Chemistry of Natural Dyes of Batik Crafts Colouring Process

S Wahyuningsih¹, Rahmawati², S R Handayani³, Setyaningsih⁴, Ponimah⁵
¹,³,⁴ Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Surakarta, Indonesia
² Economic and Business Faculty, Sebelas Maret University, Surakarta, Indonesia
³ Faculty of Visual Arts and Designs (FSRD), Sebelas Maret University, Surakarta, Indonesia
E-mail: sayeki@mipa.uns.ac.id, rahmaw2005@yahoo.com.

Abstract. By Fixation technique, we found the increasing stability of natural color. The aim of the study was to evaluate the performance of dyes anthocyanin, mangiferin, curcuma longa, Indigi fera and tannin (tingi) in batik dyeing. The medium was optimized by conditioning of natural dyes from amount quantity of extracted dyes in several condition: acid condition, base condition and also complexation during fixation process usually done in Batik dyeing. It was concluded that the color values were found to be influenced by the addition of namely mordants as complexation agent, consequently different fashion hues were obtained from the same dye extract using different mordants. The chemistry aspect such as an absorption in UV Visible region of each dyes and Infra Red absorption have been studied, and also a typical of fixation model should be noticed as a chemistry of dyes.

1. Introduction
Batik products with natural colours have potential as export commodities. The quality of batik products continues to be developed not only in business management, networks or marketing channels, increasing skills of craftsmen but also production facilities, production process technology, motive design innovations, and colouring materials innovations. Raw material for batik production including fabric (prime cotton, mori cloth, primis fabric, super silk fabric, chemical colorants, and wax fragments, batik mixture (caustic soda, sodium carbonate, HCl, TRO, Al₂O₃, and starch). By understanding of chemical processing occurring along processing, quality and colour behaviour will be maintenance well.

Natural textile dyes are generally obtained from extracts of various parts of plants such as roots, wood, leaves, seeds or flowers. Batik craftsmen have known many plants that can color textiles, such as: Indigo tree leaves (Indigofera), in of soga tingi trees (Ceriops candolleana arn), tegeran wood (Cudraina javanensis), turmeric (Curcuma), tea (Tea), noni roots (Morinda citrifelia), soga jambal skin (Pelthophorum ferruginum), kesumba (Bixa oreleana), guava leaves (Psidium guajava). However, until now there has never been reported standardization of coloring preparations using natural dyes, as well as testing the color quality resulting from natural coloring. Standardization of natural coloring preparations from various source materials will greatly determine the homogeneity of coloring.

Natural dyes are comprised of dyes and pigments that are obtained from various parts of plants including roots, bark, leaves, flowers, and fruit [1]. The major applications are coloring of food, leather, wood, and natural fibers like wool, silk, cotton, and flax. Natural dyes may have a wide range of shades. Dyeing with natural dyes, however, normally requires the use of mordants, which are
metallic salts of aluminum, iron, chromium, and copper, among others, to ensure a reasonable color fastness to sunlight and washing [2]. The metal ions of these mordants can act as electron acceptors for electron donors to form coordination bonds with the dye molecules, making them insoluble in water [3]. The use of natural dyes cuts down significantly on the amount of toxic effluent resulting from synthetic dye processes. The use of natural dyes in textile applications is growing rapidly, reflecting the strict environmental standards being established in many countries, and the concern about the health hazards associated with synthetic dyes, for example, the recent ban on the use of azo dyes by the European Union, has also increased the scope for the use of natural dyes [4].

2. Experimental

The natural dyeing techniques and materials that have been conducted and characteristic colour and their spectrum have been studied. The material and their processing including:

a. Natural plant source for natural colouring include: anthocyanin dyes from flowers, tannin from tingi wood and also secang wood, chlorophyll from green leaf, indigo from indigofera fermentation

b. Extraction of natural dyes was carried out by about 1000 grams of natural coloring sources were put into 10 liters of water and boil so that the remaining volume of water is 5 liters. Then filtered to get a solution of natural dyes

c. Dyeing processing technique: dyeing processing technique for physical and chemical interaction between dyes and cotton materials. In mordaning process, the cloth was boiled in water with a ratio of alum:water about (100 g alum :17 liters of water) to tie the Fe$^{2+}$ ions to the fabric (wool, cotton, silk) for 1 hour. Leave it for overnight, them dried out. For colouring, natural dyes used as a comparison of cloth: dye = 1:30 (w/w). The coloring process was done by repetitive dipping technique (10 times or more)

d. Chemical reaction of fixation: alum (Al$_2$(SO$_4$)$_3$), tunjung (FeSO$_4\cdot$7H$_2$O), or lime (CaO) solution for binding process were prepared for fixation through complexation (also copigmentation) mechanism.

e. Influence of pH condition during colouring processing techniques from natural plant was carried out by the addition of alum, tunjung, acetic acid or lime solution in natural dye source in an exact amount, the pH will be decrease or increase to compensate the H$^+$ and OH balance along colour expression of dyes.

3. Result and discussion

3.1 Chemistry behaviour of natural plant source for batik colouring process

3.1.1. Anthocyanin

There are many natural colours for colouring batik processing including anthocyanin group, tannin group and also chlorophyll group. Anthocyanins are responsible for the red, purple, and blue colours found in a variety of fruits, vegetables, cereal grains, and flowers. Unfortunately, anthocyanin pigments are highly unstable and are totally unsuitable for dyeing textiles. It should be related to the structure and the interaction between dye and cotton materials. The mechanism behind the destruction of anthocyanins in acid condition has been the subject of some debate, but in acid condition anthocyanin give a intensive red color [5]. Anthocyanin in various pH have chemical structure illustrated in Figure 1.
At a lower pH, anthocyanidins such as cyanidin are highly soluble in water due to the formation of flavylium cation which appear as red (Figure 1(a)). But in high pH (Figure 1(a)), formation of anion form is dominant, because of the deprotonation OH\(^{-}\) group. Anthocyanins degraded to each other by direct interaction of anthocyanin with acid, but it will be probably, by free radical formation pathway, cleave the flavylium core structure of anthocyanins. This condition triggers instability of anthocyanin and results in color destabilization dye. Stabilization of anthocyanins can be attempted by copigmentation using metal ions. Metal complexation is the clear pathway for increase stability. This idea is as in the fixation in Batik colouring process. Ascorbic acid also acts as a co-pigment. Thus, improved colors are obtained with the intrinsic protection of ascorbic acid from oxidation, and also in fixation process, usually using Alum (\(\text{XAl(SO}_4\text{)\cdot12 H}_2\text{O}\)) \(\text{X= K}^+\), \(\text{NH}_4^+\), tunjung (\(\text{FeSO}_4\)) or lime (\(\text{CaO}\)). Temperature also can help to retain the color intensity of anthocyanin, with the increase in temperature the greater degree in anthocyanin destruction. We suggest that the speedy destruction of anthocyanin in higher temperatures could be due to hydrolyzation of 3-Glycoside structure, which has a protective effect in unstable anthocyanin [6].

Anthocyanins are stable at low pH. It becomes less stable when exposed to heat, causing a loss of color and browning. In solution, anthocyanins molecules are present in an equilibrium between the colored cationic form and the colorless pseudo base. pH is very important for the color of anthocyanins, some anthocyanins are red in acid solutions, violet or purple in neutral solutions, and blue in alkaline pH. The reason for this is right here this structure of the anthocyanins (red circle) is called flavylium cation the reason, at low pH the cyanidin molecule is protonated and forms a positive ion or cation, as the pH increases the molecules become deprotonated, at high pH the molecule forms a negative ion or anion [7]. This is the reason that most colorants containing anthocyanins can only be used at pH values below pH 4. Figure 2 show the UV Vis Spectras of anthocyanin before and after isolated from rose flower. Fourier Transform Infra Red absorption (FTIR) of anthocyanin was shown in Figure 3.
Figure 2. UV Visible Absorption spectra of (a) extracted anthocyanin dye (b) isolated anthocyanin dye. Anthocyanin dye extracted and isolated from rose flower. UV-Vis Absorption spectra was measured in acid condition of 0.1 M HCl in methanol.

Figure 3. FTIR Absorption of Antocyanin dye isolated from rose flower

The basic colours anthocyanin as blue, purple, red and orange colours has correlation with the number of hydroxyl groups and with the number of methoxyl groups in anthocyanin. The number of methoxyl groups in anthocyanin in different source is different. By fixation using acidification, colour expression will be different that depend on the amount of acid have been used. But the heating step in colouring process will decrease stability of anthocyanin structure. Another strategy for improving colours of anthocyanin based natural dyes is purification step in initial step before colouring processing. By this way, it will reduce sugar content and also many compounds that influence colour stability. Table 1 give an illustration about a shifted of absorbance of extracted and isolated anthocyanin that influence of colour and colour intensity.

Table 1. List of maximum absorbance UV Visible of extracted and isolated anthocyanin dye related to Figure 2.

| Wavelength (nm) | Anthocyanin |
|-----------------|-------------|
|                 | Extracted   | Isolated  |
| \(\lambda_1\)   | 256         | 288       |
| \(\lambda_2\)   | 329         | -         |
| \(\lambda_3\)   | 526         | 526       |

3.1.2. Mangiferin dye
Mango (Mangifera indica L.) is a medicinal plant that belongs to the Anacardiaceae family. Mangiferin is one of the dominant polyphenols in mango leaves that has a function as a natural dye for batik craft and has several pharmacological properties such as antioxidants, anti-bacterial, and anti-fungi [8-9]. Thus, the use of material in natural textile coloring is expected to provide 2 (two) benefits at once, namely coloring and providing protection from attacks by free radicals and microorganisms. Figure 4 show the UV Vis Spectras of mangiferin from mangi leaves and FTIR of mangiferin was shown in Figure 5.
We observed of the colours of curcuma dye in various pH in Figure 7. Curcuma extracts were further treated by ball milling process due to decreasing the particle size and also improved solubility curcuma in water. Differences of colour and intensity were occurred related to structural change in pH value.
Functional groups | Wavenumber (cm\(^{-1}\))
---|---
O-H Streching | Curcumin | Curcumin-Al
---|---|---
3500.8 | 3406.28
Vibrasi C=O | 1627 | 1625
Vibrasi C-O | 1602 | 1585
1282 | 1267

Figure 7. UV Visible Absorption spectra of extracted curcuma dye. Curcuma prepared in nanosize using ball milling method and measured in pH (a) pH 9, (b) pH 7 (c) pH 5 (d), pH 3 (e), pH 1 (f), without milling.

Figure 8. FTIR Absorption of curcuma (a) After complexation with alum (b) before complexation with alum.

Protonated form was occurred in low pH, isoelectric form was occurred in medium pH, while deprotonated form was occurred in high pH (Figure 9). The FTIR spectra of curcuma before complexation and after complexation with alum were shown in Figure 8. In fixation process for dying the Al-curcuma was formed as in Figure 10.

Figure 9. Protonated form was occurred in low pH, isoelectric form was occurred in medium pH, while deprotonated form was occurred in high pH.

Figure 10. Complex formation of Al-curcuma in fixation process of batik dying.
3.1.4. Indigofera

Surprisingly the only satisfactory long-lasting natural blue dye is indigo. However, indigo is not a naturally occurring plant pigment, and must be manufactured by fermenting plants that contain the appropriate precursor chemicals. In principle the production of indigo is a simple process; however in practice it is very difficult to produce a deep blue dye.

Indigofera arrecta, commonly known as Bengal Indigo, Indigo, Natal Indigo, or Java Indigo, is a tropical small shrub of herb growing up to 4 m in height with partly woody stems and slightly hairy leaves. It has pink or brown flowers. It is a major source of the blue dye ‘indigo’. Indigofera arrecta, originated in tropical Africa but is now distributed widely throughout the tropics. Widely distributed throughout the continent from Senegal to Somalia, south to S. Africa. Also extending into Arabia. According to Heyne, 1927, the Dutch introduced it to Java in about 1860. It tolerates altitudes up to 2700 m [12].

![Figure 11. UV Visible Absorption spectras of indigo dye and indigo dye after addition fixation compounds of Alum(xAl(SO₄)₂·12H₂O); x = K⁺, NH₄⁺), Tunjung (FeSO₄), lime (Ca(OH)₂) and acetic acid.]

![Figure 12. FTIR absorption spectras of indigo dye]

| Functional group       | Wavenumber (cm⁻¹) |
|------------------------|-------------------|
| O-H, -NH₃, -NH stretching | 3500 – 3100       |
| C=C aromatic           | 1600              |
| C-N amine              | 1350 – 1000       |
| C-H aromatic           | 900 – 690         |

Based on indigo structural in acid and in basic condition (Figure 13), the structure were difference in acid and base conditions, due to protonated and deprotonated form. Alum, tunjung and acetic acid give acid condition and accelerate protonated form indigo structure that give a specific color intensity.

![Figure 13. Basic structure of Indigo (a) acid condition (b) basic condition]
The UV Visible absorption of indigo dye show that the maximum absorption peak is at a wavelength in the range 550 – 700 nm. The strong absorption in almost visible range give deep blue color of indigo. The permitted electronic transition of $\pi \rightarrow \pi^*$ and also $n \rightarrow \pi^*$ of chromophore group of indigo dye give high intense of blue absorption [13]. Color intensity related to the fixation condition using alum $(x\text{Al(SO}_4\text{)}_2\cdot12\text{H}_2\text{O}; x = K^+, \text{NH}_4^+)$, tunjung $(\text{FeSO}_4)$, and acetic acid.

3.1.5. Tannin from tingi
Tannic acid (tannin) is a common mordant used in the dyeing process for cellulose fibres such as cotton, often combined with alum and/or iron (tunjung). Quercitannic acid is one of the two forms of tannic acid found in oak bark and leaves. The other form is called gallotannic acid and is found in oak galls. Tannic acid is a specific commercial form of tannin.

The bark of soga tingi which contains tanin as natural coloring substances can be used as a substitute for synthetic dyes for Batiks. Tingi (Ceriops tagal) bark was highly potential as tanning materials due to high tannin concentration. The results showed that the tingi bark contains tannin level 70.91% and non-tannin levels 10.63%. Tannins from tingi bark were classified as proanthocyanidins (condensed tannins) type and the absorption values obtained maximum value at wavelength 490 nm. The FTIR spectral data indicated that tingi tannins contained hydroxyl group ($\nu\text{ O-H}$; $\delta\text{ N-H}$) in the area (3467.418-3057.025) cm$^{-1}$, aromatic group ($\nu\text{ C-H}$) in the area of 2875.733 cm$^{-1}$, $\nu\text{ C=O}$ (ester group in tanned material) in the area (1747.442-1612.422) cm$^{-1}$, $\nu\text{-OH}$; $R\text{-COO}$- in the area of 1444.626 cm$^{-1}$ and $\delta(\text{SO}_4\text{)}^\text{2-}; R\text{-SO}$; $R\text{-SO}_3\text{H}$ in the area (1112.823-1062.729) cm$^{-1}$. The coloring substances are subsequently analyzed by UV-Vis spectrophotometry. The coloring substances made of soga tingi bark is applied by adding fixation compound such as alum, lime, and tunjung. Fixation soga tingi dye with tunjung produce black color, lime produces a brown color, and alum produces a reddish-brown color. The color of fixation dyes were occured from chemical interaction produce complexes compound between them.

![Figure 14. UV Visible Absorption spectras of tingi dye before and after addition fixation compounds of Alum $(x\text{Al(SO}_4\text{)}_2\cdot12\text{H}_2\text{O}; x = K^+, \text{NH}_4^+)$, Tunjung $(\text{FeSO}_4)$, lime $(\text{Ca(OH)}_2)$ and acetic acid.](image-url)
As a resume, anthocyanin (rose flower), mango leaves (Mangifera indica), javanese curcumin (Curcuma zanthorrhiza), indigo fera, soga tingi bark (tannin), and javanese soga bark (secang) gives the final color as listed in Table 2.

Table 2. Natural dye applied and final color applied

| Natural dyes                          | Color          |
|--------------------------------------|----------------|
| Anthocyanin (rose flower)            | Red            |
| Mango leaves (Mangifera indica)      | Light brown    |
| Javanese curcumin (Curcuma zanthorrhiza) | Yellow        |
| Indigo fera                          | Blur           |
| Soga tingi bark (tannin)             | Brownish red   |
| Javanese soga bark (secang)          | Red            |

4. Conclusion

In conclusion, natural dye has different chemical characteristics. The treatment process in the fixation in the batik coloring process has the respective influence on the color and color intensity. So the traditional coloring treatment process still requires chemical knowledge related to color expression.

Reference

[1] Allen R L M 1971 Colour Chemistry (London UK: Nelson)
[2] Robertson S M 1973 Dyes From Plants (New York USA: Van Nostrand Reinhold)
[3] Mongkholrattanasit R, Krystúfek J, Wiener J, and Studničková J 2011 Fibres and Textiles in Eastern Europe 19(2) 90–95
[4] Sivakumar V, Vijaeeswarri J, and Anna J L 2011 Industrial Crops and Products 33(1) 116–122
[5] Wahyuningsih S, Ramelan A H, Wardani D K, Aini F N, Sari P L, Tamtama B P N, Kristiawan Y R 2017 IOP Conf. Ser.: Mater. Sci. Eng 193 012047
[6] Laleh G H, Frydoonfar H, Heidary R, Jameei R and Zare S 2006 Pakistan Journal of Nutrition 5(1) 90-92
[7] Wahyuningsih Wulandari S L, Wartono M W, Munawaroh H, and Ramelan A H 2017 IOP Conf. Ser.: Mater. Sci. Eng. 193 012047
[8] Masibo H and He Q 2008 Compr. Rev. Food Sci. Food Saf 7 309-319
[9] Ribeiro S M R and Schieber A, Bioactive compound in mango (Mangivera indica L.) R R Waston, V R Preedy ed London Academic Press
[10] Ghoreishian S M, Maleknia L, Mirzapour H and Norouzi M 2013 Fiber Polym 14 201-207
[11] Zhou Y, Zhang J, Tang R, and Zhang J 2015 Ind Corp Prod 64 224-232
[12] Plan for a future. Indigofera hochst ex a rick. https://pfaf.org/user/Plant.aspx?LatinName=Indigofera
[13] Wahyuningsih S 2017 IOP Conf. Ser.: Mater. Sci. eng 193 0120048