Utilization of Teak Leaf Waste as an Environmentally Friendly Dyes

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Abstract. As the second largest teak producer in the world, the abundance of teak leaf waste in Indonesia is inevitable. However, until now the effort to convert this material into functional products with high economic value is still very limited. In this study the potential utilization of teak leaf waste as an environmentally friendly dyeing material for the batik industry is examined. To be applied, extraction of teak leaves is carried out in a water solvent. Optimization of dyeing in cotton fibers is done by involving the use of positively charged alum mordant which can bridge the reaction between cotton fibers and antosianin in teak leaf extract which are both dominated by negative charges. The results showed the appearance of a light brown color on all cotton fibers, both fixed with iron (II) sulfate, alum and lime. However, the intensity of the color produced by each fixer varies in the range of 57.94% -84.62%. In line with this, the resulting fastness also varies on the staining scale 3 and 4. Dyeing with the highest intensity and fastness results from fixation using iron (II) sulfate. While alum and lime fixers tend to produce opposite intensities and fastness. This value shows the high potential of teak leaf waste material to be developed as a substitute for synthetic dyes with high toxicity in cotton fiber dyeing.

1. Introduction

The re-use of environmentally friendly and non-toxic biological resources has regained its popularity in various fields of life as community awareness of environmental and health issues increases. Natural dyes sourced from plants, insects/animals and minerals are one example of this type of product, which is not only renewable and sustainable, but also capable of producing products with minimum environmental impact [1]. However, the discovery of synthetic dyes in 1856, has led to the use of natural dyes dropped sharply [2]. The market share of synthetic dyes worldwide reaches 23 billion US dollars for a total production volume of around 1.3 million tons [3] and it is estimated that only 1% of the total world textile is dyed with natural dyes. In its development, the application of synthetic dyes has damaged the environment and triggered a number of health problems because of their toxic and carcinogenic properties. This condition has induced the reappearance of non-toxic natural dyes that are environmentally friendly as an alternative/co-partner to some extent against synthetic dyes [4]-[5].

Teak (Tectona grandis) is one of the most valuable timber-producing species in the world, with total cultivation reaching three million hectares. The distribution of these commodities is dominated by tropical or sub-tropical countries, including Indonesia. Specifically, teak plantations in Indonesia cover more than one million ha with annual logging of 8,000-10,000 ha [6]. As a by-product of this intensive
plantation activity, large amounts of teak leaf waste will be produced. But unfortunately, until now the use of teak leaves is limited to food packaging. Yet according to [7], teak leaves contain several pigments, especially anthocyanins which can be used as natural dyes. The high anthocyanin natural pigment content in teak leaves has triggered the appearance of red color in preparations [8].

The extraction efficiency of the natural dyes is very dependent on the raw material and the operational conditions of the process, such as pH, temperature, time, raw material/solvent ratio, and particle size. Furthermore, natural dye extraction methods can be classified based on the media used in extraction, such as aqueous, non-aqueous, organic, and aqueous-organic mixtures. This can be done in a variety of pH, temperature and duration. In this study, the extraction of dyes from teak leaf material was carried out with reference to previous publications, namely using a water solvent with a raw material/solvent ratio of 1/10 and an operating temperature of 100 °C [9]-[10].

Not only operational conditions of extraction, the quality of natural dyeing is also determined by the suitability of the preparation (washing and mordanting), dyeing and fixation procedure applied. The stages of washing and mordanting will ensure that cotton fibers are in optimal conditions for dyeing. While the suitability of the dyeing and fixation method will produce high intensity and color fastness [11]-[14]. This study aims to obtain operational conditions that are able to produce the best quality cotton colors from teak leaf extract.

2. The material and methods

2.1. Material

Some text. Materials needed in this study include Turkey Reddish Oil (TRO, ≥17%) which is used to minimize the presence of contaminants in fibers, purchased from CV. Dunia Kimia (Surabaya, Indonesia), alum (Al2(SO4)3.18H2O, ≥17%) and soda ash (Na2CO3, ≥48%) which serve to bridge the reaction between fibers with natural dyes, each obtained from PT. Brataco Chemistry and CV. Water (Surabaya, Indonesia). Teak leaf material which is used as raw material for natural dyes is obtained from the environment around Universitas Negeri Surabaya. Meanwhile, fixer compounds, including iron (II) sulfate (FeSO4.7H2O, d 2.84 g/cm3), and calcium oxide (CaO, ≥90%), which are required for color locking, each was purchased from PT. Nusa Indah Megah and Mitra Water (Surabaya, Indonesia). Especially for alum fixers, materials used are in the same specifications with used as mordanting agents.

2.2. Pre-treatment

These pre-treatment stages include washing using TRO and mordanting of the cotton fibers using alum and soda ash, with procedures that refer to previous publications [11]-[14].

2.3. Dyeing

The natural dyeing of cotton fibers is carried out using the pre-mordanting method, which is done by preceding the mordanting procedure. As with pre-treatment, dyeing with teak leaf extract applied to cotton fibers also refers to previously published procedures [11]-[14]. In Fig. 1 the visual appearance of teak leaf extract which will be applied for dyeing cotton fibers.

Figure 1. Color shades of aqueous extract of teak leaf material with concentration: (a) 1 time; (b) 2 times; and (c) 4 times more concentrated
2.4. Dyeing
Dyeing of cotton fibers using teak leaf extract is ended with fixation using materials: (a) iron (II) sulfate, (b) alum and (c) lime. The fixation procedure performed also refers to previous publications [11] - [14], but with a few additions. In addition to applying each fixer to the dyeing results using teak leaf extract, multilevel dyeing and fixation were also carried out, in order to determine the fixation method that is capable of producing the best color intensity and fastness.

![Diagram of dyeing and fixation processes](image)

**Figure 2.** Process illustration: (a) single dyeing & fixation; and (b) multilevel dyeing & fixation

2.5. Characterization
Characterizations include: (1) maximum wavelength analysis using Pharmaspec UV-1700 UV-Visible Spectrophotometer to ensure the dominance of anthocyanin compounds in teak leaf extracts. The appearance of maximum absorbance at wavelength 527 nm will ensure this dominance (Wirajana et al, 2016); (2) color intensity analysis using Shimadzu UV-2401-PC Diffuse Reflectant Ultraviolet (DRUV) Spectrophotometer to evaluate color intensity resulting from variations in fixer types. In general, high reflectance values from this analysis indicate low color intensity in cotton fibers; (3) fastness analysis.
using the Gray staining scale method to evaluate the effectiveness of extraction, pre-treatment, dyeing and fixation in minimizing color loss. The results of this analysis are in the form of number 1 (bad); 1-2 (bad); 2 (not good enough); 2-3 (not good enough); 3 (fair); 3-4 (good enough); 4 (good); 4-5 (good); and 5 (very good).

3. Results and discussion

Anthocyanin is a pigment found in the form of aglycone as anthocyanidin and glycone as a sugar bound by glycosidic. This dye is stable at acidic pH, which is around 1-4. In this condition, anthocyanins produce orange, pink, red, purple to blue colors [15]-[16]. Anthocyanins are polar dyes [17]. Anthocyanin is more soluble in water than in non-polar solvents and this characteristic aids the extraction and separation process [18].

Anthocyanin is not the only color compound contained in teak leaf extract. This is in line with what was published by [19], which reported the existence of beta carotene, foefitin, pelaronidin, and clorofilid compounds in this extract. However, the appearance of bluish color in the extract is predicted to be related to anthocyanin dominance. To ensure this, an absorption analysis of electromagnetic radiation is carried out and the results, show the maximum absorbance at wavelengths 504 nm. This ensures the dominance of the anthocyanin role in the production of bluish color in teak leaf extract. In accordance with the anthocyanin molecular structure shown in Fig. 3, the appearance of bluish color in teak leaf extract is closely related to the presence of two types of chromophore groups, namely C=C and C=O.

![Anthocyanin molecular structure](image)

**Figure 3.** Anthocyanin molecular structure

In batik production, fabric becomes one of the raw materials that determines the quality of batik and dyeing. The use of the right type of fabric will result in the appearance of specific types of motifs that are targeted as a result of the application of dyes resist and ease in the removal process as soon as the dyeing is done. The use of fabric types with the dominance of specific functional groups will also determine the high or low dyes compounds that can be bonded to the fabric fibers. The higher the suitability, the higher the intensity and color fastness produced.

In batik production, the type of fabric used is known as mori. Mori is a fabric made from cotton yarn. Based on the level of smoothness, mori or cotton fabric is divided into four groups, namely: primisima, prima, blue, and gray/blaco. In this research, the raw material used for the dyeing standardization using teak leaf extract is a type of prima mori. Various types of treatment in spinning cotton yarn into fabric become the background of the importance of washing treatment before dyeing.

In this study, prima mori washing was carried out using TRO. Turkey Red Oil is also known as sulfated castor oil. This material is the only type of oil that can be dispersed in water. This material is made by adding sulfuric acid to castor oil, and is considered the first synthetic detergent. The presence of polar and non-polar groups in TRO allows the dissolution of all types of contaminants found in the fabric. The availability of contaminant-free mori raw material will optimize the reaction between hydroxide (-OH) functional groups in fabric fibers with alum which in this case acts as a mordant. Fig. 4 shows an illustration of the difference in the effectiveness of the entry of mordanting agents into the raw material of fabrics that get and do not get washing treatment using TRO.
Mordanting is a process carried out to provide an intermediate compound which acts as a bridge for the optimal reaction that occurs between the fabric fibers with natural dyes so that the affinity of the dye to the fabric fibers increases. Basically, cellulose fibers which are generally negatively charged do not have the ability to absorb dyes that have a similar charge, so the presence of intermediate compounds is very necessary in this case. In this study, mordanting was carried out using alum and soda ash material.

Teak leaf extract contains a natural pigment called anthocyanin [20]. Anthocyanins are polyphenols which are known as the largest and most important group of water-soluble dyes [21]-[22]. The color intensity of anthocyanin is influenced by the number of hydroxyl and methoxyl groups in their molecular structure. When the hydroxyl group dominates the molecular structure, the color produced becomes more bluish, and vice versa, when the methoxyl group dominates, the reddish color feel increases [23].

In batik production, especially the lorod (dyes resist removal) stage performed at relatively high temperatures, the potential for color loss will increase. To improve color fastness in this case, fixation
is needed. Fixation is a color locking process that is done by adding metal complex materials. For this purpose, in this study three types of fixer compounds were used, including iron (II) sulfate, alum and lime. Furthermore, to find a fixation method that is more capable of producing higher color intensity and fastness, a multilevel dyeing and fixation procedure is performed, as shown in Fig 2.

Fig. 5 shows the color shades produced by teak leaf extract on mori fibers. These results indicate the appearance of grayish color in alum fixation results, as well as the appearance of colors that tend to brownish on fixation results using lime and iron (II) sulfate. The difference in the color shades that appear in the extract and the fabric are predicted to be triggered by the synergism that is formed, especially by the mordant and the dyes molecular structure. The appearance of reddish color in the extract is more influenced by the presence of C=C and C=O chromophore groups on the anthocyanin molecular structure, while the grayish and brownish color that appears on the fiber is more triggered by the chromophore combination of the mordant (C=C, S=O and C=N in alum, Ca=O in lime and S=O in iron (II) sulfate) and anthocyanin compounds.

Fig. 6 shows the color shades resulting from the multilevel dyeing and fixation application. The application of this procedure produces a stronger color, where fixation using alum produces a reddish brown, lime fixation produces a dark brown, while iron (II) sulfate fixation produces a blackish brown. The application of multilevel dyeing and fixation procedures tends to enrich the type of chromophores involved in the absorption of electromagnetic radiation in the UV visible spectrum.

To ensure the colors quality produced by each dyeing procedure and the use of various fixers, a color intensity and fastness analysis has been carried out. The results (see Table 1) show the higher color intensity and fastness produced by multilevel dyeing and fixation procedures. The complexity of the reactions formed in this dyeing procedure has produced significant obstacles to the entry of the environmental negative impacts, such as high heat when drying using direct sunlight and ironing, as well as chemical compounds during washing.

An interesting phenomenon arises from the results of the color intensity and fastness analysis, where although it produces the lowest color intensity (57.94%), alum fixers are able to offer color fastness that is actually better than lime, although still lower when compared to the fastness which is produced by an iron (II) sulfate. Similar results were also found in the color intensity and fastness resulting from the multilevel dyeing and fixation methods. This condition is predicted to be closely related to the size of the alum fixer molecule. With molecular sizes much larger than lime, alum particles are able to block the entry of environmental negative effects that tend to increase the potential for color loss. However, the large molecular size has also created the effect of space tightness which causes fewer alum molecules capable of binding to dyes.

**Table 1.** The color intensity and fastness resulting from variations in the dyeing method and fixer type

| Cotton Fiber Sample | Fixer Type     | Color Intensity (%) | Fastness (scale) |
|---------------------|----------------|--------------------|------------------|
| **Single Dyeing & Fixation** | | | |
| CF-1                | Alum           | 57.94              | 4 (Good)        |
| CF-2                | Lime           | 81.00              | 3 (fair)        |
| CF-3                | Iron (II) sulfate | 86.62              | 4 (Good)        |
| **Multilevel Dyeing & Fixation** | | | |
| CF-4                | Alum           | 76.65              | 4-5 (Good)      |
| CF-5                | Lime           | 82.47              | 3-4 (Good enough) |
| CF-6                | Iron (II) sulfate | 96.07              | 4-5 (Good)      |

4. Conclusions

Teak leaf trial use for batik natural dyeing has been done. To get the best color quality, pre-treatment has been applied including washing using TRO and mordanting using alum and soda ash. Visual shades of grayish and brownish colors that vary has been produced from the application of the pre-mordanting
method, both with a single or multilevel dyeing. The use of iron (II) sulfate, alum and lime fixers has produced a color intensity in the range of 57.94%-86.62% for single dyeing and 76.65%-96.07% for multilevel dyeing. The results of the overall analysis showed the dominant quality of dyeing accompanied by fixation using iron (II) sulfate.

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