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Extraction of Natural Dyes from Cocoa Pod Husk (*Theobroma cacao L.*) using Ultrasound-Assisted Extraction as a Natural Fabric Dye

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Abstract

Natural dyes are one of the popular choices for textile dyes today. One part of the plant that has the potential to produce natural dyes is cocoa pod husk (*Theobroma cacao L.*) because it contains several secondary metabolite compounds, such as tannin which produces a brown color. The extraction method used in this research is Ultrasonic Assisted Extraction (UAE). This study aims to obtain the highest yield of natural dye extracts from cocoa pod husk by varying solvent types, extraction time, and material-to-solvent ratios using the UAE method. In addition, the types of compounds contained in extracts of natural dyes and color results on cotton fabrics were also obtained. The extraction process was carried out using several types of solvents, namely methanol, ethanol, acetone, and distilled water with varying extraction times of 30, 60, and 90 minutes. The research results show that the solvent that can extract the best natural dyes was ethanol with a yield of 11.43% and an extraction time of 90 minutes. Variable ratios of material to 96% ethanol solvent were also observed, namely at ratios of 1:5, 1:6, 1:7, and 1:8 for extraction times of 30, 60, 90, and 120 minutes. The research results were obtained for the ratio of material to ethanol solvent; 1:8 (w/v) and extraction time 120 minutes with a dye yield of 12.29%. The results of the UV-visible spectrophotometry analysis were obtained that the maximum wavelength of cocoa pod husk extract was 656.5 nm with an absorbance of 0.532. The results of the Gas Chromatography-Mass Spectrometry (GC-MS) analysis were obtained that the dye compound in the cocoa pod husk was tannin. Tannin compounds are natural dyes that can be applied to fabrics and will reduce the use of synthetic dyes. The application of dye extracts to cotton fabrics produced a brown color.

Keywords: natural dyes, extraction, cocoa pod husk, ultrasonic-assisted extraction, tannin

1. Introduction

The global demand for dyes increases annually. Currently, there are more than 10,000 dyes commercially available. The annual production of dyes worldwide is around 70.000.000 tons/year (Markandeya et al., 2017). The textile industry is the largest consumer of dyes in the world. Textile coloration processes typically involve synthetic dyes. Synthetic dyes from both heavy metals and petroleum derivatives adversely affect health. Synthetic dye waste poses significant environmental risk because of its potential to cause pollution. This material is hazardous because certain dyes can break down into substances that are both carcinogenic and toxic. Synthetic dyes generally contain azo compounds. This compound is not environmentally friendly and is toxic to the body. Unlike natural dyes, colors are formed by secondary metabolite compounds, including those from plants. These substances differ in the types of chemical bonds in their compounds and the energy of their color absorption. The advantage is that natural dyes are safe and environmentally friendly.

Natural dyes can be obtained from the roots, stems, leaves, flowers, and fruits of plants and these dyes are biocompatible and biodegradable. Dyeing cotton fabrics or fabrics made from natural materials with natural dyes can avoid the environmental problems associated with the use of chemical dyes and synthetic fibers, and meet the need for sustainable development (Li et al., 2024).

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In Indonesia, there are many plants as a source of natural dyes. One plant that has the potential to be a source of dye is the cocoa plant (*Theobroma cacao L*). The part of the cocoa plant that can be used as a natural dye is the cocoa pod husk. Cocoa plants are found in many tropical areas, such as Indonesia. Based on 2020 statistical data, the total area of cocoa plantations in Indonesia is around 1,508,956 Ha, with cocoa production of around 720,660 tons (Badan Pusat Statistik, 2020).

The chocolate plant produces fruit that is processed into chocolate products. In the process of processing chocolate products from cocoa, cocoa pod husk (CPH) is the main waste, according to Arroy et al. (2017), this side product accounts for more than 76%. Between 76% to 86% of the entire weight of a cocoa pod is attributed to its husk. Despite this substantial proportion, only a minor fraction of this waste material has been effectively utilized. This cocoa pod husk has the potential to be utilized due to its composition, which includes protein, carbohydrates, fats, lignocellulose, pectin, alkaloids, and phenolic compounds such as anthocyanidins and pigments (Dewi et al., 2022). Cocoa pod husk (CPH) is the main by-product of the cocoa industry and is a source of bioactive compounds. It is estimated that for every ton of dry cocoa beans produced, 10 tons of wet CPH are produced. Because the number is quite large, processing cocoa waste is still a challenge, generally, CPH is only used as fertilizer by leaving it directly in the soil until it decomposes (Ramos et al., 2023)

There are already several researchers who have researched cocoa pod husk. Valadez-Carmona et al. (2018) have researched about supercritical-CO_2 extraction method with ethanol solvent to extract phenolic compounds from cocoa pod husk. The optimal extraction conditions involved operating at 60°C and 299 bar pressure, with an ethanol concentration of 13.7%. under these conditions produces a yield of 0.52% and a total phenolic content of 12.97 mg in Gallic Acid Equivalents (GAE)/gram of dry extract. In the other study, it was stated that there are phenolic or polyphenolic compounds in the cocoa pod husk (Karim et al., 2014).

The presence of phenolic compounds in cocoa pod husk pigment has the potential to be used as a natural dye in textiles. One of the natural dyes of phenolic compounds is tannin, which is a secondary metabolite of polyphenolic compounds found in plant parts (Das et al., 2020). The process method chosen will influence the results of the phenolic content extracted from the cocoa pod husk. According to Pisitsak et al. (2016), tannins can cause brown color in cotton fabric. The extraction of tannin from *Tamarindus indica L* seeds was carried out by (Prabhu and Teli, 2014) as a natural mordant for textiles.

In general, tannin is extracted using hot water as a solvent. However, some researchers also use the solvents acetone, diisopropyl ether, ethyl acetate, ethyl ether, methanol, and ethanol. There are several advanced methods are available for the extraction of tannin, such as supercritical, ionic liquid-assisted microwave, infrared-assisted, and hot water extraction methods (Das et al., 2020). Meanwhile, Helmy (2020) states that new techniques or methods for extracting natural dyes include ultrasonic extraction, microwave extraction, and utilization of enzymes. The ultrasonic or microwave method has been successful in increasing the extraction rate, and the temperature of the extraction process is lower compared to traditional heating methods.

Extraction using the ultrasonic method has also been carried out by several researchers. Ribeiro et al. (2023) conducted research using the UAE method to extract tannin from the bark of the *Stryphnodendron astringents* (Barbatimao) plant more efficiently than conventional methods. Silva et al. (2021) extracted tannin from the *Cytinus hypocistis L.* plant using the Heat-Assisted (HAE) and UAE methods. The HAE method gave a result of 200 mg of tannin in 95.1 minutes, a temperature of 46.4°C, and an ethanol concentration of 74.3%, while the UAE gave a result of 178 mg in 18.7 minutes, with a power of 327.4 W, and an ethanol concentration of 69.3%. Although HAE provides higher results, the UAE method takes less time.

Other researchers, Sivakumar et al. (2011) were conducted to investigate the extraction of natural dyes from various plant sources utilizing ultrasound technology. The materials used in this research are plants that contain natural dyes such as green wattle bark (*Acacia decurrens*), marigold flowers (*Tagetes erecta*), pomegranate skin (*Punica granatum*), 4 o'clock flower (*Mirabilis jalapa*) and cock's comb flower (*Celosia cristata*). In this research, extraction was carried out using ultrasound and using a magnetic stirrer. The research results showed that there was a significant increase in the yield of extracted dyes by 13-100% for different plant materials using ultrasound compared to a magnetic

stirrer. Therefore, dye extraction using ultrasound can be used to extract dyes from plant materials more quickly and effectively.
Haerudin et al. (2020) researched the influence of variations in temperature, pH, and extraction duration on the quality of dyes from cocoa pod husk extract (*Theobroma cacao L.*) which were applied to cotton and silk fabrics for batik fabric. This research was carried out with variations in extraction temperature (60, 80, and 100°C), variations in extraction pH (acid pH 4, alkaline pH 10, and at neutral pH namely pH 7), variations in extraction time (1, 2, and 3 hours), and variations type of fabric (cotton and silk). In this research, the method used still uses conventional methods, namely by boiling or extraction with water as a solvent. The results of this research do not focus on the coloring results alone, but the treatment given has a significant influence on achieving optimal dark colors and striking differences in color testing. Specifically, the extraction treatment at a temperature of 100°C, alkaline pH 10, and a time of 3 hours produced the highest dark color. The color fastness test shows an average value of 4.5, which indicates it is still in the good category. The resultant is a dark salmon color, characterized by a blend of red and yellow hues.

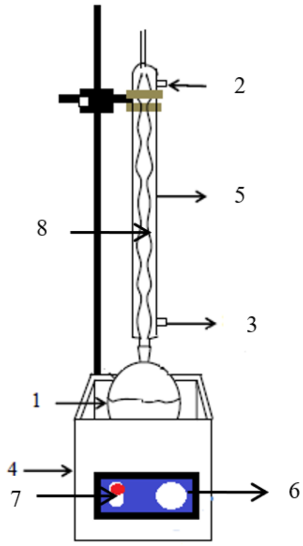
Rodiah et al. (2021) researched the extraction of cocoa pod husk from the mesocarp and exocarp using NaOH solution (0.2-0.8 M) and extraction time (2-10 minutes) with microwave-assisted extraction. The research results showed that using 0.8 M NaOH for 4 minutes significantly increased the dye yield, namely 82.15% for mesocarp and 97.15% for exocarp. This research also investigated the application of tannic acid at different concentrations (2.5%, 5%, and 7.5%) as a mordant on cotton fabric. The dyeing process was conducted at a temperature of 40 °C for 60 minutes.

The primary aim of this research was to optimize the extraction of natural dyes from cocoa pod husk using ultrasonic-assisted extraction, considering various solvents, material-to-solvent ratios, and extraction durations.

2. Methodology

2.1. Materials

The experiment was carried out at the Laboratorium Terpadu dan Sentra Inovasi Teknologi (LTSIT) at the University of Lampung, Bandar Lampung. The materials used in the research were cocoa pod husk obtained from Desa Teluk Dalem, East Lampung. Distilled water, lime, alum and ferrous sulfate were supplied by Brataco chemicals, Bandar Lampung. Ethanol 96% (w/w), methanol 96% (w/w), acetone 96% (w/w) were supplied by Merck. Lime, alum, and ferrous sulfate were used as fixator materials, which were liquids for fixation in fabric dyeing. The series of equipment used for extraction with UAE is shown in Figure 1.



(1) single neck round bottom flask, (2) inlet water, (3) outlet water, (4) ultrasonic batch cleaning, (5) condenser (6) timer, (7) heater, (8) stative and clamps

Figure 1. Ultrasonic-assisted extraction

2.2. The Extraction Process on Cocoa Pod Husk

The husk of the cocoa pod underwent a thorough cleaning process to remove any impurities before being finely chopped into small pieces. The cut material was then left to dry under sunlight until it reached a state of complete dryness. Subsequently, the dried material was examined, revealing a water content of 10.3% (w/w) and an ash content of 10% (w/w). The dried cocoa pods were then ground using a blender until they became powder and sifted using a 60-mesh sieve.

The extraction process began by weighing 50 grams of dried cocoa pods using an analytical balance, placing them in a flask, and adding 400 mL of solvent using a 500 mL beaker glass. In this first step of the experiment, the solvents used varied, namely distilled water, ethanol, methanol, and acetone. The extraction procedure occurred at a temperature of 70°C. The extraction duration was determined upon reaching the temperature of 70°C and varied at 30, 60, and 90 minutes using ultrasonic asissted extraction.

In the next experiment, ethanol was utilized as the solvent for extraction, and the material-to-solvent ratio was varied at a ratio of 1:5, 1:6, 1:7, and 1:8. The extraction operation was conducted at a constant temperature of 70°C, while the duration of extraction was being varied at 30, 60, 90 and 120 minutes. The UAE method can occur with ultrasonic waves to extract natural dyes from the cocoa pod husk. Filter paper was used to separate the residue from the solution after the extraction process was completed. To obtain dye extract from the solution, use a rotary vacuum evaporator. This procedure was conducted under conditions of 70°C and a pressure of 200 mbar. The dye extract obtained was in paste form, then cooled with a desiccator and weighed until the weight was constant.

Analysis of research results was carried out at the Laboratorium Botani, Biology Department and LTSIT, University of Lampung. The tools that used to analysis were UV-Vis Spectroscopy and GC-MS

2.3 The Analysis

The analysis of the results of natural dye extracts carried out in this research was UV-Vis Spectrophotometric analysis and GC-MS analysis. The UV-Vis Spectrophotometry test aimed to identify the peak wavelength of the produced natural dye extract. This wavelength was used to analyze the chromophore groups contained in the extract according to the absorption band of the compound to be searched for. The type of spectrophotometer used was a Double-beam type Shimadzu UV-1800. Meanwhile, The GC-MS test was designed to confirm the presence of chromophores through UV-visible spectro-photometric analysis. With this GC-MS test, the compounds contained in the extract will be detected. The GC-MS used was Thermo Scientific Trace 1310 Gas Chromatograph. The separation was performed using an HP-5MS UI capillary column with helium UHP as a carrier gas. The injector temperature was set at a temperature of 260°C and split flow 50 mL/min.

2.4. Application of the dye extract on cotton fabric

To produce a good color, the color dyed from the extract needed to be given a binder or fixative. The purpose of applying dye to cotton fabric was to determine the influence of the fixation solution on the color produced on cotton fabric. Based on theory, using different types of fixative materials would produce different colors too. The function of fixation was to strengthen the color of the fabric and the direction of the resulting color was by the type of metal that binds it. The fabric used was 3 sheets of primisima cotton fabric measuring 5 x 5 cm. This cloth was then dipped in a 10 g/L dye solution for 15 minutes and then dried (repeated 3 times). In the fixation process, a solution of 70 g/L alum, 50 g/L lime, and 20 g/L ferrous sulfate was made. Each cloth was dipped in a different solution so that the color results could be compared. The fabric samples were dipped in the respective fixator solution for 15 minutes and then dried.

3. Results and Discussion

3.1. Effect of Solvents

The extraction is the process of separating a component from a mixture using a solvent. The process of extracting natural dye compounds from cocoa pod husk is a solid-liquid extraction that relies on mass transfer. The dye is strongly bound to the plant cell walls therefore a suitable solvent is needed to extract the dye.

In this research, the UAE method was used because the extraction process can take place more quickly. This aligns with prior research by (Utami et al., 2021) on avocado seed extraction, using the UAE method which gave an extraction yield of natural dyes of 16.7%, with 90 minutes of extraction time using 70% ethanol solvent. The equipment used was an ultrasonic cleaning bath brand Mujigae TP-0105 with a frequency of 80 Hz, at a temperature of 70°C. The selection of extraction time in this study is also based on the study.

The following are the results of extracting cocoa pod husk with various types of solvents and extraction times of 30, 60, and 90 minutes. Many organic solvents are commonly used to extract natural pigments. The polarity of the solvent significantly influences the absorption spectra and extraction amounts of dyes (Soosairaj et al., 2024). The solvents used in this study were ethanol 96% (w/w), methanol 96% (w/w), acetone 96% (w/w), and distilled water. The choice of solvents was based on the components of dyes which were polar, so they dissolve easily in polar solvents. The extraction process was carried out at a temperature of 70°C and a material-to-solvent ratio of 1:8. Figure 2 shows that the highest yield of 11.43% was obtained using ethanol as the solvent with at an extraction time of 90 minutes. The high yield of cocoa pod husk with ethanol solvent shows that ethanol solvent can extract cocoa husk better because the compound in the extract had a similar polarity to the solvent.

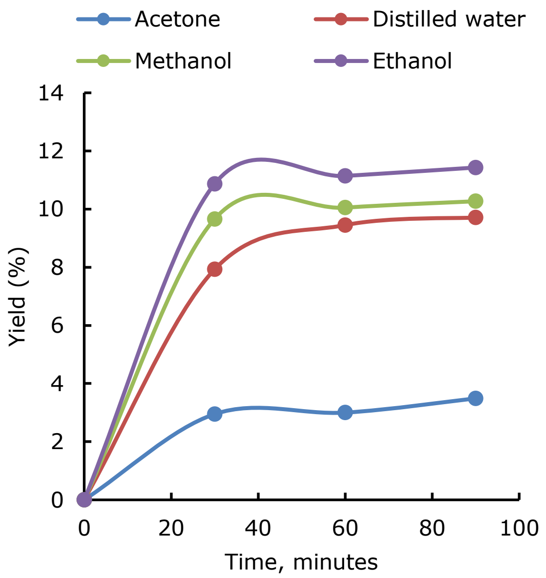


Figure 2. The yield profile of natural dyes for the type of solvents

Based on GC-MS analysis, the dye extract produced in this study is tannin. The solubility of tannins varies greatly, based on the desired target compound, solvents with different relative polarity can be selected, such as water, ethanol, acetone, or methanol. According to (Pandey et al., 2014) tannins can dissolve in water, ethanol, and methanol. In general, tannins are classified into two main groups of polyphenols, namely hydrolyzed tannins and condensed tannins known as proanthocyanidins. To extract hydrolyzed tannins generally uses water or ethanol. Meanwhile, condensed tannins have limited solubility in polar organic solvents (Fraga-Corral et al., 2020)**.**

Methanol and acetone have a polarity index of 5.1, ethanol is 5.2 and water is 10.2 (Kleiman et al., 2016). According to the calculation method contained in the reference, tannins have a polarity index of 6.05 (Gardner, John M., Morris, 2007). Thus, the closest to the polarity of tannins is ethanol so the yield of tannin extract is with ethanol solvents. The polarity of ethanol is caused by the presence of an OH group at one end of its carbon chain (Waluyo et al., 2020). While the ethyl group (CH_3CH_2) is non-polar. The non-polarity is caused by the shortness of the activated carbon in ethanol (Arsa and Achmad, 2020).

2.3. The Effect of Material to Solvent Ratio

Ethanol with a concentration of 96% was used as a solvent. The selection of the solvent depends on the outcomes of experiments comparing different types of solvents. Variables in this study include the ratio of material to solvent, including ratios of 1:5, 1:6, 1:7, and 1:8, alongside extraction durations of 30, 60, 90, and 120 minutes. Extraction procedures were conducted at a temperature of 70°C. The results obtained from the extraction of cocoa pod husk are depicted in Figures 3 and 4.

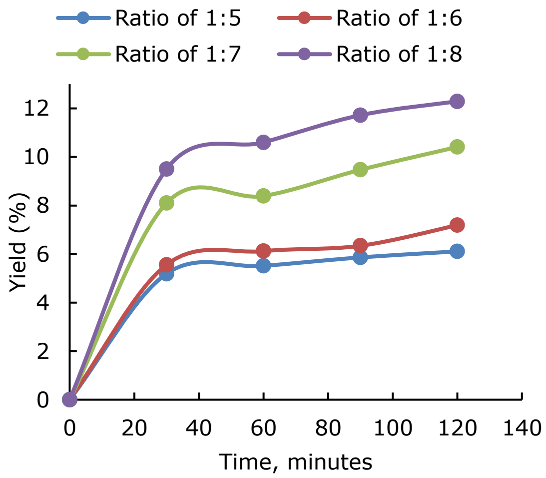


Figure 3. The yield of natural dyes results based on the material-to-solvent ratio

Figures 3 and 4 illustrate how altering the ratio of material to solvent impacts the yield of cocoa pod husk extract dye. The greatest yield, reaching 12.29%, was achieved when using a ratio of 1:8 (material to solvent ratio) during a 120-minute extraction period. Meanwhile, with the same extraction duration, yields were 6.11%, 7.69%, and 10.41% for material-to-solvent ratios of 1:5, 1:6, and 1:7, respectively. A higher material-to-solvent ratio resulted in a greater yield. This is because the contact between the solids material and the solvent will be greater when a larger volume of solvent is used, making it easier for the solvent to penetrate the solids cell and dissolve the target compound. This will continue until equilibrium in the extraction process is achieved.

Extraction results can be maximized and this is a step that needs to be considered, apart from saving time it can also reduce resources because the extract results obtained in the same amount can be achieved using less solvent and materials (Klavins et al., 2017). The ratio between material and solvent is one of the important factors that influence the extraction of bioactive compounds (Hernes et al., 2018)and plays an important role in determining the efficiency of the extraction process (Arroy et al., 2017).

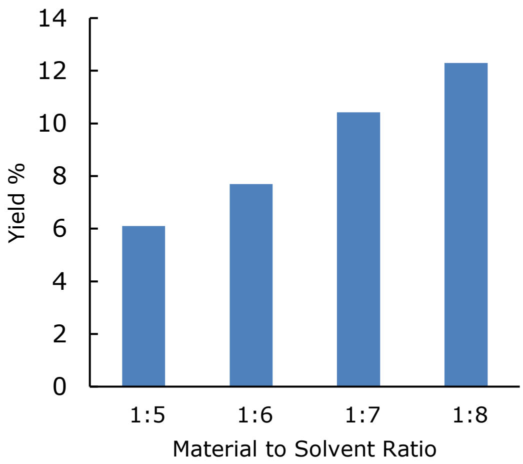


Figure 4. The yield of natural dyes results based on the material-to-solvent ratio at an extraction time of 120 minutes

This increase in yield is due to the higher the amount of solvent used, the more optimal the release of the target compound into the solvent. Septiani et al. (2021) research results are in line with this research. The results of the research showed that at a ratio of solvent to material, namely 5:1 to 8:1, there was an increase in the yield of natural secang wood dye with the distilled water solvent and the UAE method. The highest yield of 4.0% was achieved when the ratio was 8:1, the extraction time was 15 minutes, and the temperature of 60^{o}C.

Winata and Yuaninta (2015) researched the extraction of anthocyanins from mulberry fruit (*Morus alba* L.) was explored using the ultrasonic bath method, investigating the influence of extraction time and the ratio of material to solvent. The research revealed that an increased ratio of material to solvent led to higher extract yields. This phenomenon can be attributed to the enhanced contact between the material matrix and the solvent when a larger volume of solvent is employed. Consequently, the solvent can more readily permeate the material matrix cells and dissolve the desired compound. This process continues until reaching equilibrium. However, the use of excessive solvent volume needs to be avoided because it causes obstacles in the transfer of ultrasonic wave energy because of being absorbed by the solvent before it reaches the material matrix.

3.3. Effect of the Duration of the Extraction Process

This research was conducted using the UAE method with time variations of 30, 60, 90, and 120 minutes. Based on the yield results of dye extracts with variations in time, the highest extract yield was achieved at an extraction time of 120 minutes as shown in Figure 3.

Figure 3 shows a significant increase in extraction yields with an increase in extraction duration. The most effective extraction time was 60 minutes for a ratio of 1:5, as equilibrium was reached, and the relative yield showed minimal differences. However, the ratio of 1:6, 1:7, and 1:8 had not reached equilibrium time because the yield of the extract was still experiencing a significant increase.

Prolonged exposure to ultrasonic waves caused cavitation within the solution material, leading to an increase in extraction (Maran and Priya, 2015). In Winata and Yuaninta (2015) research, it was discovered that using the ultrasonic extraction technique can expedite the extraction process. This is due to the cavitation effect induced by ultrasonics, which effectively ruptures the cell walls of the material so that the extract comes out easily and achieves maximum extract yield in a significantly shorter extraction duration.

Generally, extended extraction durations tend to result in increased yield. This phenomenon occurs because prolonged extraction periods allow for more extensive interaction between the solvent and the substance being extracted. The longer the extraction time, the more heat is absorbed and the diffusion process is more intensified, thereby accelerating the extraction process.

Based on Figure 3, the extraction results exhibited a continual rise until reaching their peak under optimal conditions. For the extraction of natural dyes from cocoa pod husk, the maximum extraction yield was achieved after 120 minutes of extraction time. The increased yield of extraction is caused by the extended duration of exposure to ultrasound waves, which leads to the swelling and hydration of the solid material of the cocoa pod shell. This phenomenon arises from the cavitation effect, where microjets form on the surface of the material, potentially causing damage to the material and allowing the solvent to easily diffuse into the material matrix (Maran & Priya, 2015). The increase in yield will be observed continuously until an equilibrium condition is reached between the concentration of the compound in the material and the concentration of the compound in the solvent. Based on the results of this research, in general, the yield obtained is still increasing so it has not yet reached an equilibrium.

3.4. Analysis UV-Vis of the Natural Dye Extract

A spectrophotometer determines the wavelength of natural dyes by analyzing the correlation between absorbance and wavelength in nanometers (nm). The basic principle is that each compound absorbs or transmits light over a certain range of wavelengths. The natural dye content resulting from the extraction is proportional to their absorbance values. The maximum wavelength of the natural dye extracted is determined through this absorbance test. Qualitative tests using the UV-Vis spectrophotometry method were carried out to determine the maximum wavelength. This aims to ensure that measurements at the maximum absorption wavelength will also produce maximum absorption. In this UV visible spectrophotometer analysis test, light is used above the ultraviolet range of 185-400 nm and visible range of 400-700 nm of the electromagnetic radiation spectrum (A and Dileep, 2017).

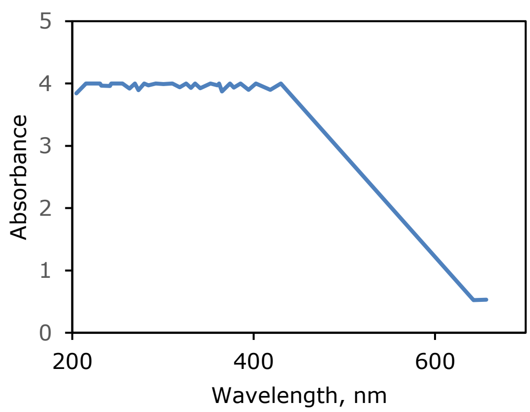


Figure 5. The result of UV-Vis Spectrophotometer analysis

The result of measuring the dye extract sample under extraction conditions with ethanol as the solvent, using a material-to-solvent ratio of 1:8, a time of 90 minutes, and a temperature of 70°C, revealed that the capable of identifying the dye in the cocoa pod husk was at 656.5 nm. This corresponded to an absorbance value of 0.532, as shown in Figure 5.

One method to predict the wavelength of a compound is by applying the Woodward-Fisher Rules equation, which considers the chemical structure of the compound (Nandgaye et al., 2023). Calculations using this method indicated that the wavelength range corresponds to tannin compounds. The UV-Vis spectrophotometry analysis results align with findings from other studies. For instance, dye extracts from mangrove fruits displayed a maximum absorbance of 0.541 at a wavelength of 675 nm, indicating the presence of tannin compounds, which produce a blue color in the 600-700 nm range (Paryanto et al., 2017). Additionally, the resonance exhibited by phenolic compounds in UV-Vis spectroscopy occurs at wavelengths ranging from 640-780 nm (Pratama et al., 2019). This supports the conclusion that the extracted dye contains phenolic compounds. The wavelength of the cocoa pod husk extract (656.5 nm) further confirms that the extract contains with more than one chromophore group, such as tannins, which are phenolic or polyphenolic in nature.

3.5. Analysis GCMS of the Natural Dye Extract

The natural dye extract from cocoa pod husk, obtained from the extraction process, was further analyzed using GC-MS for both qualitative and quantitative analysis. Gas Chromatography (GC) is effective for identifying the constituents of the cocoa pod dye extract, while Mass Spectrometry (MS) quantifies the compounds present in the extract.

The GC-MS detector converts certain molecular properties of organic compounds into electric current, which is transmitted to a recorder to produce a chromatogram. This chromatogram enables both qualitative and quantitative analysis. Qualitative analysis involves comparing the sample retention time with laboratory standards in GC-MS, while quantitative analysis is carried out by calculating the area and height of the chromatogram peaks.

The measurement of the dye extract sample under extraction conditions using ethanol, a material-to-solvent ratio of 1:8, a time of 90 minutes, and a temperature of 70°C, produced a chromatogram with peaks corresponding to the sample's properties and the detector type. The GC-MS analysis results, presented in Table 1, revealed that the cocoa pod husk extract contains 31 organic compound components. The area of each peak was determined and compared to the total peak area to calculate the percentage composition of each component.

Three which had the largest percentage with significant % area in the extract: n-hexadecanoic acid ($C_{16}H_{32}O_2$) with 18.227% area, having a molecular weight of 256 g/mol, I-(+) -Ascorbic acid 2,6-dihexadecanoate ($C_{38}H_{68}O_8$) with 18.227% area and a molecular weight of 652 g/mol, and oleic acid ($C_{18}H_{34}O_2$) with 16.277% area and a molecular weight of 282 g/mol.

The presence of phenolic compounds in the extract is indicated by several compound structures, as evidenced by the chromophore groups present. The three dominant compounds in cocoa pod husk extract contain hydroxyl groups and other groups (such as carboxyl). This is a characteristic of tannin compounds which are defined as polyphenols that have hydroxyl groups and other groups.

Table 1. Organic compound contained in dye extract detected by GC-MS measurement

No	**RT**	Organic Compound	**Rel. Area (%)**
1	7,29	Hexane, 2,2,3-trimethyl-	0,966
2	7,29	Decane,2,2,3-trimethyl-	0,624
3	25,42	Phenol, 4,6-di(1,1-dimethylethyl)-2-methyl-	0,264
4	25,42	2,4,6,-tris(1,1-dimethylethyl)-4-methylcyclohexa-2,5-dien-1-one	0,191
5	25,42	Buthylated Hydroxytoluene	0,137
6	28,78	Phenethylamine, N-methyl-beta.,3,4-tris(trimethylsiloxy)-	0,348
7	28,78	Benzeneacetic acid,. Alpha., 3,4-tris[(trimethylsilyl)oxy]-, trimethylsilyl ester	0,211
8	28,78	Terbutaline, N, trifluoroacetyl-o,o,o-tris(trimethylsilyl)deriv	0,140
9	30,94	Thieno[3,2-c]pyridine, 3-bromo-	0,324
10	30,94	2-Bromobenzothiazole	0,286
11	30,94	2-(2-Bromo-phenyl)-acetamide	0,069
12	36,34	Pentadecanoic acid, 14-,methyl-, methyl ester	4,424
13	36,34	Pentadecanoic acid, 13-,methyl-, methyl ester	2,681
14	36,34	Hexadecanoic acid, methyl ester	1,892
15	37,29	n-hexadecanoid acid	18,227
16	37,29	I-(+)-Ascorbic acid 2,6-dihexadecanoate	18,227
17	37,29	Isopropyl palmitate	9,944
18	39,70	9,12-octadecadienoic acid. (Z,Z)-,methyl ester	1,030
19	39,70	9,12-octadecadienoic acid,methyl ester	0,789
20	39,70	8,11-Octadecadienoic acid, methyl ester	0,478
21	39,82	9-Octadecanoid acid (Z)., methyl ester	0,973
22	39,82	12-Octadecenoic acid, methyl ester, (Z)	0,821
23	39,82	10-Octadecanoic acid, Methyl ester	0,789
24	40, 32	Octadecanoid acid, Methyl ester	3,664
25	40,32	Heptadecanoic acid, 16-methyl-, methyl ester	0,878
26	40,32	Heptadecanoic acid, 15-methyl-, methyl ester	0,672
27	40,68	Oleic Acid	16,277
28	40,68	9,12-Octadecadienoic acid (Z,Z)-	2,469
29	40,68	E-9-Tetradecenoic acid	0,672
30	41,09	Oleic Acid	9,065
31	41,09	Octadecanoid acid, 2-(2-hydroxyethoxy)ethyl ester	2,471

3.6. Natural Dyes on Cotton Cloth

To make good dyes, it's necessary to bond or fix the colored dyes with a binding or fixing agent. This binding agent can produce different colors when applying natural dyes to fabric. In this research, lime, alum, and ferrous sulfate binding agents were used. The natural dye that has been extracted is then dissolved using water.

Cotton cloth measuring 5 x 5 cm was immersed in a natural dye solution at room temperature for 15 minutes. Following this, it was air-dried in a shaded area, avoiding direct sunlight exposure. The dyeing and drying process was repeated 3 times. After that, dip it in a fixator solution, namely lime, alum, and ferrous sulfate.

Figure 6. The result of the application of natural dye on cotton cloth

Based on the experimental findings obtained using natural dyes derived from cocoa pod husk, it was found that natural dyes can dye cotton fabric brown because they contain tannin compounds as shown in Figure 6. As a result of dyeing cocoa pod husk extract, cotton fabric can be dyed well and gives a brown color, because it contains tannins. The conjugated double bonds in polyphenols (acting as chromophores) and the presence of OH groups (acting as auxochromes) in tannins cause them to impart a brown color to materials. This property allows tannin extracts to be used as natural textile dyes (Sylvi and Merlin, 2020). The dye will be absorbed into the fabric fibers and settle in the fibers throughout the dyeing process.

Figure 7. The final fixation color of the dyed cotton cloth (a) lime; (b) alum; (c) ferrous sulfate

Figure 7 indicates that natural dyes undergo color changes when a fixative is added. Fixation is a process to strengthen the color so that it does not fade easily. When adding lime $Ca(OH)_2$, the resulting color is darker than before the fixation solution was added. The addition of alum ($Al_2(SO4)_2$) gives a brown color that is similar to the base color before fixation. Meanwhile, when adding ferrous sulfate ($FeSO_4$), the color becomes blackish brown, which is very different from the color before being given the fixation solution.

From the dyeing on the cotton fabric, it can be applied to the dyeing on the written batik fabric. By using natural dyes, the process of making batik becomes more environmentally friendly because it reduces the synthetic dyes used so far. Artisans of written batik can utilize the waste of cocoa pod husk and make their natural dyes. It's just that the amount of waste from cocoa pod husk is still limited and this natural dye cannot be produced on a commercial scale.

4. Conclusion

This research found that the optimal condition for extraction was using ethanol as the solvent, with a material-to-solvent ratio of 1:8 and an extraction time of 90 minutes, yielding 11.43%. By varying the ratio of material to solvent, the results were obtained at a ratio of 1:8 with an extraction time of 120 minutes producing a dye extract yield of 12.29%. The results of the dye extract were analyzed using UV-Vis Spectrophotometry and GC-MS. The results of the Spectrophotometry analysis were obtained that the maximum wavelength of cocoa pod husk extract is 656.5 nm with an absorbance of 0.532. The results of the GC-MS analysis were obtained that the dye compound in the cocoa pod husk was tannin. Apart from that, the color produced from cocoa pod husk extract is brown. A light brown color is imparted to the fabric upon the addition of an alum fixator. The fabric's color changes to light brown when the alum fixator is added. Meanwhile, the addition of a lime fixator results in the brown color of the fabric becoming darker (dark brown), and then the addition of a ferrous sulfate fixator shows a change in color to blackish brown.

Author contribution

Conceptualization, H.U.; Formal analysis, K.H.; Investigation, A.F.P.; Project administration, A.A.A.; Supervision, Y.D.; Writing – original draft, A.M.; Validation, S.G.; Writing –review and editing, H.U.

Data availability Statement

Available on request to the corresponding author.

Declaration of Competing Interest

The author declares that there is no competing of interest regarding the publication of this manuscript.

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