

# Development of Eco-friendly Dyeing Process Based on *Caesalpinia sappan* L. Bark, *Cocos nucifera* Fiber and *Leucaena leucocephala* Leaves

N. Kusumawati<sup>a,\*</sup>, M.M. Sianita<sup>a</sup>, A.B. Santosa<sup>b</sup>, Supari Muslim<sup>b</sup>, A.R. Sella Auliya<sup>c</sup>

<sup>a</sup> *Departement of Chemistry, Universitas Negeri Surabaya, Ketintang, Surabaya, 60231, Indonesia*

<sup>b</sup> *Departement of Electrical Engineering, Universitas Negeri Surabaya, Ketintang, Surabaya, 60231, Indonesia*

<sup>c</sup> *Departement of Chemistry, Airlangga University, Mulyorejo, Surabaya, 60115, Indonesia*

Corresponding author: \*nkusumawati82@yahoo.com

**Abstract**—Natural dyes have begun to regain attention due to biodegradable nature and low negative impact on human health and the environment. Besides, the continuous development of color shades variants from several natural sources of newly available abundant natural dyes and their ability to produce high color intensity and high wash fastness has become a major consideration of their use in textile dyeing. This study has evaluated the potential utilization of *Caesalpinia sappan* L bark, *Cocos nucifera* fiber, and *Leucaena leucocephala* leaf as a single and combination natural dye material. In particular, the extracts of these natural dye materials are used to dye the cotton fibers by involving mordanting stages using alum and fixation using iron (II) sulfate, alum, and calcium oxide compounds. The quality of the resulting dyeing was evaluated by the intensity of the color and wash fastness against wet washing. The dyeing results showed the appearance of varied shades of color with the dominance of the typical reddish color of *Caesalpinia sappan* L. While the results of the analysis using *Diffuse Reflectance Ultraviolet* (DRUV) and the wash fastness using the staining scale method showed high color dyeing with the color intensity in the range 53.55% - 94.34% with wash fastness in the staining scale range 2 (less) – 4 (good). Specifically, in contrast to the behavior of dye AB, the AC staining scale increases with increasing dye C added (up to 50%) and decreases when dye C added increases to 75% (dye AC3).

**Keywords**— Textile; natural dyes; *Caesalpinia sappan* L; *Cocos nucifera*; *Leucaena leucocephala*.

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## I. INTRODUCTION

Over the past few years, many industries, particularly the textile industry, have been heavily criticized for their role in polluting the environment [1], [2]. This is directly related to the textile industry's use of large amounts of synthetic dyes [3]–[5]. Several synthetic dyes facts that are considered more economical have superior fastness properties, varied color shades, and greater reproducibility has become the main background of the dominance of the synthetic dyes used in various industries [6]–[8]. However, dyeing using a large number of synthetic dyes is known to have the potential to produce a toxic waste that negatively affects the aquatic ecosystem and has mutagenic, carcinogenic, and toxicological properties in human health [9]–[13]. In the increasing phenomenon of environmental destruction and deterioration of the world's public health quality, environmentally friendly non-toxic natural dyes reappear as a choice of 'Green

Chemistry' as a substituent/complement of synthetic dyes to some extent [14]. In recent years, large-scale research [15]–[17] has been undertaken globally to explore the natural dye preparation procedures from a variety of sources, both plants, animals, and minerals as well as optimizing its utilization by suppressing its limitations on textile fiber dyeing.

Nowadays natural dyes primarily derived from plants; because of its abundant availability, biocompatibility, low toxicity, green approaches, and eco-friendly properties have gained worldwide popularity for use in textiles [18]–[21]. Natural dyes can be obtained from the extraction of certain parts of the specific plant [22]–[28], such as roots, rhizomes, seeds, bark, leaves, flowers, or fruit. Many plant parts such as *secang* (*Caesalpinia sappan* L.) bark, coconut (*Cocos nucifera*) fibers, and *lantoro* (*Leucaena leucocephala*) leaf can be used as a source of natural dyes [29]–[33].

Water-soluble *braziline flavonoids* are the main source of red dye on *Caesalpinia Sappan* Linn. or *Sappanwood* (family

Leguminosae) [34]–[36]. The extract has been used extensively as a natural dye, especially in the textile industry due to its low toxicity and low cost [37]–[39]. *Sappanwood* extracts in addition to functioning as a natural red dye, also show great benefits as antibacterial agents [38], [40]–[42], antioxidants [38], [43]–[45], and pharmacological activity [46]. Also, *braziline* is easily oxidized by light to form a very red *brazilein* [35], [38]. Characterization with UV-Vis spectroscopy and  $\mu$ -spectrofluorimetry revealed that in its acid form, *brazilein* chromophores provide maximum absorption, excitation, and emission respectively at wavelengths of 446, 475 and 536 nm and 540, 548 and 560 nm when deprotonated. When complexed with  $Al^{3+}$  the wavelength values are changed to 510, 520, and 585 nm, respectively.

*Cocos nucifera* or coconut fiber has fiber with a strong structure that is not easy to rot or moldy and durable [45], [47]. Indonesia is the biggest coconut-producing country in the world [48]. But unfortunately, coco fiber processing has not been done optimally, where every year only 15% of the total abundance of processed coconut husk, while the rest will be left to accumulate as waste that will eventually dry up and then burned [49]. This condition is unfortunate, considering coconut husk is part of the coconut husk that can be used as a natural dye because of the flavonoid type water-soluble tannin content. This dye will give off a reddish-brown color and gradation depending on the type of mordant and fixer compound used [50]. Characterization with UV-Vis spectroscopy revealed that *Cocos nucifera* fiber extract provides maximum absorption at wavelengths of 385.41 nm and 380.79 nm when complexed with  $Al^{3+}$ .

*Leucaena leucocephala*, commonly called *petai china*, is a kind of shrub from the Fabaceae family (Leguminosae, legumes). *Leucaena leucocephala* is a plant that is easy to find in the tropics, such as Indonesia. Similarly, with coconut husk, *Leucaena leucocephala* leaf material has not been used as much of the fruit that is widely used as a raw material of traditional Indonesian food. This material contains many phenolic compounds in high concentrations, especially types of *tannins* and *mimosine*, making it a potential natural dye material. As with most tannins, tannin chromophores in *Leucaena leucocephala* leaf will also produce a reddish-brown color and a gradation, according to the type of mordant and fixer applied [51], [52]. Characterization with UV-Vis spectroscopy revealed that *Leucaena leucocephala* leaf extract provides maximum absorption at wavelengths of 417.84 nm and 387.50 nm when complexed with  $Al^{3+}$ .

Dyeing using natural dyes is generally accompanied by several problems such as narrow shade range and lower fastness. The utilization of mordant compounds is one effort that can be done to overcome these problems. In addition to increasing the affinity between the dye compound and the fabric fibers, the application of mordant may cause hue changes of a number of specific dyes. Application of different mordant types to the same dye compound can darken, brighten, or alter the final color significantly [53], [54]. The colorimetric properties of the dyeing results including lightness ( $L^*$ ), redness-yellowness ( $a^*$ ), blueness-greenness ( $b^*$ ), chroma ( $c^*$ ), hue ( $h^\circ$ ) and color strength (K/S) are strongly influenced by the chemical properties, both mordant and fiber compounds and the forming ability of metal

complexes with dyes and fibers [55]. Mordanting is generally capable of improving dye performance by producing a wide spectrum of shades on a variety of natural fibers as well as synthetic fibers with increased color intensity and fastness [56], [57].

One of the colored fabric qualities can be seen from the fastness. Besides mordanting optimization, fixation is another way that can be done to improve fastness through the color locking process on fiber. Fixation is generally done by adding metal complex materials, such as iron (II) sulfate ( $FeSO_4 \cdot 7H_2O$ ), aluminum sulfate, or alum [ $Al_2(SO_4)_3 \cdot 18H_2O$ ] and calcium oxide (CaO). However, the application of the fixation process in the final stages after dyeing also has the potential to darken, brighten, or alter the color significantly as it does with mordanting. This is triggered by the presence of several chromophores in the fixer compound used, which will lead to the appearance of a specific hue when the absorption of light occurs [58]–[61].

The current research focuses on producing dyed fabrics using red pigments from *sappanwood* extract and reddish-brown producing pigments from *Cocos nucifera* fiber and *Leucaena leucocephala* leaf extract separately and as a combination dye. This study is the first report on the dyeing carried out by combining the *braziline* and tannin compounds, the two dominant pigments in the three raw materials used. To find out the effect of both pigments' combination on the quality of cotton dyeing, the color production is done through the use of composition 75%/25%; 50%/50%; and 25%/75% both for a combination of *sappanwood* bark extract with *Cocos nucifera* fiber and *Leucaena leucocephala* leaf extract. Meanwhile, the color production using a 100% composition in *sappanwood* bark, *Cocos nucifera* fiber, and *Leucaena leucocephala* leaf extract was applied as a comparative color needed to determine the extension of the color spectrum resulting from the pigment combination process. Besides, achieving optimum color strength and creating a wide colors spectrum is done by forming bridge compounds between cotton and pigment using mordant alum, which has aluminum as a central atom with a three-valence positive charge application color-locking using 3 types of fixer compounds. Furthermore, the interaction between fabric fibers, mordant alum, combinations of pigments, and fixer compounds, which have not been previously reported, have been investigated. An analysis of the effect from three different fixer compound uses was also performed to determine the suitability of interactions between pigment combinations with fixers in generating color spectrum expansion and increased strength and fastness.

## II. MATERIAL AND METHOD

### A. Washing Process

Cotton fibers to be dyed must go through a washing process to remove contaminants attached. Thus, the appeal of mordant alum to fabric fibers increases. The following procedure does the washing of cotton fibers. The 2.57-gram cotton fiber is immersed in a 2 gram/liter Turkey Red Oil (TRO, Dunia Kimia, Indonesia) solution for 6 h. Furthermore, three times were rinsing using distilled water to remove the mordant residue that does not interact with cotton fibers. The cotton fiber washing procedure was ended by drying the cotton fibers in the open air for 24 hours [3], [11].

### B. Mordanting Process

After going through the washing stage, the cotton fiber preparation process continues with the mordanting using aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , Brataco Chemistry, Indonesia) and soda ash ( $\text{Na}_2\text{CO}_3$ , Water, Indonesia). The mordant solution is made by dissolving 8 grams of alum and 2 grams of soda ash in 1 liter of distilled water. The stirring process using a magnetic stirrer was applied to ensure the homogeneity of the solution. The solution is then heated to boiling, and into it is added 2.57 grams of cotton fiber. The process of heating process continued for 1 hour. To optimize the interaction that occurred with alum mordant, cotton fibers were left submerged in a mordant solution for 24 hours. In the next step, cotton fibers are rinsed (not squeezed) three times and then dried and ironed. Ironing of cotton fibers is done to get a uniform fiber orientation. After that, the cotton fibers are ready to be dyed using natural dyes [3], [11].

### C. Dyeing Process

After going through the washing and mordanting, cotton fibers are ready to be dyed using water extract of *Sappanwood* bark (Dwi Jaya, Indonesia), *Cocos nucifera* fiber (Berkah, Indonesia), and *Leucaena leucocephala* leaf (Bengawan Solo riverbanks, Indonesia). Table 1 shows the operational conditions for the dyeing [11], while Table 2 shows the natural dyes extract compositions.

TABLE I  
THE OPERATIONAL CONDITIONS FOR DYEING PROCESS

	Condition
Material to liquor	1/35 (gram/mL)
Temperature	Room temperature
The weight of cotton fiber	0.85 gram
Dyeing time	50 minutes

TABLE II  
THE NATURAL DYES EXTRACT COMPOSITIONS

	Compositions (wt.%)		
	<i>Sappanwood</i>	<i>Cocos nucifera</i>	<i>Leucaena leucocephala</i>
A	100	0	0
B	0	100	0
C	0	0	100
AB1	75	25	0
AB2	50	50	0
AB3	25	75	0
AC1	75	0	25
AC2	50	0	50
AC3	25	0	75

### D. Fixation Process

To improve the fastness of natural dyes, after going through the staining stage, the cotton fibers must go through fixation using three types of fixers, including iron (II) sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , Nusa Indah Megah, Indonesia), alum, and calcium oxide ( $\text{CaO}$ , Mitra Water, Indonesia). The fixer solution was prepared by dissolving 50 grams of each fixer material in 1 liter of distilled water. The solution was allowed to age for 24 hours and then from the solution was taken a transparent solution. The fixation process is carried out by immersing the cotton fibers in the fixer solution for 10 minutes. To determine the resulting color difference, a fixation of 0.85 grams of cotton fibers was performed in 30

mL of iron (II) sulfate, alum, and calcium oxide solution respectively. In the next step, each cotton fiber is rinsed three times using distilled water and then dried in the open-air [11].

### E. Characterization

To determine the pigment characteristic in the water extract from *Sappanwood* bark, *Cocos nucifera* fiber, and *Leucaena leucocephala* leaf, wavelength analysis was done with maximum electromagnetic wave absorption Pharmaspec UV-1700 UV-Visible Spectrophotometer. The maximum wavelength region ( $\lambda_{\text{max}}$ ) will show the dominant pigment contained in the water dye extract of each raw material. Each dye's CieLab coordinates ( $L^*$ ,  $a^*$ ,  $b^*$ ) were directly measured using a *spectrophotocolorimeter* (*Tintometre*, Lovibond PFX 195 V 3.2, Amesbury, UK). In this coordinate system, the  $L^*$  value is a measure of lightness, ranging from 0 (black) to 100 (white); the  $a^*$  value ranges from -100 (greenness) to +100 (redness) and the  $b^*$  value ranges from -100 (blueness) to +100 (yellowness). Besides, at this stage, cotton fiber also analyzed the intensity and fastness to determine the quality of the colors resulting from the combination of pigment and three different fixer compounds. Color intensity analysis was performed using Shimadzu Diffuse Reflectance Ultraviolet (DRUV) UV-2401-PC Spectrophotometer, while the fastness analysis was performed using the staining scale method. The higher color intensity will generally result in lower reflection percentages in the analysis results using DRUV.

## III. RESULTS AND DISCUSSION

### A. Dyes Extract Characterization

A, B, and C dyes, each prepared as cotton fiber pigments by extracting dyes from *Sappanwood* bark, *Cocos nucifera* fiber, and *Leucaena leucocephala* leaf. Consequently, A dyes exhibit characteristic properties of the red-pink color of *brazilein flavonoids*, which appear as red chromophores as oxidized forms of *braziline* from *Sappanwood* bark (Fig. 1a). The red-pink color with maximum wavelength at 538.57 nm, as shown in Fig. 3a, is red ( $a^*$ ) higher than 19.00 (Table 1). Meanwhile, B and C dyes exhibited characteristic properties with a typical reddish-brown tannin flavonoid, as shown in Fig. 1b and Fig. 1c. However, compared to *Cocos nucifera* extract, *Leucaena leucocephala* extract showed a darker color. Also, the occurrence of reddish-brown *Cocos nucifera* showed redness in color ( $a^*$ ) for 12.16. The redness in color values is lower than *Leucaena leucocephala*, which has a  $a^*$  value of 17.40.

The UV-Vis spectrum of the AB1 dye extract shows the maximum absorption at the wavelength 538.34 nm with a bathochromic shift (0.23 nm) of the A dye wavelength. Theoretically, adding 25% tannins of the B dye has led to the increasing quantity of chromophores and auxochrome in the AB1 dye. However, what should be noted is that the increase in tannin levels in AB dye will occur along with a decrease in *brazilein* levels and based on the results of the analysis it is suspected that there is a close relationship between the molecular size and the success of the fiber in binding dye molecules. The larger the size of the dye molecule is predicted to increase the barriers to fabric fibers to maximize the binding of the dye molecules. As shown in Fig. 2 (a), the molecular structure of *brazilein* has 2 types of chromophores

(C=C and C=O) and 2 types of auxochrome, ie -OH and C-O. Meanwhile, in Fig. 2 (b) it appears that although it has the same chromophore and auxochrome properties, the tannin molecular structure exhibits the higher quantity of the corresponding chromophores and auxochrome. The quantity of chromophores and auxochromes increases with increasing tannin levels to 50% and 75%, as found in AB2 and AB3 dyes, respectively. The increase in the number of chromophores and auxochromes is predicted to be capable of inducing an increase in the number of electronic transitions, especially those involving the non-bonding orbital ( $n \rightarrow \pi^*$ ) and  $n \rightarrow \sigma^*$ , which leads to a shift maximum wavelength and shades of color that appear. However, the higher effect of space difficulties that arise along with the increase in tannin content, which reaches its peak in the composition of the AB2 dye has triggered conditions where the bond formed between the fabric fibers and dyes molecules becomes minimum to produce a brighter color accompanied by lower redness ( $a^*$ ) and yellowness ( $b^*$ ). The opposite phenomenon was detected when tannins dominated the AB3 dye extract. Increased tannins accompanied by decreased levels of *brazilein* appear to produce brighter shades, but with increasing levels of redness and yellowish. Thus, it can be reported that comparable levels of *brazilein* and tannins in the AB dye extract will produce a mutually nullifying effect. Slightly different from the conditions caused by the addition of tannins from *Cocos nucifera* extract, the addition of tannins from the *Leucaena leucocephala* extract, as seen in the AC1-AC3 dye composition, shows a lower magnification (0.02 nm) shift of the A dye wavelength. The condition is predicted to be triggered by mimosine pigment, which produces a complementary effect with tannins in the dye. This complementary effect is getting stronger because of the smaller molecular size of mimosine, which reduces the effect of space difficulties, which can inhibit the binding of dye molecules by fabric fibers. The presence of mimosine, with the molecular structure as shown in Fig. 2 (c), in AC1-AC3 extract has enriched the auxochrome variety of AC1-AC3 dyes, wherein the molecular structure of mimosine has N-H chromophores absent in AB1-AB3 dyes. This is the cause of the difference in bathochromic shifts that occur in AC1-AC3 dyes when compared to AB1-AB3 dyes. The condition also shows that in addition to increasing orbital quantities, the presence of mimosine has enriched the number of chromophores and the quantity and variety of auxochromes involved in the electronic transition of AC1-AC3 dyes when adsorbing light energy. These conditions make mimosine as one inducer of a larger bathochromic shift in AC1-AC3 dyes. This condition is following the color look of the extract is getting closer to the typical brown tannin.

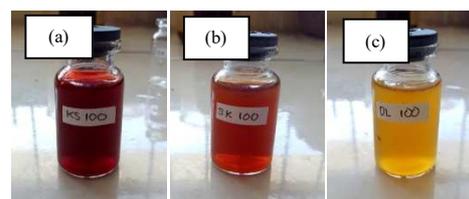


Fig. 1 Scheme of (a) *Sappanwood* bark; (b) *Cocos nucifera* fiber; (c) *Leucaena leucocephala* extract

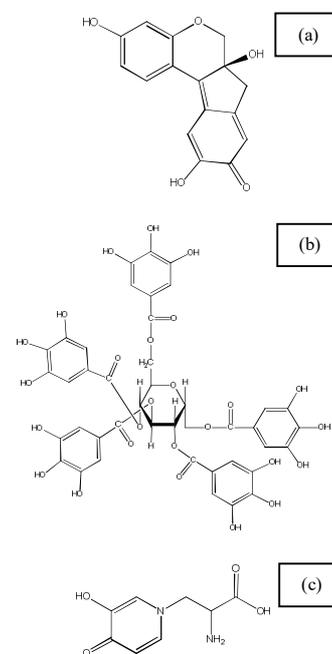
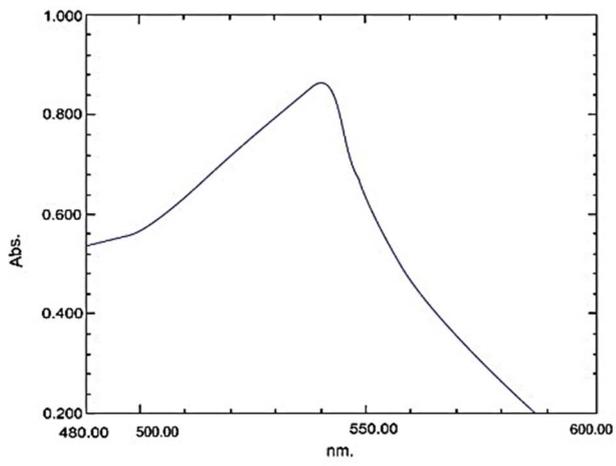


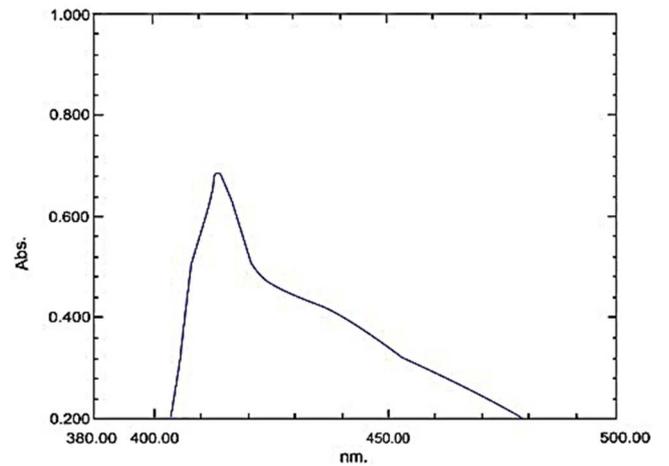
Fig. 2 Scheme of (a) *brazilein*; (b) *tannin*; (c) *mimosine* molecular structure

### B. UV-Visible Spectra

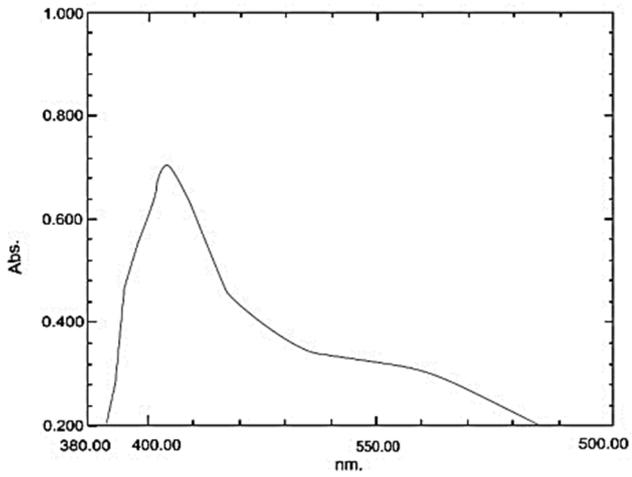
The UV-Vis spectrum of *Sappanwood* bark (A) dye extract showed  $\lambda_{max}$  at 538.57 nm. These results confirm the presence of *brazilein* pigment in the *Sappanwood* bark extract. These results correspond to  $\lambda_{max}$  data of *brazilein* flavonoids at 540 nm reported by the ref. [28]. Meanwhile, the UV-Vis spectrum analysis results of *Cocos Nucifera* fiber and *Leucaena leucocephala* leaf extract showed the maximum absorption at 384.41 nm and 417.84 nm. The difference in maximum wavelength between *Cocos Nucifera* fiber and *Leucaena leucocephala* leaf extract has strengthened the prediction of the presence of mimosine pigment as a complement of tannin in C dye extract. Fig. 3 shows the UV-Vis spectra of the A, B, C, AB1-AB3, and AC1-AC3 dye extracts.



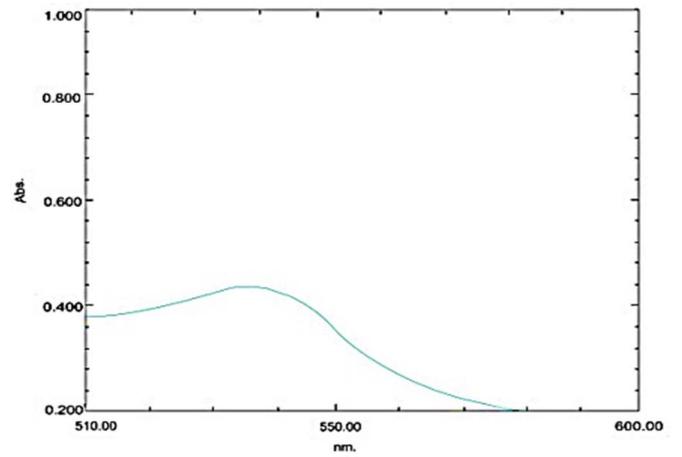
A



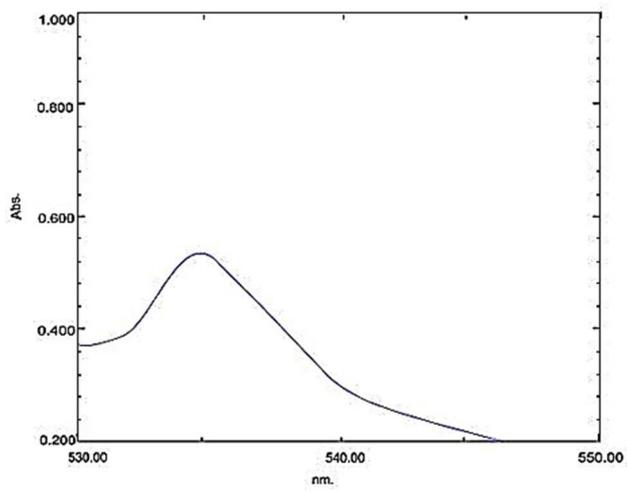
B



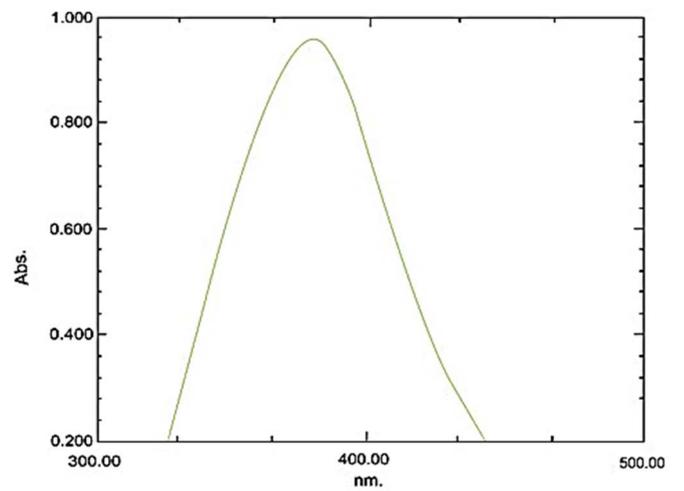
C



AB1



AB2



AB3

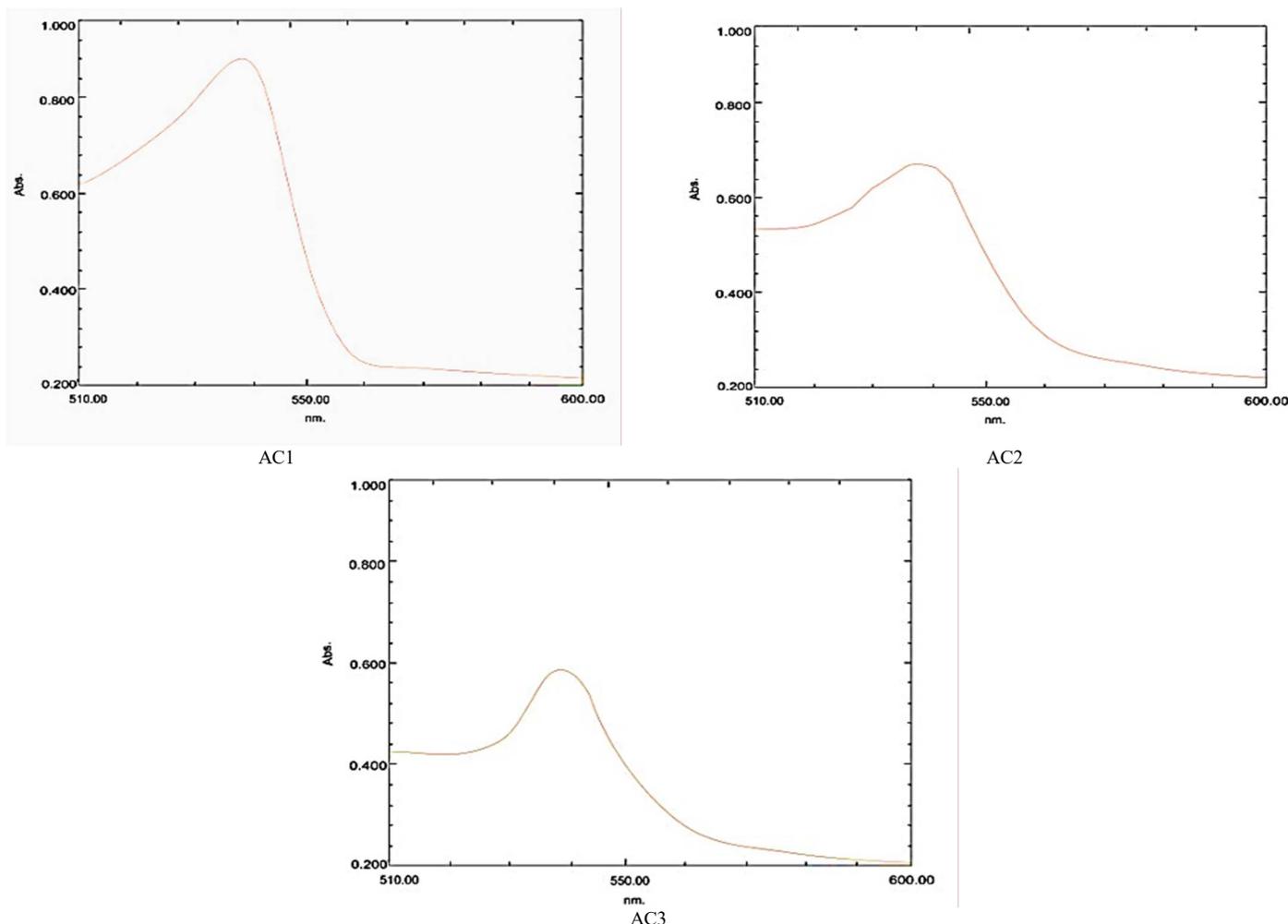


Fig. 3 UV-Visible spectra of dyes

Table 3 shows the colorimetric parameters of different compositions of dyes extract. The colorimetric analysis results showed that elevated levels of tannin pigment from *Cocos nucifera* fiber extract on AB1-AB3 dyes had resulted in a decrease in the brightness value from 47.34 in A dye, being respectively of 41.35 in AB1. It is closely related to the bathochromic events or maximum absorption shifts to higher wavelength regions triggered by an increase in the number of chromophores and auxochrome occurring as a result of tannin pigment added from *Cocos nucifera* to then synergize with *brazilein* pigment from Sappanwood bark extract. The same trigger has induced an increase in redness and yellowness value along with an increase in tannin content from *Cocos nucifera* fiber extract into *Sappanwood* bark extract. In general, almost the same phenomenon is detected in AB3 dyeing results. However, balanced levels of *brazilein* and tannin pigments in AB2 dyes have given rise to a mutually nullifying effect that minimizes the number of bonds between fabric fibers with both pigments, which increases the color brightness accompanied by a decrease in redness and yellowness compared to the colors produced by AB1 and AB3 dyes or when one of the pigments dominates. In detail, the results of dyeing using AB2 dye have brightness 49.95 with the  $a^*$  and  $b^*$  notation values of 24.80 and 9.22, which are 9.90% and 29.18% lower compared to the  $a^*$  and  $b^*$  color

notation values produced by AB1 dyes; and 20.89% and 54.56% lower than AB3 dyes.

TABLE III  
COLORIMETRIC PARAMETER OF DIFFERENT DYES COMPOSITIONS

	CieLab Coordinate			
	L*	a*	b*	dE*ab
A	47.34	19.02	6.97	56.25
B	78.42	12.16	28.64	37.68
C	69.00	17.40	37.20	51.27
AB1	41.35	27.26	11.91	65.61
AB2	49.95	24.80	9.22	56.46
AB3	52.57	29.98	14.25	57.75
AC1	52.80	23.67	6.22	53.03
AC2	64.64	29.68	16.69	48.98
AC3	64.06	27.74	15.64	47.89

Note : L\* : brightness; a\* : (red = +ve, green = -ve); b\* (yellow = +ve, blue = -ve)

The corresponding conditions were detected in the analysis results of the AC1-AC3 colorimetric parameters. Brightness value ( $L^*$ ) of AC1-AC3 dye showed an increasing trend along with elevated levels of tannin from *Leucaena leucocephala* leaf extract added to *Sappanwood* bark extract. However, as described in the preceding section, the presence of mimosine pigment as a tannin complement in *Leucaena leucocephala* leaf extract has triggered an increase in the number of chromophores as well as the quantity and diversity of auxochrome which is bonded to the fabric fibers and induces

less significant maximum wavelength shifts in AC1-AC3. However, in contrast to the dyeing phenomenon by AB2, the results of dyeing using AC2 dyes produce an increase in brightness, accompanied by an increase in the  $a^*$  and  $b^*$  notation values compared to AC1. The decrease in brightness, although not significant, together with a decrease in the notation values of  $a^*$  and  $b^*$  was only detected after an increase in tannin and mimosine levels in the dye reached the maximum (AC3). The decrease in CieLab coordinate in this condition is thought to be closely related to the minimum presence of brazilein pigment in the AC3 dyes, which has led to a decrease in the resulting redness and yellowness color. More specifically, this is reinforced by the results of the analysis showing the more dominant level of redness of AB3 and the yellowness level of AC3 dyes.

### C. Fourier Transform Infra-Red Spectroscopy

To confirm the presence of red-pink chromophore from brazilein, the FT-IR spectrum showed adsorption at wavenumbers  $1635.71 \text{ cm}^{-1}$  from C=C aromatic stretching (Fig. 4 and Table 4). Based on these adsorptions, the FT-IR analysis confirmed the presence of chromophores C = C. Meanwhile, the presence of auxochromes -OH in the brazilein structure has been confirmed by the appearance of respective absorption at wavenumbers  $3265.86 \text{ cm}^{-1}$ . The absorption details arising from the analysis of FT-IR A dyes are shown in Figs. 4 and Table 4.

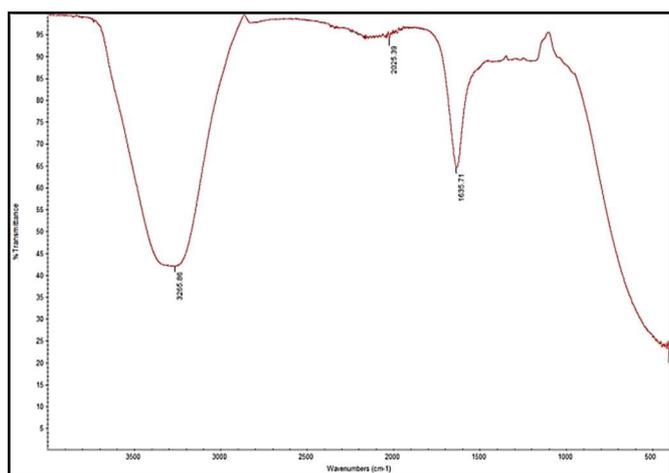
In addition to brazilein, FT-IR analysis was also applied to confirm the presence of reddish-brown chromophore from tannins, both in B and C dyes. Specifically for C dye, the FTIR analysis has been very useful for confirming the predicted presence of mimosine pigments as tannins complement the extracts. The FT-IR result of B dye shows that the absorption does not differ significantly from A dye. The absorption at wavenumber  $1636.05 \text{ cm}^{-1}$  of C=C aromatic stretching has confirmed the presence of heterocyclic compounds with the

aromatic ring of the tannin molecule. These of FT-IR FTIR result has also confirmed the presence of C=C chromophores of tannin molecules. Meanwhile, the emergence of -OH and -CO auxochromes in tannin molecular structure has been confirmed by peak incidence at wavenumbers  $3265.04 \text{ cm}^{-1}$  and  $2154.48 \text{ cm}^{-1}$ . The only characteristic differentiation between brazilein and tannin is a peak that appears at wavenumber  $2154.48 \text{ cm}^{-1}$  which indicates the presence of C-O functional groups typical of the ester group.

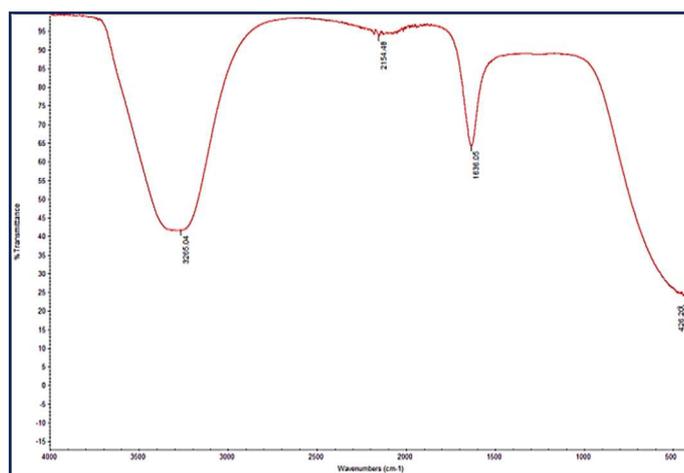
Especially for the results of C dye analysis, the appearance of the peak in wave number  $1636.19 \text{ cm}^{-1}$  indicates the presence of C=C chromophore and N-H auxochrome. This result further strengthens the results of the DRUV and UV-Vis spectrophotometers analysis which show a lower bathochromic shift to the maximum wavelength of the A dye. The condition has triggered the appearance of C dye that has lower brightness as well as higher redness and yellowness values than the B dye. This is closely related to the similarity of the chromophores and auxochromes quantity between A dye and C dye compared to that of B dye. This has induced the similarity of the electronic transitions occurring in A dye and C dye as compared to the B dye when adsorbing light.

TABLE IV  
FT-IR VIBRATION ASSIGNMENT OF DYES

Vibration assignment	Wavenumber ( $\text{cm}^{-1}$ )				
	A	B	C	AB1	AC1
-OH	3265.8 6	3265.0 4	3279.5 7	3269.2 0	3281.7 3
C=C stretch, aromatic	1635.7 1	1636.0 5	1636.1 9	1633.2 7	1635.7 2
N-H ( $1^\circ$ amine)	-	-	1636.1 9	-	1635.7 2
C-O ester	-	2154.4 8	2129.9 7	2147.8 8	2162.9 5



A



B

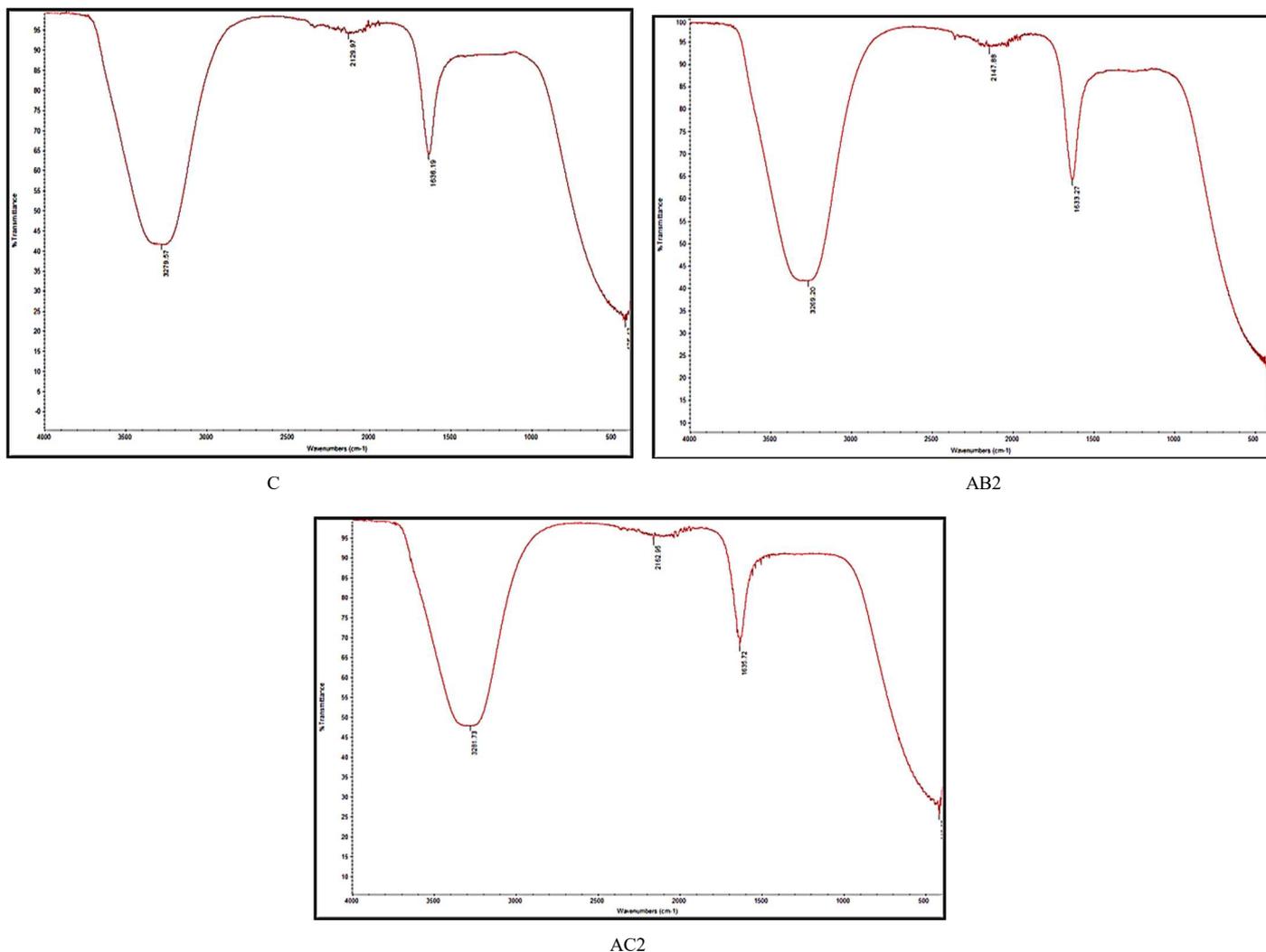


Fig. 4 FT-IR spectra of dyes

#### D. Diffuse Reflectance Ultraviolet (DRUV)

The effect of the dye composition on the variety of shades, strength, and fastness was studied by varying the B and C dye as the mixture of the A dye which became the main dye in this study (with a ratio of 75/25; 50/50; 25/75) and by using 3 types of fixer compounds to enrich the original shades of the *Sappanwood* bark extract. Fig. 5 and Fig. 6 show the shades and reflectance values of the colors produced by each color combination and type of fixer. In general, higher reflection percentages will result in higher color intensity.

Implementation of dyeing ending with the fixation process using three different fixer compounds proved to have enriched the shades produced by the A dye. The physical appearance of the dyeing results in Fig. 5 shows the appearance of dark brown for fixation with iron (II) sulfate and red for both other fixation, alum, and calcium oxide. The combination of the presence of specific chromophores and auxochromes from dyes and fixers used is predicted to induce the appearance of specific colors from the use of each fixer. Fig. 7 appear different types of chromophores in the three fixer types of compounds used. In fixer iron (II), sulfate and alum appear to have S=O chromophore and S-O auxochrome, whereas there is only 1 type of chromophore in the calcium oxide fixer, ie Ca=O. The only difference between fixer iron (II) sulfate and

alum is in the higher quantity of chromophore and auxochromes in the alum fixer.

Different patterns of influence emerged from the application of three different types of fixers to dyeing using B and C dyes. The dyeing results using B dye indicate the appearance of blackish brown, light brown, and dark brown resulting from the use of fixers iron (II) sulfate, alum, and calcium oxide. Similar to the results, dyeing using C dye denotes the appearance of gray, light yellow, and yellow in color resulting from the use of fixers iron (II) sulfate, alum, and calcium oxide. Despite having the same pigment content, B and C dyes show the appearance of different shades, though not significantly. This is closely related to the presence of mimosine pigment as a differentiator of pigment content in B and C dyes. Besides, the presence of mimosine pigments in addition to tannins in C dye has induced the appearance of similar colors with higher brightness and yellowness and lower redness values in C dye compared with B dye. This finding is relevant to the results of the colorimetric parameters and DRUV analysis shown in Table 5 - Table 7. More specifically, the DRUV data have shown a lower reflectance percentage of the shades produced by the C dye, both terminated by fixation using iron (II) sulfate, alum, and calcium oxide.

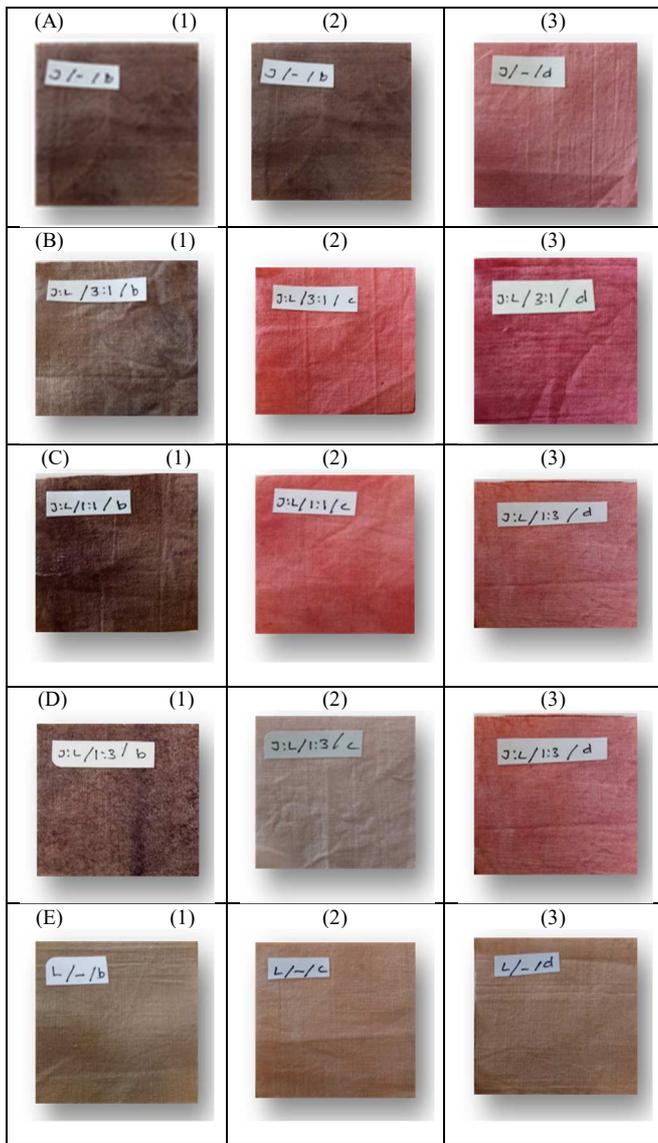


Fig. 5 Physical appearance of : (a) A; (b) AB1; (c) AB2; (d) AB3; (e) B dyes with fixer : (1) iron (II) sulfate; (2) alum; and (3) calcium oxide

When adding more B dye to A dye, each cotton fiber sample gives shades of light brown, light red, and pink colors that fade respectively on the dyeing result fixed with an iron (II) sulfate, alum, and calcium oxide fixer, as shown in Fig. 5. This condition indicates that the addition of B dye with various compositions has tended to enrich the shades of A dyes produced through the creation of shades gradations predicted due to the interaction competition between brazilein pigments from A dye and tannin pigments from B dye. Increases in B dyes levels in the dye composition will produce shades with a lower brightness for dyeing, which ends with fixation using iron (II) sulfate, while the application of alum and calcium oxide fixers results in increased brightness shades. This finding is relevant to the results of the colorimetric parameters analysis shown in Table 5 and the color reflectance shown in Table 7. Overall, increases in the B dye amount added have been shown to increase the percentage of reflectance from the dye. This condition shows a decrease in color intensity in dyeing with increasing tannin levels.

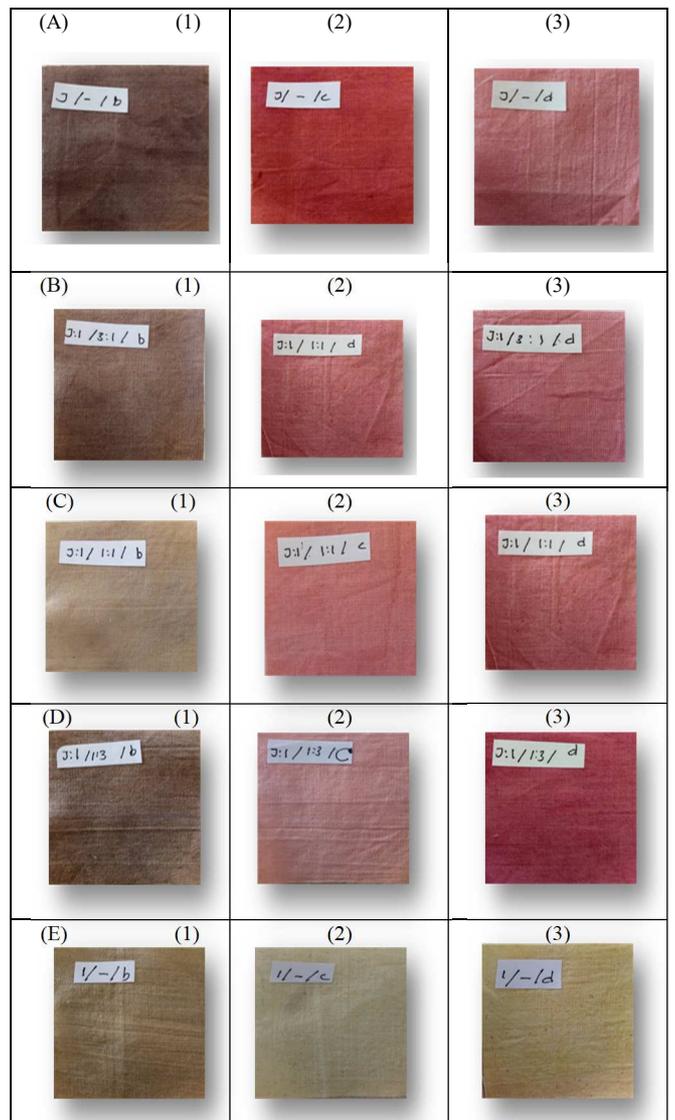


Fig. 6 Physical Appearance of : (a) A; (b) AC1; (c) AC2; (d) AC3; (e) C Dyes with Fixer: (1) iron (II) sulfate; (2) alum; and (3) calcium oxide

Similar to the results obtained from the combination of A and B dyes, the result of an A and C dyes combination has triggered the appearance of the shades of blackish brown, dark pink, and light pink that fade respectively on the dyeing result fixed with an iron (II) sulfate, alum, and calcium oxide fixer, as shown in Fig. 6. This condition indicates that the addition of C dye with various compositions has tended to enrich the shades of A dyes, which produce through the creation of shades gradations predicted due to the interaction competition between brazilein pigments from A dye and combination of tannin and mimosine pigments from C dye. Increased levels of C dye used in dyeing give varying results in CieLab coordinate. On the results of dyeing using AC which ends with fixation using iron (II) sulfate detected to give color shades increasing brightness, while the use of alum and calcium oxide fixers, each of which results in the emergence of color shades with stable and decreasing brightness. This finding is relevant to the results of the colorimetric parameters analysis shown in Table 5 and the color reflectance shown in Table 6. In general, increases in the C dye amount added have been shown to increase the percentage of reflectance from the

dye. This condition shows a decrease in color intensity in dyeing with increasing tannin and mimosine levels.

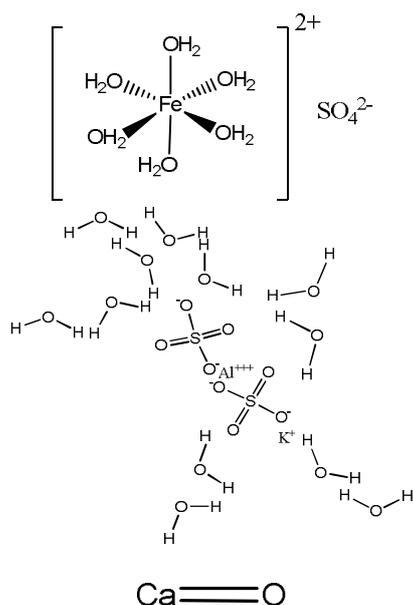


Fig. 7 The molecular structure of the fixer: (a) iron (II) sulfate; (b) alum; and (c) calcium oxide

TABLE V  
A COLORIMETRIC PARAMETER OF DIFFERENT DYES COMPOSITIONS AND FIXER

	CieLab Coordinate			
	L*	a*	b*	dE*ab
A – Iron (II) sulfate	53.00	5.92	4.80	53.55
A – Alum	54.49	26.40	12.70	61.87
A – Calcium oxide	67.49	22.43	12.64	61.87
B – Iron (II) sulfate	62.76	6.16	14.90	64.80
B – Alum	74.99	14.50	24.50	80.21
B – Calcium oxide	85.29	9.94	22.47	88.76
C – Iron (II) sulfate	68.76	5.90	19.13	72.62
C – Alum	83.84	1.18	31.80	89.67
C – Calcium oxide	81.09	2.62	41.40	91.08
AB1 – Iron (II) sulfate	43.08	6.79	7.13	44.19
AB1 – Alum	52.74	39.91	20.26	69.18
AB1 – Calcium oxide	44.32	29.90	9.09	54.32
AB2 – Iron (II) sulfate	38.19	7.09	9.25	39.93
AB2 – Alum	56.98	36.36	21.03	70.79
AB2 – Calcium oxide	53.51	23.26	9.92	59.20
AB3 – Iron (II) sulfate	31.28	7.81	8.52	33.35
AB3 – Alum	87.90	12.41	12.20	89.60
AB3 – Calcium oxide	60.65	28.57	15.35	68.78
AC1 – Iron (II) sulfate	56.00	6.83	11.23	57.52
AC1 – Alum	67.58	32.23	17.27	76.83
AC1 – Calcium oxide	67.59	22.11	11.00	71.95
AC2 – Iron (II) sulfate	70.97	6.08	14.39	72.67
AC2 – Alum	67.56	34.75	20.60	78.71
AC2 – Calcium oxide	65.46	23.08	10.17	70.16
AC3 – Iron (II) sulfate	49.90	5.74	7.14	50.74

AC3 – Alum	67.32	33.03	29.48	80.57
AC3 – Calcium oxide	42.09	29.26	8.16	51.91

Note : L\* : brightness; a\* : (red = +ve, green = -ve); b\* (yellow = +ve, blue = -ve)

TABLE VI  
DRUV OF THE DYES WITH DIFFERENT COMPOSITIONS

	Reflectant (%)	Intensity (%)
A	8.31	94.34
B	42.77	59.88
C	26.29	76.36
AB1	11.51	91.14
AB2	15.94	86.71
AB3	12.67	89.98
AC1	28.94	73.71
AC2	28.11	74.54
AC3	37.17	65.48

TABLE VII  
THE REFLECTANCE OF DYES WITH DIFFERENT COMPOSITION AND FIXER TYPE

	Reflectant (%)	Intensity (%)
A – Iron (II) sulfate	23.36	79.29
A – Alum	14.94	87.71
A – Calcium oxide	21.76	80.89
B – Iron (II) sulfate	18.01	84.64
B – Alum	36.47	66.18
B – Calcium oxide	33.81	68.84
C – Iron (II) sulfate	16.70	85.95
C – Alum	30.89	71.76
C – Calcium oxide	23.86	78.79
AB1 – Iron (II) sulfate	10.15	92.50
AB1 – Alum	21.79	80.86
AB1 – Calcium oxide	17.77	84.88
AB2 – Iron (II) sulfate	28.13	74.52
AB2 – Alum	30.80	71.85
AB2 – Calcium oxide	31.41	71.24
AB3 – Iron (II) sulfate	23.69	78.96
AB3 – Alum	28.99	73.66
AB3 – Calcium oxide	49.10	53.55
AC1 – Iron (II) sulfate	18.49	84.16
AC1 – Alum	40.35	62.30
AC1 – Calcium oxide	27.09	75.56
AC2 – Iron (II) sulfate	23.72	78.93
AC2 – Alum	24.57	78.08
AC2 – Calcium oxide	21.16	81.49
AC3 – Iron (II) sulfate	21.89	80.76
AC3 – Alum	30.52	72.13
AC3 – Calcium oxide	20.90	81.75

### E. Staining Scale

The wash fastness properties of the nine dyes compositions of the focus in this study are illustrated by the staining scale in Table 8(a)-(b). It appears that the original dyes, including A, B, and C dyes, each capable of inducing the appearance of specific shades with staining scale values of each are equal to 2-3 (less); 3 (enough), and 3 (enough). The wash fastness properties of the dyes are important to evaluate to determine the ability of each dye to maintain its existence in the mixture through competition with its companion dye in interacting with the alum mordant, which mediating the interaction between the cotton fibers and the dye.

Compared with B and C dyes, A dye has the lowest wash fastness. In the early stages of adding B dye to A dye (AB1 dye), the dye staining scale value is constantly detected at the value/range 2-3 (less). The constant value of this staining

scale continues to hold up to 50% of the B dye added to the mixture (AB2 dye). The increase in staining scale values begins to appear in the addition of 75% of the B dye into the mixture (AB3 dye). By comparing the staining scale values of A and B dyes as the origin dyes of this combination, it can be seen that tannin pigment (B dye) competitiveness is superior to that of brazilein pigment in A dye.

The pattern of color behavior appears on the dyeing results using a combination of A and B dyes, both of which then ends with fixation using iron (II) sulfate, alum, and calcium oxide. The appearance of shades is strongly influenced by the mutually supportive or mutually exclusive properties between the chromophores and the auxochromes, which are either owned by dyes or fixers. This is evidenced by the same pattern of similarity formed between the AB1 and AB2 dyes terminated by fixation using all three types of fixers used with the result of A dye with the same three fixer types. Similarly, the resultant dye behavior produced by the AB3 dye having similarities to the B dye produced from the same fixer. This finding is in line with the similarity of the three colorimetric parameters (brightness, redness, and yellowness) produced by AB1 and AB2 dyes with A dye and AB3 dye with B dye.

The evaluation result of the C dye addition to the A dye (AC dye) shows that when into the A dye is added a small amount of C dye (AC1 dye), the staining scale value of the dye is constantly detected at the value/range 3 (enough). However, in contrast to the behavior of the AB dye, the staining scale has increased with increasing C dyes added (up to 50%) and has decreased when the C dyes added raise to 75% (AC3 dye). This condition is predicted to occur due to the presence of mimosine pigment as a tannin complement in the C dye. As has been explained previously, the presence of mimosine pigment, one of which has enriched the auxochrome variety, through the presence of the -CN and -NH bonds. The presence of nitrogen atoms with high electronegativity will tend to strengthen the interaction with mordant alum and minimize the potential of staining scale decrease in dyeing results using this type of dye. This suggests a synergistic or mutually reinforcing effect between chromophores and auxochromes, both owned by brazilein as well as tannins and mimosine pigments. This finding is also in line with the physical appearance of AC1, AC2, and AC3 dyes, which still show similarities with the A dye through the emergence of typical gradations of brazilein pigment. This result is reinforced by the similarity of the brightness, redness, and yellowness values, as shown in Table 5, between the dye A with the AC1, AC2, and AC3 dyes.

The better behavior is shown by the wash fastness resulting from AB and AC dyes with iron (II) sulfate as fixers compounds. However, the opposite phenomenon can be observed from wash fastness, which decreases when dyeing ends with fixation using alum and calcium oxide. Thus, the use of three different fixers is not only influential on the shades variation and colorimetric parameters, but also the wash fastness. The wash fastness is influenced by the strength of interaction, either between fabric fibers with mordant alum, mordant alum with specific dye, or dye with each type of fixer used. However, if further investigated, the application of iron (II) sulfate fixer as soon as the dyeing process is completed is detected capable of producing the best wash fastness through the appearance of a specific shade with the highest staining

scale value, ie 4 (good). To provide a more complete illustration of the interactions that occur in the dyeing process using *Sappanwood* bark, *Cocus nucifera* fiber, and *Leucaena leucocephala* leaf extract, in Fig. 8- Fig. 16 appears interaction between cotton fiber, mordant, pigment, and each type of fixer.

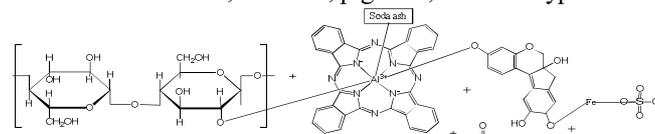


Fig. 8 The interaction of the dyeing process using brazilein pigment with iron (II) sulfate fixer

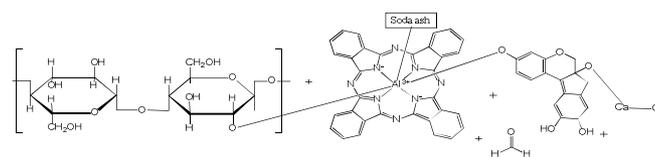


Fig. 9 The interaction of the dyeing process using brazilein pigment with alum fixer

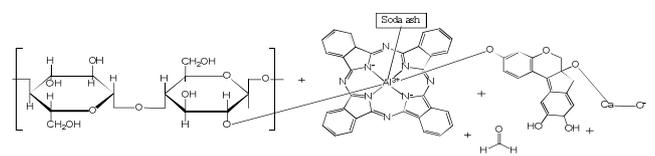


Fig. 10 The interaction of the dyeing process using brazilein pigment with calcium oxide fixer

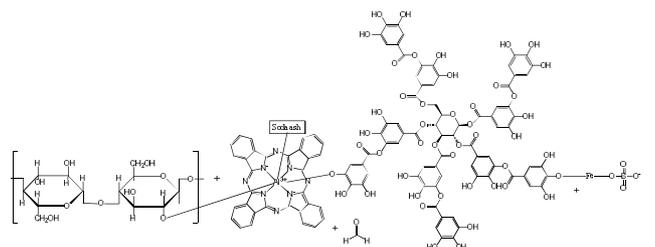


Fig. 11 The interaction of the dyeing process using tannin pigment with iron (II) sulfate fixer

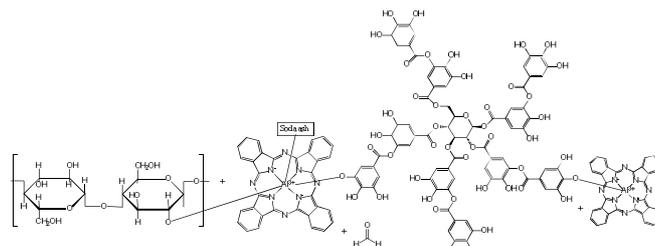


Fig. 12 The interaction of the dyeing process using tannin pigment with alum fixer

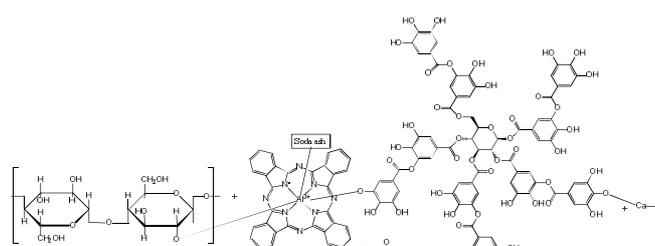


Fig. 13 The interaction of the dyeing process using tannin pigment with calcium oxide fixer

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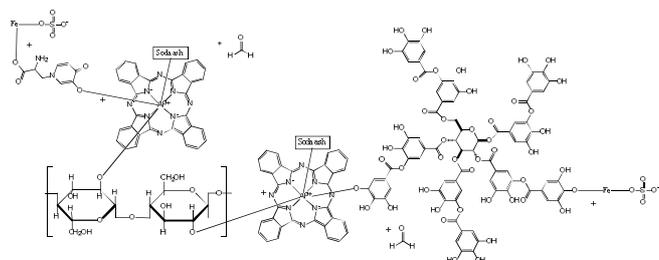


Fig. 14 The interaction of the dyeing process using tannin and mimosine pigment with iron (II) sulfate fixer

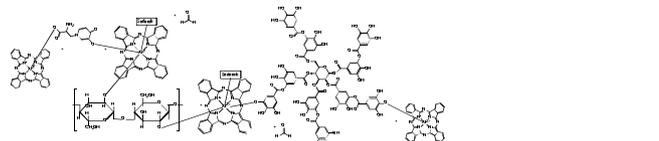


Fig. 15 The interaction of the dyeing process using tannin and mimosine pigment with alum fixer

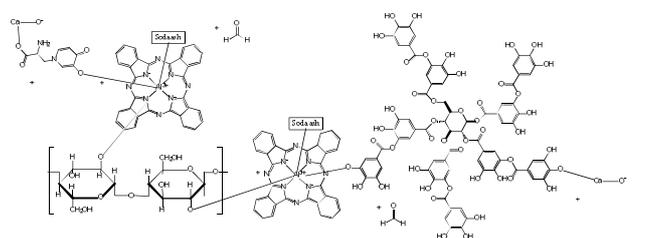


Fig. 16 The interaction of the dyeing process using tannin and mimosine pigment with calcium oxide fixer

## IV. CONCLUSIONS

The cotton dyeing in this study was carried out using natural dyes from an extract of the *Sappanwood* bark, *Cocus Nucifera* fiber, and *Leucaena leucocephala* leaf. It was found that all three had maximum absorption at 540 nm; 384.41 nm; and 417.84 nm; which confirmed the presence of brazilin pigments in the *Sappanwood* bark extract tannins on the extract of *Cocus Nucifera* fiber and *Leucaena leucocephala* leaf. In addition to tannins, mimosine pigment is detected as a tannin companion in *Leucaena leucocephala* leaf extract characterized by detection of wavelength differences wherein extract of *Cocus nucifera* fiber *Leucaena leucocephala* leaf is capable of producing maximum absorption. Increased levels of *Cocus Nucifera* fiber extract in combination with *Sappanwood* bark have resulted in specific results on color percentage reflectance, brightness, redness, and yellowness. This condition is associated with an increase in the type and quantity of chromophores and auxochromes in a combination of brazilin and tannin pigments. It has been the same for dyeing using a combination of brazilin pigment with tannin and mimosine from *Leucaena leucocephala* leaf extract. This condition is associated with the presence of mimosine pigment in addition to tannin in *Leucaena leucocephala* leaf extract, which has improved the quality of interaction, especially with mordant alum to improve the quality of the resulting dyeing. In addition to the dye composition, applying three different fixer types to this dyeing process has enriched the shades and produced specific colorimetric parameters with significantly affected wash fastness.

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