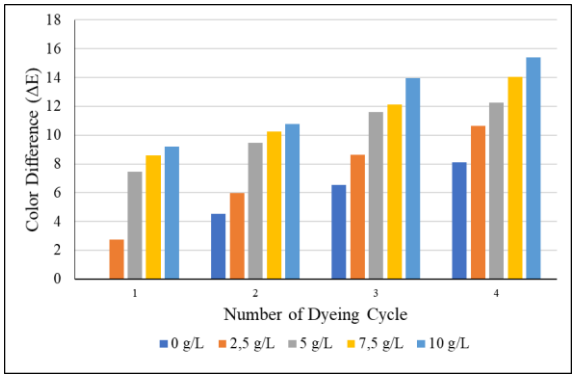


Figure 2. ΔE values of fabric dyeing with betel nut at various concentrations of chitosan

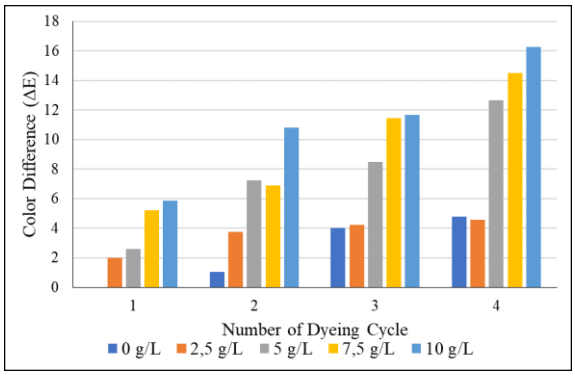


Figure 3. ΔE values of fabric dyeing with spurred mangrove at various concentrations of chitosan

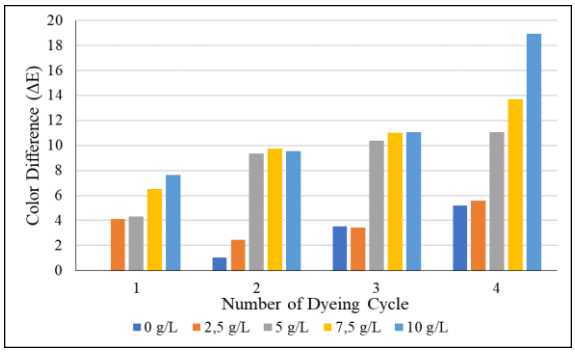


Figure 4. ΔE values of fabric dyeing with baheda at various concentrations of chitosan

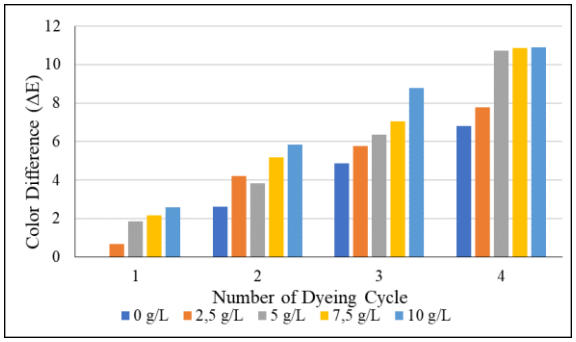


Figure 5. ΔE values of fabric dyeing with mangrove at various concentrations of chitosan

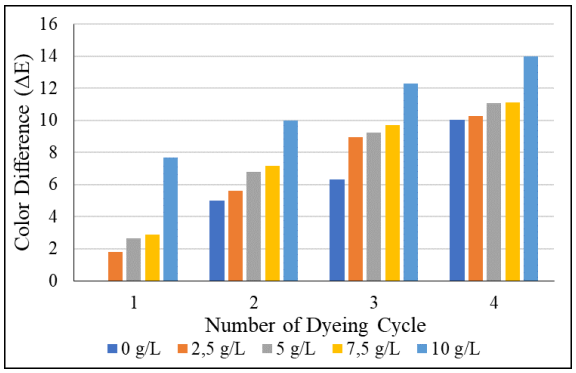


Figure 6. ΔE values of fabric dyeing with mahogany at various concentrations of chitosan

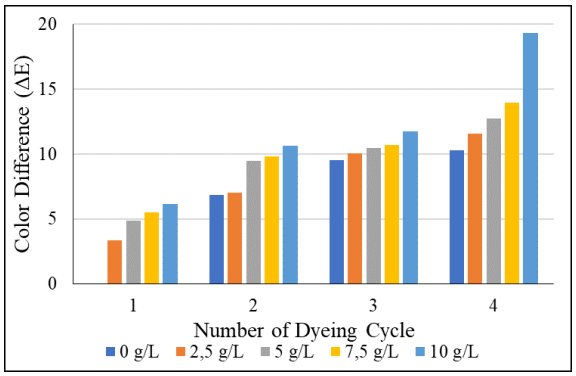


Figure 7. ΔE values of fabric dyeing with copperpod at various concentrations of chitosan

The ΔE value of betel nut dye with a concentration of 10 g/L is obtained at 15.40. The highest ΔE value at a concentration of 10 g/L chitosan was higher than the ΔE value at different amount of concentrations. Spurred mangrove dye with a concentration of 10 g/L resulted the ΔE value at 16.26; baheda gave

value at 18.97; then mangrove obtained the result at 10.87; continuing with mahogany led to the ΔE value at 14.01; and lastly, copperpod could reach the ΔE value at 19.33.

The amine group in chitosan affect the increase of the dye amount which was absorbed into the cotton fabric and created empty sites to be filled with tannin (Mehrparvar *et al.*, 2016; Singh and Sheikh, 2020; M.el-Zawahry *et al.*, 2021). The cotton fabric had a low affinity with the dye since both of them had the negative charges (anion) in the solution. At that point, chitosan which had positive one (cation) began to be a mordant for fabrics by creating bonds between anion and cation under acidic conditions. Therefore, in this study, it's functioned as a bridge between the cotton fabric and tannins. (Xiao, 2018) and formed hydrogen bonds with a cotton fabric and ionic bonds with dyes (Zhou *et al.*, 2020). Figure 8 show the chemical bond mechanism between cotton, chitosan, and tannin.

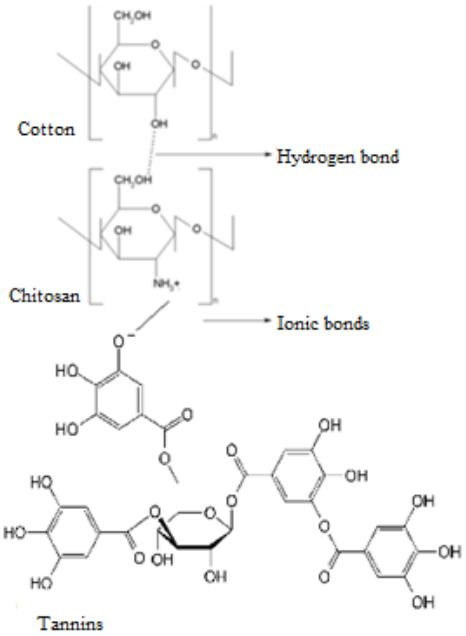


Figure 8. Chemical bonding structure between cotton fabric, chitosan, and tannin

Sunlight Fastness Results

The analysis of sunlight fastness or resistance of the fabric dyed was stated as the greyscale value. The test results are presented in Table 3. The fabric dyed with natural dyes and treated without chitosan reached the fastness value with a greyscale scale of 2-3 to 3 which imply sufficient values. However, in the same kind of dyed fabric which was through the chitosan mordant process showed the increase of the fastness value of 4 to 4-5, which imply good fastness towards the sunlight.

Table 3. Fastness Resistance Test Results

Natural Dyes	Sunlight Fastness	
	Untreated	Chitosan
Betel nut	2 – 3 (Fair)	4 (Good)
Spurred mangrove	3 (Fair)	4 (Good)
Baheda	3 (Fair)	4 – 5 (Good)
Mangrove	3 (Fair)	4 – 5 (Good)
Mahogany	3 (Fair)	4 – 5 (Good)
Copperpod	2 (Bad)	4 (Good)

CONCLUSIONS

The use of chitosan can increase the dye absorption cotton dyeing with natural dyes of tannins from various sources. In the dyeing process with chitosan concentration of 10 g/L, betel nut succeeded in reaching the ΔE value at 15.40; then, spurred mangrove could obtained 16.26; after that baheda reached 18.97; next, mangrove succeeded in getting the ΔE value at 10.87; continuing with mahogany could raise the ΔE value at 14.01; and the last, copperpod got the ΔE value at 19.33. Furthermore, chitosan also increases the sunlight fastness, test obtained a *greyscale* value in range of 4-5 (good).

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