Use of *Tectonagrandis* Leaf Extract in Colouring Silk Cloth Material Based on pH and Mordant Variations

A Rosyida¹,² and Suranto¹

¹Department of Environmental Science Graduate Program, Universitas Sebelas Maret, St. Ir. Sutami 36 A Kentingan Jebres Surakarta 57126, INDONESIA, ²Textile Chemistry Program. Akademi Teknologi Warga, St. Raya Solo Baki, Km 2, Kwarasan Solo Baru Sukoharjo 57552, INDONESIA.

E-mail: kenur.rosida@gmail.com

Abstract. One of the very potential use of plant natural colour in the industrial activities was Anthocyanin. This substance contains in a number on plant organs such as *Tectona Grandis* (Fabaceae) particularly in their leaf materials. In order to get this secondary metabolism, the aim of this research was to find out the optimum condition of mordant and the pH combination in producing natural colour of *Tectonagrandis* leaf extract. To get this chemical substance, 1 kilogram of young leaves were cut into smaller size and soaked in 7 litre of H₂O for 12 hour⁹. The solution was then boiled for 15 minutes. To get the best colour, variations of pH (5, 7 and 9) respectively were applied. The results showed that purple to redness were resulted when pH 5 and no additional mordant was added. Conversely the greyness to black, were produced when ferrosulphate were added. When the addition of alum was made the redies purple will appear. These colours were considered quite good quality under examination of grey and staining scales (4-5) after treated by both wet and dry rubbing methods. The test for wash fastness resulted in sufficiently good value of color change (value of 3 on Grey Scale standard), while test for staining demonstrated good staining (value of 4 on Staining Scale standard). This early finding was quite promising to be applied in the near future in providing natural colours for industrial purposes.

1. Introduction

As one of countries with abundance of sufficiently potential natural resources, Indonesia presents itself as a powerful country in the provision of nature-derived raw materials. However, the management of the natural resources has not yet been maximal, whereas in fact, they were traditionally managed by our ancestors. Natural dye plants belong to natural resources potential to be used for textile dye in Indonesia, particularly for development of natural, imitive, cultural, and exclusive products, as well as for raw materials with high economic value in textile industries. Now days, sources of natural dyes have been being obtained from such parts of plants as barks, fruit, flowers, timbers, leaves, and roots. In addition, natural dyes can also be derived from fungi, algae, bacteria [1]. However, after synthetic dyes had been invented in 1856 by W.H. Perkins, they started to be widely used [2]. Synthetic dyeing techniques are shifting to the use of natural dyes due to easier process and various yielded colors.

It is estimated that more than 10,000 different synthetic dyes all this time has been being used in industries and more than 7 x 10⁵ tons of synthetic dyes is produced in all over the world every year [3]. Based on sequence and production volume, azo dyes are the most widely produced coloring
substances, with the percentage of 60-70% of all coloring substances produced all over the world [4], but they have toxic effects, particularly carcinogenicity and mutagenic occurrence [5]. The increase in needs of synthetic dyes will be comparable to the rise in water and soil pollution, as well as in environmental pollution [6] since in textile industries, ± 200,000 tons of dyes, or ranging between 10-50% of the use, are lost to effluents every year during the dyeing and finishing operations due to the inefficiency of the dyeing process [7]. The generated liquid waste contains heavy metal which presents as the primary pollutant [8]. Several dyes are very toxic and mutagenic in nature, and their presence in aquatic environment may resist penetration of sunlight and prevent vegetative photosynthesis, leading to O2 deficiency and limiting beneficial uses of rivers such as drinking and irrigation [9,10,11]. The use of aromatic and heterocyclic dyes with complex and stable chemical structures causes the dyes to be difficult to degrade when mixed with other pollutants in wastewater [11,12]. There has been no method which is able to efficiently remove colors and toxic substances from dye containing waste water [13].

Anthocyanin contents in teak leaves serve as natural dyes which produce more various and attractive colors. Figure 1 presents a chemical structure of anthocyanins, while Table 1 demonstrates anthocyanin components [14]. The molecular structures of anthocyanins demonstrate that natural dyes extracted from teak leaves belong to unsaturated organic compounds and flavonoids. Their main structures are characterized by two benzene rings (C6H5) connected to three carbon atoms [15]. The three carbon atoms are bonded by an oxygen atom to form a ring between two benzene rings. In a solution, anthocyanins exist in equilibrium forms depending on pH condition. Such equilibrium forms include flavylium cation, carbinol base, chalcone, quinoidal base, and anionic quinoidal base. At the most acidic pH, anthocyanins exist predominantly as flavylium cation contributing to the most stable condition and colorful form. As pH increases above 4, the anthocyanins turn either yellow (chalcone), blue (quinoidal base), or colorless (carbinol base).

![Chemical structure of anthocyanins](image)

**Figure 1.** Chemical structure of anthocyanins.

The purpose of this research was to apply young teak leaf extracts as natural dyes on silk, and to find out the colors resulted from the use of various pH and different mordant. The dyeing was done by soaking at room temperature using different methods to obtain more optimal results in coloring.

2. Experimental

2.1 Materials and Methods

Plant materials: Young teak leaves were collected from Baki Sukoharjo.

Research locations: The research was conducted at finishing laboratory and evaluation laboratory of textile chemistry of AkademiTeknologiWarga of Surakarta, as well as finishing laboratory of PT. Danliris, Sukoharjo during Mei - September in 2014.

2.2 Extraction process of natural dyes

The extraction process was done by preparing 1 kg of young teak leaves collected from the forth or fifth leaf. The leaves were then whased using flowing water and chopping down into small sizes and than 7 L of water was added and boiled for 15 minutes. The solution was the leaved to dry and straining the solution to an extract.
2.3 Preparation of Mordant Solution
Mordant solution was obtained by dissolving alum/ferrous sulfate in cold water with concentration of 5g/l, and stirring constantly to perfectly dissolve the alum/ferrous sulfate.

2.4 Dyeing process
The dyeing process was done in glass beaker with vlot of 1:30. The extract solution of teak leaves was firstly put into the glass beaker and 1 cc/l of wetting substance (TRO) was added and stirred until homogeneous. After that, the silk was put into the glass beaker and processed at room temperature for 30 minutes. Next, 5 g/l of salt/NaCl was added into the solution. The dyeing was done for 45 minutes at room temperature, and then acid/alkali was added according to various pH. The dyeing was continued at room temperature for 30 minutes. The colored silk was then squeezed and fixated in the mordant (alum/ferrous sulfate) solution for 15 minutes. For nonmordant silk, after being dyed, the silk was directly washed, but for mordant silk, after mordanting, the silk was soap, washed and dried.

2.5 Testing dyeing result
Several tests carried out to samples of dyed fabrics included the test for wash fastness (SNI.080285-98), the test for rub fastness (SNI.080288-89), as well as the test for darkness of color.

3. Result and Discussion

3.1 The Results of Dyeing
The results of the experiment indicated that teak leaves contribute to purple, reddish-purple, and grayish-black colors of silk fibers due to the from anthocyanin contents. Anthocyanins give permanent colors to silk since the dyed fabrics were not proved to be discolored after frequent washing. Therefore, they could be considered to fulfill requirements to be utilized as textile dyes.

During the coloring, silk fibers are soaked in extract solution of teak leaves to stimulate the swelling of fibers, and therefore pores in the fabrics will open and anthocyanins enter the fibers. The anthocyanins will be then absorbed by and bonded with such reactive groups in fibers as amino (NH$_2$), hidroxyl (OH) and carboxyl (COOH) groups. Such bonds with silk fibers will get be more abundant and stronger after fixation using alum/ferrous sulfate than those in dyed fabrics without fixation. It is proved by the fact that fixated fabrics will have darker color and be uneasy to be discolored when being washed. Dyed fabrics without fixation will turn light purple or pink.

3.1.1 Light Fastness. The test for light fastness was performed using spectrophotometer. The results of the test revealed several measurement results, one of which is DL value, a lightness value indicating comparison between darkness/lightness of color and the used standard values. DL value can be either negative or positive. The positive value denotes that batch has lighter color than standard fabrics, while the negative value signifies that batch has darker color. The standard fabrics refer to white undyed silk.

Table 2 presents DL value of dyed silk. It is clear from the testing results that on dyeing with the addition of fixative agent/alum, purple to reddish-purple colors were obtained. On fabric samples dyed using acidic pH (5), purple silk with higher DL value than those dyed using neutral pH (7) and basic pH (9) was obtained. The fixation using alum does not result in color changes since alum (Al$_2$(SO$_3$)$_3$)$_2$ belongs to colorless chemical compound. The results of fixation itself will only strengthen previous color resulted from dyeing.

The dyeing with the addition of fixative/mordant agent ferrous sulfate resulted in grayish-black color. Different darkness levels of color of silk dyed in extracts of teak leaves will be obtained if the silk is dyed in solutions with different pH. On silk dyed in solution with acidic pH (5), a fabric with the highest DL value was obtained, while on silk dyed in solution with either neutral (7) or basic (9) pH, similar color with different darkness levels of color was obtained. On silk with no fixation, higher DL value than acidic pH was obtained.
Table 1. Reflectance of silk fabric dyed with *tectonagrandis* leaf extract.

| Type of plants | pH | Fixation treatment | Results of the test for darkness of color (DL) |
|----------------|----|-------------------|---------------------------------------------|
|                |    |                   | 1      | 2      | 3      | 4      | 5      | 6      |
| Teak leaves    | 5  | without           | -36.23 | -38.64 | -38.54 | -29.12 | -29.15 | -29.38 |
|                | 7  | fixation          | -34.84 | -37.97 | -37.84 | -29.07 | -28.41 | -29.02 |
|                | 9  |                   | -34.00 | -37.69 | -37.82 | -28.32 | -26.91 | -27.56 |
|                | 5  | Fixation using    | -45.64 | -49.86 | -48.76 | -42.30 | -38.86 | -35.79 |
|                | 7  | alum              | -44.13 | -45.13 | -44.92 | -38.52 | -37.37 | -34.89 |
|                | 9  |                   | -36.97 | -44.64 | -44.51 | -35.27 | -36.91 | -34.07 |
|                | 5  | Fixation using    | -62.82 | -63.73 | -63.93 | -58.22 | -59.69 | -54.73 |
|                | 7  | ferrous sulfate   | -57.58 | -62.23 | -62.32 | -53.73 | -58.96 | -52.67 |
|                | 9  |                   | -57.48 | -62.04 | -62.16 | -50.11 | -58.71 | -48.37 |

**Description:**
- **L** = Lightness
- **DL+** = Batch has brighter color than fabrics standard
- **DL-** = Batch has darker color than fabrics standard

Higher DL value than acidic pH is obtained since the basic solution may lead to the formation of groups allowing to form cross bonds on protein structures, in which serine residues will form a residues [16]. This may lead to a reduction in reactivity of silk fibers towards anthocyanins during the dyeing. Although the formed residues are small in number, but they exert an influence on DL value of the dyeing results.

On dyeing without fixative mordant agents, light purple or pink was obtained although the dyeing was done in different pH (5,7, and 9). Lighter color is obtained when most of the anthocyanins entering silk fibers after dyeing leave from fibers during washing process. It happens since there is no fixative agent which is able to strongly bind anthocyanins in fibers. As a consequence, the release of pigments of teak leaves can easily occur during washing.

Table 2. Color properties and shades of the silk fabrics dyed with *tectonagrandis* leaf extract.

| pH | Fixation treatment | Results of testing using spectrophotometer |
|----|--------------------|------------------------------------------|
|    |                    | 1 | 2  | 3  | 4  | 5  | 6  | 1  | 2  | 3  | 4  | 5  | 6  |
|    |                    | 1 | 2  | 3  | 4  | 5  | 6  | 1  | 2  | 3  | 4  | 5  | 6  |
| 5  | Without fixation   | Da* | Da*  | Da*  | Da*  | Da*  | Da*  | Da*  | Db*  | Db*  | Db*  | Db*  | Db*  |
| 7  | fixation           | +17.54 | +14.75 | +14.37 | +16.02 | +14.25 | +12.99 | -3.18 | -8.34 | -8.50 | -2.76 | -0.11 | -0.71 |
| 9  |                   | +18.39 | +15.05 | +15.17 | +16.74 | +14.97 | +13.65 | -5.13 | -9.15 | -9.06 | -3.44 | -0.91 | -2.22 |
| 5  | Fixation using     | Da* | Da*  | Da*  | Da*  | Da*  | Da*  | Da*  | Db*  | Db*  | Db*  | Db*  | Db*  |
| 7  | alum               | +18.90 | +16.43 | +16.30 | +16.27 | +14.31 | +13.05 | +4.36 | +0.38 | +0.50 | +5.84 | +8.20 | +6.57 |
| 9  |                   | +17.59 | +14.94 | +14.83 | +15.10 | +14.06 | +12.31 | +1.80 | +0.31 | +0.12 | +2.12 | +8.14 | +4.60 |
| 5  | Ferrous sulfate    | Da* | Da*  | Da*  | Da*  | Da*  | Da*  | Da*  | Db*  | Db*  | Db*  | Db*  | Db*  |
| 7  |                   | +14.58 | +14.91 | +14.75 | +13.92 | +13.52 | +12.12 | +0.94 | +0.64 | +0.72 | +4.39 | +8.61 | +1.45 |
| 9  |                   | +1.38 | +1.26 | +1.22 | +1.50 | +0.54 | +1.04 | -2.96 | -2.79 | -2.85 | -2.46 | -1.72 | -2.10 |
| 7  |                   | +2.05 | +1.44 | +1.35 | +1.58 | +0.47 | +1.33 | -3.01 | -2.15 | -2.60 | -2.28 | -1.68 | -1.55 |
| 9  |                   | +2.08 | +1.53 | +1.62 | +1.85 | +0.31 | +1.35 | -3.11 | -2.06 | -1.94 | -2.21 | -1.47 | -1.40 |

**Description:**
- **Da+** = red color direction
- **Db+** = yellow color direction
- **Da-** = green color direction
- **Db-** = blue color direction

Table 3 indicates color properties and shades of the dyed silk. The results of testing using spectrophotometer revealed that all of color directions indicate red (Da+). Da* value of fabrics treated either without fixation or with alum is greater, this means that the red color direction of dyed silk is stronger than that of dyed silk with smaller Da*, which is dyed silk with fixative agent of ferrous sulfate. Db* values are either negative or positive. All of dyed silk either without fixation or with
fixation using ferrous sulfate have negative values, indicating that the color direction of the dyed silk is blue. On dyed silk with fixation using alum, Db+ value shows yellow color direction.

The all experiments of dyeing silk with extract teak leaves that if fixated using different fixative agents but similar pH, silk dyed in extracts of teak leaves will result in different color and color direction. However, if fixated using similar fixative agents but different pH, same colors with different DL values will be obtained.

3.1.2 Wash Fastness. Colors resulted from dyeing are permanent. Table 4 details that the test for washing fastness on silk dyed in extracts of teak leaves with different pH and fixative agents generally resulted in almost similar Grey Scale values. On silk with fixation using alum and ferrous sulfate with different pH (5, 7, 9), value of 3 (sufficiently good) was obtained, while on silk with no fixation, colour changes value of 2-3 (less good). The mean score colour staining on silk dyed either without fixation, with fixation using alum, or with fixation using ferrous sulfate with different pH (5, 7, 9) is 4 (good), meaning that dyed silk has good value of colour staining.

Sufficiently good Grey Scale values on the test washing fastness appear due to the entrance of pigments of teak leaves (anthocyanins) contained in natural dyes during dyeing to fibers. They are then bonded and together form complex compounds. Although the bond is in the form of hydrogen bond, fixative agents enable to lock and precipitate anthocyanins in silk fibers to avoid them to release and to discolor batch during the test for washing fastness. Therefore, sufficiently good value of washing fastness was obtained. Meanwhile, on silk dyed without fixation, smaller value of color change/ Grey Scale was obtained (2-3/ less good). It is no surprising because there exists no fixative agent which binds and locks anthocyanins in silk fibers. As a consequence, during washing the release of some anthocyanins occurs due to less strong fiber-anthocyanin bonds (only in the forms of hydrogen bonds) and causes discoloration.

| Test Sample | Variance of dyeing | Washing Fastness | Colour changes | Colour Staining |
|-------------|--------------------|-----------------|----------------|-----------------|
| pH | Fixation treatment | GS | CD | SS | CD |
| 1. Acidic (pH : 5) | without fixation | 2-3 | 4.2 | 4 | 4.0 |
| 2. | alum | 3 | 3.0 | 4 | 4.0 |
| 3. | ferrous sulfate | 3 | 3.0 | 4-5 | 2.0 |
| 4. Neutral (pH : 7) | without fixation | 2-3 | 4.2 | 4 | 4.0 |
| 5. | alum | 3 | 3.0 | 4 | 4.0 |
| 6. | ferrous sulfate | 3 | 3.0 | 4 | 4.0 |
| 7. Basic (pH : 9) | without fixation | 2-3 | 4.2 | 4 | 4.0 |
| 8. | alum | 3 | 3.0 | 4 | 4.0 |
| 9. | ferrous sulfate | 3 | 3.0 | 4-5 | 2.0 |

Rubfastness. Table 5 points out results of the test rubbing fastness. It indicates that the test on test rubbing fastness silk dyed either with fixation or without fixation in different pH resulted in Staining Scale value of 4-5 (good). The table shows that the dyed silk had good resistance to rubbing fastness. Similarly, all fabrics treated either with or without fixation in different pH had Staining Scale of 4 (good). Thus, both dry and wet rubbing resulted in good Staining Scale values. The good staining value appears since pigments of teak leaves (anthocyanins) entered to thus fibers and bonded. As a consequence, it is difficult for anthocyanins to escape despite an attempt of rubbing surfaces of fabrics/fibers. This gets rid of discoloration during the test for rubbing fastness.
Table 4. Rubbing fastness of dyed silk fabrics with extract teak leaves.

| Test Sample | Variance of dyeing | Fixation treatment | Dry Rubbing | Wet Rubbing |
|-------------|--------------------|--------------------|-------------|-------------|
|             | pH                 |                    | SS CD       | SS CD       |
| 1.          | acidic (pH : 5)    | without fixation   | 4-5 2.0     | 4-5 2.0     |
| 2.          |                    | alum               | 4-5 2.0     | 4 4.0       |
| 3.          |                    | ferrous sulfate    | 4 4.0       | 4 4.0       |
| 4.          | neutral (pH : 7)   | without fixation   | 4-5 2.0     | 4 4.0       |
| 5.          |                    | alum               | 4 4.0       | 4 4.0       |
| 6.          |                    | ferrous sulfate    | 4-5 2.0     | 4 4.0       |
| 7.          | basic (pH : 9)     | without fixation   | 4-5 2.0     | 4-5 2.0     |
| 8.          |                    | alum               | 4 4.0       | 4 4.0       |
| 9.          |                    | ferrous sulfate    | 4 4.0       | 4 4.0       |

Description: GS = Grey Scale SS = Staining Scale CD = Color Difference

4. Conclusion
One of the very potential use of plant natural colour in the textile industrial activities was anthocyanin. The dyeing silk fabrics with the addition of fixative agent ferrous sulfate resulted in grayish-black color, but the dyeing with the addition of fixative agent alum resulted in purple to reddish-purple colors. On dyeing without fixative mordant agents resulted light purple or pink. Fixation is proved to improve wash fastness and rubfastness on dyed silk fabrics and the use of different pH on dyeing will influence fixation of dyes and light fastness. The use of acidic pH proved to fabric treated with fixation/ mordant (alum and ferrous sulfate) resulted in dyed fabric with the highest light fastness value.

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