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Extract of *Centella asiatica* Leaves as a Biomordant in Cotton Dyed with Natural Dye *Bixa orellana*

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Abstract. Natural dyeing is a promising process to reduce environmental pollution caused by the use of synthetic dye. Seed of *Bixa orellana* (Kesumba) contain bixin compound which can be extracted to give a beautiful orange color in textile. The application of *B. Orellana* seed extract to textile, especially cotton, is limited by their low color fastness. To help dye fixed in cotton fiber, mordant from metal salt is usually applied, but metal based mordant can promote severe pollution to the environment. In this study, extract of *B. orellana* seed was used as a natural dye and extract of *Centella asiatica* leaves (Pegagan) were used as a biomordant in cotton dyeing. Both raw materials were extract using water as a solvent. Tannin contained in *Centella* leaves could give a mordanting effect in cotton. Influence of *Centella* concentration (50, 150, 250 gr/L) and pH (4, 6, 8) during mordanting process (fixation) were studied and were compared with the use of Alum mordant. Response Surface Methodology (RSM) with the help of Minitab 16. Was used for optimization of the mordanting process. Color strength (K/S), wash fastness and light fastness property of each sample were evaluated. Functional group present in samples dyed were analyzed with Fourier Transfer Infra-Red (FTIR). In general, mordanting with *Centella* leaves extract can increase wash and light fastness (scale 3 to 3-4) of dyed sample without losing orange color character of *Bixa,* compared with non-mordant sample (3). Mordanting in pH 8 give highest color strength K/S, followed by pH 4 and pH 6. This whole process of dyeing and mordanting with natural resource will conduct the development of sustainable technology in textile industry.

INTRODUCTION

The use of environmentally friendly and sustainable both material and process in all industry are gaining popularity. In textile industry, development of natural dyeing is of interest. *Bixa orellana* (also popular as achiote, annatto and kesumba) has been known as a colorant plant, native to tropical America. *Bixa* seeds extract can gives beautiful orange color shade coming from orange pigment (bixin, norbixin, and others carotenoid). Bixin is fat soluble and norbixin is hydrosoluble [1]. *Bixa* extract are mostly used in food industry (butter, margarine and cheese). Application in textile dyeing however, is still small. Bixin has weak affinity for adsorption onto fiber. To overcome this problem, mordanting process (pre and post mordant) using metallic mordant are commonly applied.

Mordant could improve dyeing properties by enhance chemical interaction between dye and metal. Metal and dye could bind each other through coordination bond to form complex. The size of this complex is bigger than the dye alone, thus it could attach stronger onto fiber due to its more insolubility. However, employing metallic mordant in dyeing can promote severe environmental problem and health problem in the textile user [2]. Finding alternatives mordant which more ecofriendly is necessary.

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(a) (b)

FIGURE 1. Fruits of *B. orellana* (a) and Leaves of *C. asiatica* [3] (b)

Biomordant are natural material that contain metal ion(s), tannin, tannic acid, etc. that acts as a mordant in natural dyeing. Biomordant source is either plant with high tannin contain or metal hyper accumulating plant. Several biomordant was successfully employed in natural dyeing (almond shell extract [4,5], pomegranate extract [6], acacia, hena and turmeric [7]).

Tannins are water soluble polyphenolic compounds of higher molecular weight (about 500-3000) containing phenolic hydroxyl groups, with the ability to form effective crosslink between protein and other macromolecules. Tannins play an important role in cotton dyeing to retain coloring matter permanently [8]. Tannin can be classified as hydrolysable tannins (gallotannins) and condensed tannins [9].

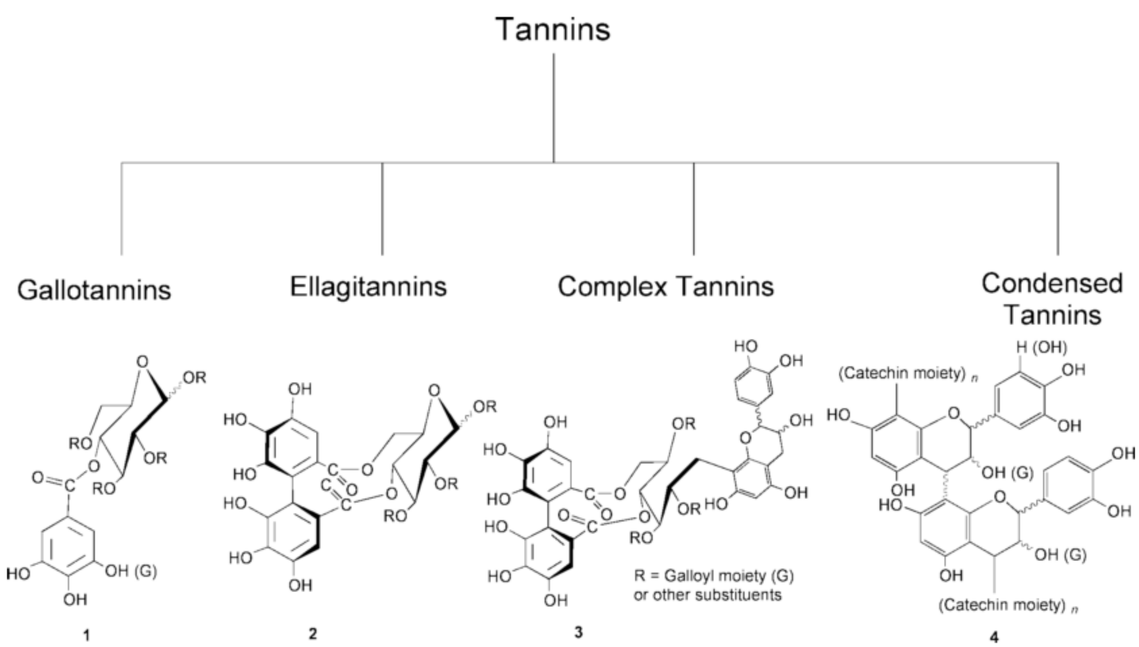

FIGURE 2. Classification of tannins [9]

Centella asiatica is a native plant of Indonesia that belongs to family of Apiaceae. The plant extract is rich of tannins, flavonoid, phenolic, and various active compounds [10]. The polyphenols in *Centella* found to be 150 mg tannic acid/100 g of *Centella* [11].

The main objectives of this study are to study the potential of *Centella* leaves extract to be used as biomordant, to reveal alternatives to metallic mordant in dyeing of cotton fabric using *Bixa* seed extract. Mordanting process was done after dyeing (post-mordanting). The effect of concentration of *Centella* extract and pH of mordanting process to the color strength (K/S) and fastness properties (wash and light fastness) was studied. Color strength (K/S) as a response variable was evaluated using response surface methodology (RSM).

MATERIAL AND METHODS

Materials

C. asiatica leaves, *B. orellana* seeds, cotton (Primisima), aquadest, sodium hydroxide (NaOH, Sigma), citric acid ($C_6H_8O_7$, technical food grade), *Turkey Red Oil* (TRO), and alum (or tawas in Javanese) ($Al_2K_2(SO_4)_4$). Detail plant used in this research is in Tabel 1.

TABLE 1. Plant Specification

	Natural dye	Bio mordant
Common name	Kesumba, Annatto, Achiote	Pegagan
Botanical name	*Bixa orellana*	*Centela asiatica*
Kingdom	Plantae	Plantae
Order	Malvales	Apiales
Family	Bixaceae	Apiaceae
Used part	Seeds	Leave

Methods

Extraction of color from Bixa Orellana seeds and Dyeing

Seeds of *B. orellana* were collected from fresh fruit and then extracted with water in ratio of 1:6 kg seed/l water. The extraction process was carried at temperature of 60°C for 2 hours. The solution was then filtered to separate the extracts and residues. The filtrate was then called a natural dye solution and used for dyeing.

Cotton fabric was weighed then soaked in 1 gram/L TRO solution to remove the dirt, with material to liquor ratio (MLR) 1:50 for 30 minutes then dried. Cotton were dyed with the extract solution with MLR 1:20 at room temperature for 15 minutes then air dried. The dyeing cycle was repeated 3 times.

Biomordant preparation and mordanting

Different mass of Pegagan leaves (50, 150 and 250 grams) were cleaned with water and then cut into small pieces. Each sample was taken in a flask filled with 1 liter of aquadest. Extraction was carried out by squeezing the leaves for 20 minutes at room temperature and then filtered. The filtrate was then called biomordant solution. The mordanting process were carried out at different pH condition (4,6, and 8) in each mass of leaves extracted, by adding citric acid and sodium hydroxide solution (0.5 M) to control the pH. Alum solution was made with a concentration of 50 g/ L of aquadest at room temperature until all alum dissolved. The mordanting were done by dipping the fabric for 15 minutes in each mordant solution with MLR 1:20 for 15 minutes, and then air dried.

Determination of Color Fastness

Light fastness of dyed sample was test according to AATCC 16e-2004 method. Wash fastness was test according to ISO 105-C06:1994 (2010). The dyed sample were evaluated in term of color scale using grey scale.

Determination of Color Strength

The measurement of color strength expressed as K/S was done using the Kubelka-Munk equation (Equation (1)).

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

where K is the absorption coefficient, R is the reflectance of dyed sample, and S is scattering coefficient. The reflectance of dyed fabric was measured with spectrophotometer (Shimadzu, UV-2401-PC, instruction manual ISR-2200).

Optimization of mordanting process

The present work involves optimization of different parameters governing the mordanting process. Optimization have been done using Response surface methodology (RSM). RSM can evaluate multiple parameter and their interaction. It can also reduce the number of experiments [12].

In this study, the optimization of mordanting process was carried out by two chosen independent varibles including concentration of *Centella* leaves and pH of mordanting. The range and levels of variables are given in Table 2. The responses of the system were color strength (K/S) and fastness (wash and light fastness). The quadratic equation model was expressed to Equation (2).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} {x_i}^2 + \sum_{i=1} \sum_{j=1+1} \beta_{ij} x_i x_j + e \quad (2)$$

where

Y response (dependent variable)

β_0 constant coeeficient

β_i β_{ii} β_{ij} coefficient for the linear, quadratic, and interaction effect

x_i x_j factors (independent variables)

e error

Two factors were studied, and their low and high levels are given in Table 2. Minitab 18 was used for regression and graphical analysis of the data obtained. Scheme of experiment and the result were done according to the design in Table 3.

TABLE 2. Experimental range and levels of independent process variables

Independent variable	**Range and levels (ceded)**		
	-1	**0**	**+1**
Centella concentration (gr/L) [A]	50	150	250
pH mordanting process [B]	4	6	8

RESULTS AND DISCUSSION

Bixa seeds extract contain bixin, norbixin and others carotenoid. Around 80% of total colorant in extract is bixin. Extraction of *Bixa* seeds in water should maintained in temperature below 100°C because in above 100°C, the color will change from orange to yellow [1].

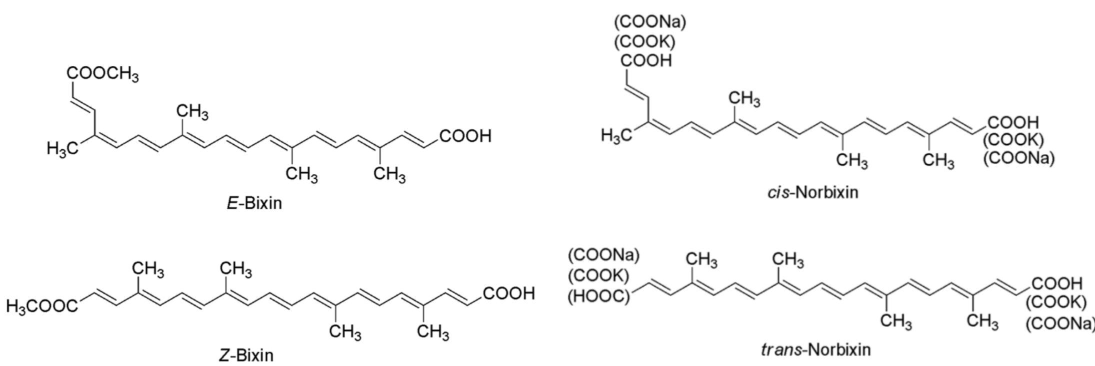

FIGURE 3. Chemical structure of bixin and norbixin [1]

Interaction between bixin and norbixin to cotton substrate are proposed through hydrogen bonding (H and OH). Hydrogen bonding is weaker compared to covalent or electrostatic bond, as a result, wash fastness of *Bixa* dye in cotton without mordanting is still low (scale 3).

Tannin has the ability to precipitate protein and other macromolecules. Tannin content in extract *Centella* leaves could act as mordant by promote formation of complex between dye and tannin to form macromolecule. Complex formed has bigger molecules, resulting higher insolubility of dye in cotton which lead to have better fastness.

Mordanting cotton dyed with *Bixa* were carried out with different *Centella* leaves concentration (50, 150, and 250 gr/L) and at different pH (4, 6, and 8). Working in too acid or basic condition lead to fiber damage. Mordanting with *Centella* extrat depends on both independent variables. The results of this experiment are shown in Table 3 and Figure 4 and 5. Compared with unmordant sample, wash fastness of sample mordanted with *Centella* were higher, although still lower than alum mordant. Light fastness for all sample were almost in the same level (scale 3), unless sample mordanted with *Centella* concentration of 150 and 250 gr/L, both in pH 8.

TABLE 3. Design for two independent variables used in this study

Run no.	Coded value		Real value		Wash Fastness	Light Fastness	Reflectance (R%)	K/S
	A	B	A	B				
Undyed							98.82	0.000
Dyed no mordant							75.85	0.038
Dyed Alum mordant							88.47	0.008
Centella mordant								
1	-1	-1	50	4	3	3	77.45	0.033
2	-1	0	50	6	3-4	3	82.27	0.019
3	-1	+1	50	8	3-4	3	75.87	0.038
4	+1	-1	250	4	3-4	3	85.03	0.013
5	+1	0	250	6	3-4	3	83.13	0.017
6	+1	+1	250	8	3-4	3-4	80.39	0.024
7	0	-1	150	4	3-4	3	79.33	0.027
8	0	0	150	6	3-4	3	83.71	0.016
9	0	+1	150	8	3	3-4	74.68	0.043
10	0	0	150	6	3-4	3	84.21	0.015
11	0	0	150	6	3-4	3	79.73	0.026
12	0	0	150	6	3-4	3	86.50	0.011

Experimental design and statistical analysis

The present work involves optimization of different parameters governing the mordanting process. Optimization have been done using Response surface methodology (RSM). An empirical relationship between the response and independent variables has been expressed by the following quadratic model. The quality of the model fit was expressed by the correlation coefficient R^2, and its statistical significance was confirmed using the p value. The closer the value of R^2 to 1, the higher the quality of the model fit. P value less than 0.05 demonstrate a high significance for the model [13]. In this model, R^2 value was 0.84% which is close to 1. However, p value is only 0.186 which is higher than 0.05. This indicates the significance of the model is still low. Based on the model, the optimum K/S (0.392) is achieved in *Centella* concentration of 101.17 gr/L and pH 8.

$$K/S = 0.1207 - 0.0355\, pH + 0.000035\, concentration + 0.00308\, pH^2 + 0.000007\, pH * concentration \quad (3)$$

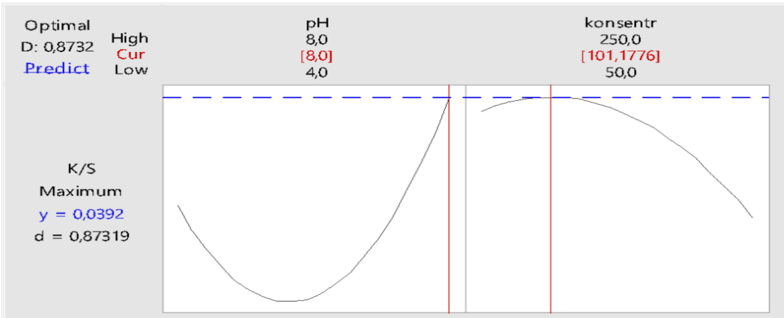

FIGURE 4. Response prediction using quadratic model in RSM

TABLE 4. Analysis variance of binominal fitting model for color strength (K/S)

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	5	0,000743	0,000149	3,17	0,186
Linear	2	0,000387	0,000193	4,12	0,138
pH	1	0,000171	0,000171	3,64	0,153
Concentration	1	0,000216	0,000216	4,60	0,121
Square	2	0,000348	0,000174	3,71	0,155
pH*pH	1	0,000304	0,000304	6,48	0,084
Concentration*Concentration	1	0,000044	0,000044	0,93	0,406
2-Way Interaction	1	0,000009	0,000009	0,19	0,691
pH*Concentration	1	0,000009	0,000009	0,19	0,691
Error	3	0,000141	0,000047		
Total	8	0,000884			

Effect of *Centella* concentration and pH of mordanting process on K/S

The contour plot and response surface of Fig.5 showed combined effect of *Centella* concentration and pH of mordanting process. It is observed that color strength (K/S) increased with the increasing pH but not with increasing concentration. Concentration and pH that gave best K/S was in a range of 50-180 gr/L and 7-8. It is showed that mordanting using high concentration of *Centella* extract would result in lower color strength. This could be because green color of *Centella* extract would decrease color strength.

In acidic pH, K/S was found higher than in neutral condition. Above pH 7, K/S increased as pH increasing. In acid and basic condition, the number of ionic site increase [14]. Increasing ionic site will promote increasing of interaction between biomordant and natural dye, which lead the formation of larger molecule complex.

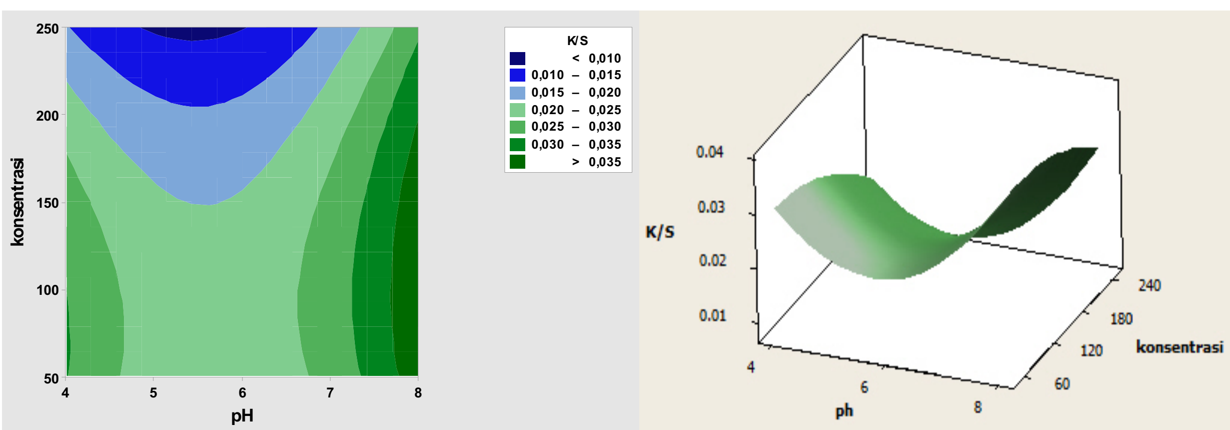

FIGURE 5. Contour plot (a) and response surface (b) showing the interaction effect of concentration and pH in mordanting process

Characterization of the cotton dyed with *Bixa* seeds extract and mordant with *Centella* leaves extract

The functional group of five samples were analyzed using FTIR. As shown in Fig 6., the sample analyzed were unmordant, mordant with alum, and mordant with *Centella* extract (concentration 250 gr/L) but in different pH (4,6, and 8). The FTIR spectral analysis of all sample show distinct peak at 3430 cm^{-1}, 2906 cm^{-1}, 1640 cm^{-1}, 1430 cm^{-1}, 1371 cm^{-1}, 1282 cm^{-1}, 1162 cm^{-1}, 1115 cm^{-1}, 1058 cm^{-1}, 667 cm^{-1} and 611 cm^{-1} respectively.

The strong and broad peak at 3430 cm^{-1} can be attributed to –OH group, which could be from cellulose and phenolic group in tannins. The peak at 2906 cm^{-1} can be assigned to –C-H bond stretching absorption of cellulose [15]. The strong peak at 1640 cm^{-1} represent –O=C stretching in carboxyl group [16]. This group both represent in bixin and tannins structure. Bending vibration at 1432 cm^{-1} and 1372 cm^{-1} were attributed to $–CH_2$ and $–CH_3$ groups. The presence of C-O-C stretch was appeared at 1371 cm^{-1} and 1282 cm^{-1} [17]. The peak at 1000-1300 cm^{-1} can be attributed to the stretching of C-O-C group of cellulose [15]. Variation of pH in mordanting using *Centella* resulted similar peak.

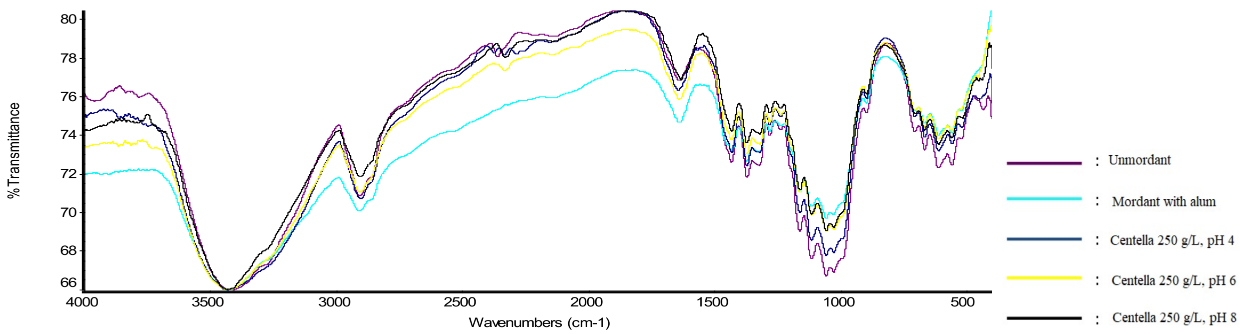

FIGURE 6. FTIR spectra of cotton dyed with seed in various mordant

CONCLUSIONS

This study showed that *Bixa* seeds extract can be used as natural dye for cotton. *Centella asiatica* leaves can be successfully applied as biomordant with better wash and light fastness properties compared to unmordant cotton. Concentration of biomordant and pH of mordanting process are important factor to achieve high quality color strength. Maximum color strength was observed at concentration 101.17 gr/L and pH 8. Under these conditions, the color strength of cotton dyed was estimated to be 0.0392. Further exploration in mordanting condition, like temperature and time of mordanting, using *Centella asiatica* is required.

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