Application of cocoa pod husk (*Theobroma cocoa* Spp) for natural dyes powder on silk batik cloth

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Abstract. The chocolate industry (*Theobroma cocoa*) in Indonesia reaches a total production of approximately 500 thousand tons. It has the potential to be used as natural dyes for the batik industry. This study aims to utilize cocoa pod husk powder on silk batik. The method was carried out by varying the concentration of maltodextrin as filler powder by 5%, 10%, and 15%, the final mordant variations (alum, calcium oxide, and ferrous sulfate) on silk cloth, and the natural dye solution of cocoa pod husk. The natural dye solution for cocoa pod skin was tested for phytochemistry to see the tannin and flavonoid content, the results of dyeing application on silk batik cloth were tested for the quality of its color resistance to washing, color strength, and color differences. The colorfastness test result showed a good category with an average value of 4-5 and the result of the color strength test showed that the best maltodextrin was 5% with a natural dye concentration of 15g / L. The results of alum mordant, calcium oxide, and ferrous sulfate (tunjung) produced colors that led to light and dark with a predominance of brown, red, and blackish brown.

1. Introduction
Natural-colored batik is increasingly popular in the world since the recognition of batik as an intangible cultural heritage of Indonesia. Apart from continuing cultural promotion, there is also an awareness of lifestyle trends in the use of environmentally friendly products. Yet on the other side, natural dyes used for batik are still limited, therefore an exploration of new sources is necessary. Cocoa pod waste is one of the sources that can be made into powder. Natural dyes powder is more practical in use and easy for shipping. Indonesia is still one of the largest cocoa producers in the world. In 2015, 593.331 tons were produced from an area of 1.709.284 hectares. Cocoa-producing regions are spread from East Java and Central Java, South Sulawesi, Southeast Sulawesi, Central Sulawesi, and Sumatra. And Sulawesi Island is the largest contributor, with the number of 62.95%, followed by Sumatera Island with 22.88% and Java Island with 5.42% [1]. Cocoa production tends to produce waste, one of which is cocoa pod waste. These wastes accumulate to rot in the area of cocoa plantations which can cause unpleasant odors to the local environment [2], although some are used as absorbents, animal feed, and others. The estimated availability of cocoa pods is around 516.259 tons. Cocoa pods contain theobromine alkaloids (3.7-dimethylxanthine) with 0.17-0.22% and tannins with 0.84% [3]. Generally, the structure of cocoa consists of four parts, the cocoa pod husk, placenta, pulp, and seeds. About 75% of one whole cocoa fruit is in the form of rinds, 23% cocoa beans, and 2% placenta [4]. The current utilization of cocoa pod is for animal feed [5], organic fertilizer, and adsorbents [6].

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The main source of plant pigment is contained in many parts of plants, such as leaves, stems, bark, flowers, fruit, root bark, fruit peels, and other parts, with different amounts and types of color-bearing compounds. The use of natural dyes now has a great demand for the batik craft industry because it is more environmentally friendly. Some types of pigments that we find around us are in the form of chlorophyll which is found in many green leaves, carotenoids, tannins, and anthocyanins. The final mordant or fixation process in the natural coloring process usually uses metal salts such as alum KAl(SO₄)₂·12H₂O, calcium oxide Ca(OH)₂, and ferrous sulfate/tunjung (FeSO₄). Besides strengthening bonds, metal salts also function to change the color of natural dyes according to the type of metal salt that binds them [7]. Textile that has been dyed with natural dyes needs to be strengthened to stay attached to the textile and not fade.

Cocoa pod husk can be used as natural dyes for batik products and non-textile natural fibers and has a fairly good fastness (value 4) [3]. Research in the process of taking dye is limited to the use of extraction technology, the disadvantages of extraction technology include the lack of stability of the dye solution during storage, which is marked by a change in the color of the solution due to the influence of bacteria and molds. Another disadvantage is that the extracted dye solution is impractical to use, as well as for dye manufacturers who are constrained in terms of shipping out of the region. Based on those shortcomings, a natural coloring powder from cocoa pods was made.

This study aims to utilize cocoa pod husk powder on silk batik for the batik industry. Natural dyes powder is more practical in storage and less moldy than in solution.

2. Materials and methods

2.1. Materials
Silk fabric, cocoa pod husk solution, batik wax, alum, calcium oxide, ferrous sulfate, and maltodextrin.

2.2. Methods
Cocoa pod husk solution available with 3 types of pH (acidic, neutral, and basic) was extracted at 100°C in 3 hours. The making of powder was processed by mixing a solution of cocoa pod husk in the amount of 5 liters each with maltodextrin (variation 5%, 10%, and 15% w/v) while stirred until homogeneous then filtered. The processing process was carried out at an inlet temperature of 240°C and an outlet temperature of 80°C, and the dye powder formula was 15g/L of water. Application of coloring in silk batik cloth utilized variations of the final mordant (alum, calcium oxide, and ferrous sulfate). The results of coloring applications on batik were tested for the quality of colorfastness against washing, color strength, and color differences (CIE L* a* b*).

3. Results and discussion
The cocoa pods husk used for the experiment were taken from farmers in the Gunung Kidul area. Then, the experiments were carried out in the Central Laboratory of Crafts and Batik process, Yogyakarta while the powderization was applied at the Center for Agro Industry in Bogor. The results of the experiments are as follows.

3.1. The cocoa pods husk solution and powder solution
Data on the tannin and flavonoid contents of the extraction solution from cocoa pods husk made in powder are shown in table 1.

The result of the extraction solution of cocoa pods husk was dried using a spray dryer to powder by adding maltodextrin. Spray drying is a product processing technology by changing the form of liquid into dry particles through a heat-drying spray media. The aim is to reduce the moisture content of the material so that the material becomes more durable, reducing the volume of material to facilitate and save transportation, pack strength, and storage costs. Spray-drying drying technology is also used to convert reactive substances into more stable materials so that the product lasts longer. Spray dryer
drying process with the addition of certain solvents, the liquid spray is brought into contact with the heating gas to evaporate the solvent where the resulting product is in the form of a particle dryer in the form of extract powder [8]. The results of the calculation of the yield of cocoa pods husk are shown in table 2.

**Table 1.** The test results for tannin and flavonoid levels of natural dyes cocoa pods husk extract.

| No | Solution sample | Tanin (µg/Ml) | Flavonoid (µg/Ml) | Total Tanin and Flavonoid (µg/Ml) |
|----|-----------------|--------------|------------------|----------------------------------|
| 1  | Acidic Cocoa (AC) | 1260.00      | 3474.98          | 4734.98                          |
| 2  | Neutral Cocoa (AN) | 880.25       | 1292.65          | 2172.9                           |
| 3  | Basic Cocoa (BC)  | 1038.00      | 3163.85          | 4201.85                          |

**Table 2.** Yield of cocoa powder.

| Variation maltodextrin | Acidic Cocoa (AC) | Neutral Cocoa (AN) | Basic Cocoa (BC) |
|------------------------|-------------------|--------------------|------------------|
|                        | Gram powder | % powder (b/vv) | Gram powder | % powder (b/vv) | Gram powder | % powder (b/vv) |
| 5%                     | 118.7       | 2.37              | 96.7        | 1.93              | 77.6        | 1.55            |
| 10%                    | 189.6       | 3.80              | 182.0       | 3.64              | 143.9       | 2.88            |
| 15%                    | 328.9       | 6.58              | 266.9       | 5.34              | 204.9       | 4.10            |

Table 2 shows that the highest yield of powder was 328.9 with the addition of 15% maltodextrin. The effect of variations in the concentration of maltodextrin as a filler in the manufacture of cocoa pods husk solution was quite influential on the yield of the dye powder produced. The higher the percentage of maltodextrin used, the more amount of dye powder obtained. Conversely, the less the percentage of maltodextrin used, the less cocoa dyes produced. The use of maltodextrin as a filler used for the manufacture of natural dyes powder with spray dryer technology was quite influential on the physical form of the resulting powder.

3.2. Application of cocoa pods husk powder for coloring on silk batik cloth
Cocoa pods husk powder was applied for coloring on silk batik cloth by doing three variations of mordant namely alum, calcium oxide, and ferrous sulfate. The mordant served to bind the cocoa dyes in the fiber so it did not fade easily and direct the color. The cocoa pods husk powder used for coloring silk batik cloth was 15g/L.

3.2.1. Color difference test (CIE L,a,b). The color difference test L, a, b was carried out from the results of the application of cocoa skin coloring on silk cloth. The color difference test method was based on the brightness (lightness) of color saturation (chroma) and color hue (hue) with L*, a*, and b* notation. The L* notation had values from 0 to 100. The higher L* value means the color approaches white and the lower L* value indicates the color is black/dark.

The notation a* represents the chromatic color of the red-green mixture, with a value of a+ (positive) from 0 to 100 indicating the direction of red, and a- (negative) value from 0 to 100 indicating the direction of green. The b* notation represents the chromatic color mixture of blue-yellow, with a value of b+ (positive) from 0 to 100 indicating the direction of the yellow color and a value of b- (negative) from 0 to 100 for the direction of blue [9].
The results of coloring with cocoa pods husk powder on silk batik cloth can be seen in Table 3. While the results of different color test L*, a*, and b* application of natural dye coloring of cocoa pods husk powder on silk batik cloth that produced the level of value notation are shown in Table 4.

Table 3, shows that the use of alum mordant, calcium oxide and ferrous sulfate produced different color directions. Ferrous sulfate mordant directed the intensity of colors that tended to be dark, alum directed the intensity of colors that tended to be bright and calcium oxide directed the intensity of colors between light and dark. The darkest color was found in the results of the powder with a mixture of maltodextrin 5% and neutral pH because the active dyes were larger and were absorbed more in the fabric. Rusdi [10] states that the addition of a filler to the solution affects the particle size and color produced in a textile fabric. Fewer fillers make the color intensity darker, conversely more fillers make the color intensity whiter.

The L* notation indicates the direction of dark brown or away from white, leading to dark/black. The L* notation of the mordant variation (alum, calcium oxide, ferrous sulfate) for all treatments that had the lowest value of 52.01 was found in the neutral 5% pH concentration of maltodextrin with ferrous mordant. While the L* notation with alum mordant for all types of color treatment lowest value 63.31 was found in the mixing of 5% maltodextrin concentration, the basic pH was the same as the L* notation with calcium oxide mordant but with the lowest value of 61.42. The a* notation all produced an a+ value indicating that the color of cocoa pods husk contained a reddish-brown color. The highest a+ value of 19.23, was found at the base pH of 5% maltodextrin concentration with calcium oxide mordant. Note b* of all test samples produced positive values which showed that the color of the cocoa pods husk powder contained a yellowish-brown color, while the highest positive b notation value of 17.08 was obtained from the treatment of acid pH, 5% maltodextrin concentration, and with Alum mordant.

3.2.2. The colorfastness test to washing. The colorfastness test for washing was applied from the results of the application of cocoa pods husk powder coloring on silk batik cloth. The test method was based on colorfastness to washing [11]. The results of the colorfastness test for washing from the cocoa pods husk powder application test sample on silk cloth are shown in Table 5.

The mordants treatment of the test sample produced an average value of 4-5 indicating a good category. This was due to the color fastness of the sample with fewer mordants so that there appeared to be no degradation of color deterioration in the test sample. The color absorbed in the textile fiber was the optimal color because the mordant bonded with the dye in the silk batik cloth fibers well and were not easily separated in washing. Ardhianti [12] states that for dyes used for dyeing to have good colorfastness, a mordant process is needed to lock the dyes that enter the fibers to increase the colorfastness. This mordant process will condition the coloring agent which has been absorbed in the material at a certain time and undergoes a complex reaction between the material with the coloring agent and the material used for mordant.

3.2.3. Color strength test. The color strength test method on silk batik cloth was measured at the maximum wavelength, at the wavelength with the smallest reflectance value (%R) indicating the maximum wavelength and if converted to the K/S value would produce the largest K/S value. The higher K/S value means the absorption of dyes by a larger material or the color is darker and vice versa, the lower K/S value means less absorption of dyes so that the color is brighter [13]. The results of the color strength test from the application of cocoa pods husk powder coloring are shown in Table 6.
Table 3. Results of coloring of cocoa pods husk powder on silk batik cloth.

| No | Sample    | Mordant          |  |  |  |
|----|-----------|------------------|---|---|---|
|    |           | Alum             | Calcium oxide | Ferrous Sulphate |
| 1  | 15gpl/NC5 | ![Image](image1) | ![Image](image2) | ![Image](image3) |
| 2  | 15gpl/AC5 | ![Image](image4) | ![Image](image5) | ![Image](image6) |
| 3  | 15gpl/BC5 | ![Image](image7) | ![Image](image8) | ![Image](image9) |
| 4  | 15gpl/NC10| ![Image](image10) | ![Image](image11) | ![Image](image12) |
| 5  | 15gpl/AC10| ![Image](image13) | ![Image](image14) | ![Image](image15) |
| 6  | 15gpl/BC10| ![Image](image16) | ![Image](image17) | ![Image](image18) |
| 7  | 15gpl/NC15| ![Image](image19) | ![Image](image20) | ![Image](image21) |
| 8  | 15gpl/AC15| ![Image](image22) | ![Image](image23) | ![Image](image24) |
| 9  | 15gpl/BC15| ![Image](image25) | ![Image](image26) | ![Image](image27) |
Table 4. Test results for different colors of the application of cocoa pods husk powder on silk batik cloth.

| No | Sample   | Alum | Calcium oxide | Ferrous Sulphate |
|----|----------|------|---------------|------------------|
|    |          | L*   | a*            | b*              |
| 1  | 15gpl/BC5| 63.31| 17.74         | 8.74            |
| 2  | 15gpl/BC10| 70.45| 13.98         | 7.13            |
| 3  | 15gpl/BC15| 73.61| 12.03         | 6.63            |
| 4  | 15gpl/AC5| 68.84| 14.02         | 17.08           |
| 5  | 15gpl/AC10| 74.57| 11.01         | 12.68           |
| 6  | 15gpl/AC15| 76.43| 9.11          | 11.95           |
| 7  | 15gpl/NC5| 69.13| 12.99         | 12.61           |
| 8  | 15gpl/NC10| 69.64| 12.63         | 11.61           |
| 9  | 15gpl/NC15| 73.01| 10.54         | 11.05           |

Table 5. Test results of the color fastness of silk batik fabric against washing.

| No | Sample   | Silk batik | Alum | Calcium oxide | Ferrous Sulphate |
|----|----------|------------|------|---------------|------------------|
| 1  | 15gpl/NC5| 4          | 4    | 4 - 5         |                   |
| 2  | 15gpl/NC10| 4         | 4    | 4             |                   |
| 3  | 15gpl/NC15| 4         | 4 – 5| 4 – 5        | 4                |
| 4  | 15gpl/AC5| 4 – 5     | 4    | 4 – 5         | 4                |
| 5  | 15gpl/AC10| 4         | 4    | 4 – 5        | 4                |
| 6  | 15gpl/AC15| 4 – 5    | 4    | 4             | 4                |
| 7  | 15gpl/BC5| 4         | 4    | 4 – 5        | 4                |
| 8  | 15gpl/BC10| 4 – 5    | 4    | 4 – 5        | 4                |
| 9  | 15gpl/BC15| 4 – 5    | 4    | 4             | 4                |

Table 6. Results of the color strength test of the application of cocoa pods husk powder on silk batik cloth.

| No | Sample   | Silk batik (K/S) | Alum | Calcium oxide | Ferrous Sulphate |
|----|----------|-----------------|------|---------------|------------------|
| 1  | 15gpl/NC5| 0.35            | 0.55 | 1.05          |                   |
| 2  | 15gpl/AC5| 0.22            | 0.37 | 0.45          |                   |
| 3  | 15gpl/BC5| 0.36            | 0.39 | 0.80          |                   |
| 4  | 15gpl/NC10| 0.42        | 0.51 | 0.86          |                   |
| 5  | 15gpl/AC10| 0.12        | 0.18 | 0.42          |                   |
| 6  | 15gpl/BC10| 0.18        | 0.18 | 0.48          |                   |
| 7  | 15gpl/NC15| 0.20        | 0.22 | 0.32          |                   |
| 8  | 15gpl/AC15| 0.11        | 0.15 | 0.34          |                   |
| 9  | 15gpl/BC15| 0.17        | 0.21 | 0.20          |                   |
The average K/S results were obtained for the use of maltodextrin and acidic, basic, and neutral pH to alum, calcium oxide, and ferrous sulfate mordants to illustrate the level of color strength. The concentration of maltodextrin on the value of color strength from the application of cocoa pods husk powder coloring on silk cloth batik which got the highest value of 1.05, powder with 5% maltodextrin concentration, neutral pH with tide mordant is shown in table 6. Kembaren [14] said that the lower use of maltodextrin filler concentration will result in better color strength, while the higher usage of maltodextrin filler concentration, the lower the color strength level will be.

Variations in the treatment of the mordant substances of alum, calcium oxide, and ferrous sulfate on the dyeing results of silk batik cloth have been shown to increase the value of different color intensities. The highest strength value was the coloration of the sample which was fixed with a color intensity which led to dark/black. Because at the time of immersion with ferrous sulfate mordant, a reaction occurred between tannins and flavonoids from dyes with Fe$^{2+}$ metal from ferrous sulfate mordant materials which produced Ferro tannate complex salts.

Table 6 shows the average K/S levels of pH (acidic, basic, neutral), the use of maltodextrin variations, and mordant variations. The results of the mean calculations are shown in table 7.

| No | Variation                | Average value |
|----|--------------------------|---------------|
| 1  | Acidic pH                | 0.26          |
| 2  | Basic pH                 | 0.33          |
| 3  | Neutral pH               | 0.50          |
| 4  | 5% maltodextrin          | 0.50          |
| 5  | 10% maltodextrin         | 0.37          |
| 6  | 15% maltodextrin         | 0.21          |
| 7  | Alum mordant             | 0.24          |
| 8  | Calcium oxide mordant    | 0.31          |
| 9  | Ferrous sulfate mordant  | 0.54          |

The dark color of the application of the natural dye of cocoa pods husk powder in silk, which was seen that the addition of 5% maltodextrin filler, gave a higher color strength value of 0.50 K/S values. The greater amount of maltodextrin produced a lower color strength value. This was because the amount of filler added affects the concentration of the dyes produced, the more amount of maltodextrin used reduced the concentration of the dye found in the color powder so that less color was absorbed in fabrics. In the manufacture of powder products, maltodextrin fillers were added to increase the volume and weight of the powder produced and the drying speed [15].

The treatment of the use of ferrous sulfate mordant produced the greatest value of 0.54 K/S on silk batik cloth. This was because the ferrous metal donor (Fe$^{2+}$) performed a complex metal reaction between tannins from natural dyes with complex salts (Ferro tannates) and formed covalent bonds so that there was a good bond between the dye with fibers and produced a high degree of color strength [16]. This shows that natural cocoa pods husk powder had a good affinity for protein fiber.

4. Conclusion
Cocoa pod husk powder can be used as a dye on silk batik and is ready to use for the batik industry. The use of maltodextrin 5% filler for cocoa pods husk powder was the best. This means that the fewer fillers will further enhance the color strength. Cocoa pods husk powder which gave the best color pigment was a neutral pH condition. The use of ferrous sulfate mordant led to dark/black color intensity, while alum mordant led to bright/yellow color intensity.
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