Natural Dyes Extraction Intended for Coloring Process in Fashion Industries

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Abstract. Recently, small scale fashion industries are growing quite rapidly in Indonesia. This is due to the continuous encouragement and facilitation by the Government of Indonesia to improve workforce in creative industry. As fashion industries depend on the availability of dyes as one of their resource, it is very important to develop a new and sustainable supply of dyes for dyeing process in fashion industries. Hence, research on the extraction of dyes from sustainable and natural resources for fashion industries are considered very important and urgent. Dyes for fashion and textile are naturally occurred in plants or parts of plants. The extraction of dyes from these sources can be conducted by using simple mixing between solvent and the plants inside a soxhlet extractor or reflux apparatus. In this study, the extraction processes of natural dyes from two materials, i.e. sappanwood, and mango leaf employing combination of maceration, soxhlet and reflux techniques were reported. The experiments were conducted to analyse the effects of extraction time and solvent to materials ratios on the yield of dyes. The experimental results showed that for all materials the optimum ratio of material and solvent was 1 : 6. In addition, the reflux followed by maceration could produce dyes that can be utilised for fabric coloring that suits the industrial needs.

1. Introduction
The textile industries have relied on synthetic color for decades since it is easy to apply to fabrics. However, the wastewater of synthetic dyes usually damages the environment, especially the body of water where it would dispose to. This phenomenon happens because of the heavy metals used for additional material to fix the color called mordant [1]. Though treated before disposal, the wastewater treatment is limited only to reduce the concentration of organic materials instead of to completely remove it.

As a result, the textile industries start getting back to natural dyes which attained through the extraction of natural sources. Two natural sources of these natural dyes that are often used in industries are Caesalpinia sappan barks which contain brazilin that gives red color and Mangifera indica leaves which contain mangiferin that gives brown color. A lot of research has been conducted to define the best method and process condition upon the extraction of those sources [2], so the standardized quality of natural dyes obtained with maximum quantity.
The extraction of *Mangifera indica* leaves using batch extraction method has been done by Chavan to determine the effects of solvent used, particle size, and temperature upon the extract percentage. The research used methanol, ethanol, and acetone as its solvent, a varied range of temperature and size of particles. The results show that methanol is the best solvent for extraction. In addition, the extract percentage increased by increasing temperature and reducing the size of particles [2]. Another study conducted by Chavan upon the different species of *Mangifera indica* by using Hapoos leaves. It gives extract percentage of 48.66%(b/b) and yield of 2.43%(b/b) while Kesar leaves gives extract percentage of 34.95%(b/b) and yield of 1.75%(b/b) [3]. On the other hand, the extraction upon Rajapuri leaves conducted by Shinde gives extract percentage of 60.71%(b/b) and yield of 3.035%(b/b) [4]. These studies exhibit that the species take part in determining the value of mangiferin extracted.

So much for *Mangifera indica*, the extraction of *Caesalpinia sappan* barks by reflux method using water and ethanol as solvent was also studied. The usage of water as a solvent gives 15.6±7.5%(b/b) yield while ethanol gives 20.5±4.7%(b/b) yield. On the other hand, Sinsawasdi proved that maceration method is more effective compared to the reflux method while using water as the solvent since Brazilin is thermostable that easily degrades at high temperature [5].

The effectivity of solvent used in the extraction of *Caesalpinia sappan* L. has been studied by Hung. The solvents compared in this study were methanol, ethanol, and water whose value of each yield were 18.8±5.4%(b/b), 20.5±4.7%(b/b), and 15.6±4.7%(b/b), respectively. It shows that ethanol is the best solvent among them [6].

Despite the previous studies on *Mangifera indica* leaves and *Caesalpinia sappan* barks, there was no research reported about the efficient method and process condition using the best solvent for both materials. Thus, this research tends to fill that gap by comparing some methods with different process condition for both natural sources.

2. Materials and methods

2.1. *Mangifera indica* leaves

*Mangifera indica* leaves being used were specifically chosen from the species *Gadung* gathered directly from the trees planted in Surabaya, Indonesia. The leaves were washed then sun dried and grinded using kitchen blender until powder were attained. The powder were screened to get 40 mesh + 70 mesh particle size and then were extracted using water and methanol as solvent. The methods employed for this extraction were maceration, reflux, and soxhlet. For each variable, samples were taken periodically then were filtered using filter paper, and the absorbances were measured using HP-8453 Double Beam UV-Vis Spectrophotometer using wavelength of 361 nm. Maceration method was coupled with mixing and was carried out until the value of the absorbance became stable with sample taken for every two hours. While reflux method was employed with time variations of 2, 4, and 6 hours. For each reflux experiment, a little amount of sample was taken every half an hour and then analysed using spectrophotometer. In addition, for soxhlet method the experiment was carried out until as little solvent as possible was left with sample taken every two hours.

2.2. *Caesalpinia sappan* barks

*Caesalpinia sappan* L. was purchased as powder then screened to get 40 mesh + 70 mesh particle size and extracted using water and ethanol as solvent. The methods employed for this extraction were maceration, reflux, and soxhlet. For each variable, samples were taken periodically then were filtered using filter paper, and the absorbances were measured using HP-8453 Double Beam UV-Vis Spectrophotometer (wavelength of 543 nm for water extract and 448 nm for ethanolic extract). Maceration method was coupled with mixing with time variations of 2, 4, and 6 hours. During the maceration processes, a little amount of samples was taken every half an hour and then analysed using spectrophotometer. While reflux method was carried until the value of absorbance became stable with sample taken for every two hours, and Soxhlet method was carried out until as little solvent as possible was left with sample taken for every two hours.
For both materials, the yields of extraction process were measured by taking the ratio between the mass of product after drying and the mass of initial material. The LC-HRMS analysis was conducted to analyse the qualitative existence of mangiferin in the extract of mango leaf and also brazin in the extract of sappan barks.

3. Results and Discussion

3.1. Mangifera indica
The extraction of dyes from mango leaf in this study has been conducted by three different processes, such as reflux at different times, soxhlet, and maceration. The yields of dyes from the experiment are presented in Table 1.

| Material     | Method            | Yield of water as solvent (wt. %) | Yield of methanol as solvent (wt. %) |
|--------------|-------------------|-----------------------------------|--------------------------------------|
| Mango leaf   | 2 hours reflux     | 2.18                              | 2.60                                 |
|              | 4 hours reflux     | 2.52                              | 2.73                                 |
|              | 6 hours reflux     | 2.78                              | 2.67                                 |
|              | Soxhlet            | 1.05                              | 6.00                                 |
|              | Maceration         | 1.53                              | 2.43                                 |

The yields data in Table 1 presents the highest yield achieved by the soxhlet method with the using of methanol as solvent. The reason for high yield when methanol applied was because of the high solubility in mangiferin [1], so methanol would be easier to dissolve mangiferin than water. On the other hand, the reflux method produced higher yield than maceration due to its material mixed with the solvent and those will face the high temperature. The reason for high temperature excellence is because of the increased of kinetic energy in the solvent will contribute to the lower solvent’s viscosity, then ease the diffusional process through the leaves’ matrix and the higher intermolecular forces within the solvent causes higher local temperature in leaves’ matrix that increase the mangiferin’s solubility. This process also supported that the materials do not degrade in high temperature [2]. In addition, it was also observed that the maximum time for Mangifera indica extraction using reflux method and water for its solvent happens in 60 minutes.

The existence of mangiferin inside the produced dyes was then analysed qualitatively by using LC-HRMS technique. The qualitative presence of mangiferin can be detected by comparing the mass (m) to charge ratio (z) from the equipment with the literature value [7]. The typical LC-HRMS patterns and the values of m/z of the sample are depicted in Figure 1 and Table 2.

3.2. Caesalpinia sappan L.
The extraction of natural dyes from sappan barks was conducted by employing water and ethanol as solvents. The presence of thermolabile chemical such as brazin in sappan wood that produces red color provide an information that extraction process at low temperature will enhance the yield and stability of the dyes. At a relatively high temperature, the oxidation of brazin into brazilein is possible that can produce brown colour, instead of red colour as expected. The yields of extraction of sappan barks are shown in Table 1.
Figure 1. Typical pattern of LC-HRMS analysis of dyes from mango leaf

Table 2. m/z values of dyes from mango leaf

| Retention time (minutes) | Area          | m/z          |
|-------------------------|---------------|-------------|
| 0.778                   | 12288712.0399 | 423.0920    |
| 3.912                   | 31460199.2237 | 423.0914    |
| 4.986                   | 2737568.1677  | 423.0919    |
| 5.366                   | 2828636.7901  | 423.0917    |
| 16.738                  | 15665.8189    | 423.0916    |

The yields data in Table 1 show that maceration method gives lower yields compared to reflux and soxhlet methods, since reflux and soxhlet employs heating process to boil the solvent while maceration does not. Heating helps rupturing cell wall making it easier for the solvent to dissolve brazillin. In addition, soxhlet method gives higher absorbance compared to reflux method on both solvent. In soxhlet method, the solvent used to extract the solute is always fresh with little or no solute, since this method utilize the vapor phase of solvent. As a result, the driving force of extraction, which is the difference of solute concentration between materials and solvent is always high, producing rapid mass transfer at any time. On the other hand, extracted solute and solvent is being mixed up in reflux method decreasing solute concentration difference resulting on lower mass transfer compared to Soxhlet method.

Although heating boost extraction rate, the prolonged exposure of heat leads to degradation of brazillin, giving red-brownish color instead of red, as brazillin is thermolabile resulting the degradation of brazillin to brazilein, which is brown-colored, in high temperature. Nonetheless, since water boiling point is higher than ethanol, the degradation of brazillin while being extracted using water occurs earlier.
than the one being extracted using ethanol. The experiment shows that even though brazilin is thermolabile, its tolerance is high enough to utilize heat upon the extraction, since heat ruptures the cell wall and assists the dissolution of brazillian into solvent. However, the effect of heating reaches its maximum after some of times, and gives reversed effect on the brazilin right after it. In terms of sappan to solvent mass ratio, we also evaluated the effect of this ratio into the absorbance and concentration of dyes. As can be seen in Table 3, the optimum mass ratio was 1:6 that could produce the highest concentration of red colour. This optimum ratio is very important to be evaluated and proposed to the fashion industries that currently still use traditional technique.

| Mass ratio of sappan to solvent ratio | Solvent | Absorbance | Concentration (ppm) |
|--------------------------------------|---------|------------|---------------------|
| 1 : 4                                | Water   | 1.042      | 1884.4              |
| 1 : 6                                | Water   | 1.071      | 1940.2              |
| 1 : 8                                | Water   | 0.687      | 1249.6              |

4. Conclusion

This research has conducted the extraction processes of yellow and red colours from mango leaf and sappan barks, respectively. The extraction process for each material required different process conditions to optimize the yield of dyes produced. The extraction of mango leaf suggested the high temperature extraction process to produce high yield of dyes. On the other hand, the extraction of sappan barks required a low temperature extraction process due to the presence of brazilin, which has a thermolabile property. In order to be utilised in industrial scale, the utilisation of water is much preferred than organic solvent like methanol and ethanol, hence the optimised ratio of 1 mass of sappan wood and 6 mass of water as solvent was also suggested from the results of this study.

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