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The Utilization of Anthocyanin Extract from Parijoto (*Medinilla speciosa*) as a Sensitizer in Dye-Sensitized Solar Cells (DSSC)

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Abstract

The research on the Utilization of Anthocyanin Extract from Parijoto (*Medinilla speciosa*) as a Sensitizers in Dye Sensitized Solar Cell (DSSC) aims to identify the presence of anthocyanin compounds in parijoto fruit and determine how much power can be generated from anthocyanin compounds as sensitizers in DSSC using variations of ethanol, methanol, ethanol-citric acid (50:50), methanol-citric acid (50:50) solvents through the maceration method for 48 hours. The highest yield was the methanol-citric acid extract from the fruit, which was 16.35%. Positive results in the identification of anthocyanin compounds that were dripped with NaOH showed a color change from red to green-blue and when dripped with HCl there was no color change. The results of the functional group characterization of the fruit ethanol extract through FTIR (Fourier Transform Infrared) analysis showed the presence of -OH groups, -C=C aromatic and -CO alcohol at a wave number of 3293 cm^{-1}, 1644 cm^{-1}, and 1019 cm^{-1}, while from the GCMS (Gas Chromatography Mass Spectrometry) analysis in the fruit ethanol extract there was a cyanidin structural framework at a retention time of 12.24 minutes with a value (m/z) of 243, and an area% of 1.09%. The power measurement on the fruit ethanol extract was 0.1516 mW and on the fruit ethanol-citric acid extract was 0.023 mW. The power generated indicates that the parijoto fruit extract has the potential as a sensitizer in the Dye-Sensitized Solar Cell (DSSC) application.

Keywords: Anthocyanin, Dye-Sensitized Solar Cell (DSSC), Extract, Parijoto (*Medinilla* sp.), Power

1 Introduction

Sunlight can be an alternative energy source that has the potential to be applied in Indonesia. This is because Indonesia is located on the equator, allowing Indonesia to be optimally exposed to sunlight throughout the year [1]. The average potential for solar radiation is around 4.8 kWh/m^2 per day. One method of utilizing sunlight is photovoltaic technology. Photovoltaic technology is one method for generating energy from sunlight. This technology uses solar cells to generate electricity [2]. The first generation of photovoltaic technology is based on crystalline silicon, the second generation refers to non-crystalline silicon or inorganic semiconductors with an energy conversion efficiency of 33.7% limited by the Shockley Queisser (SQL) limit [3]. However, this technology is constrained by expensive fabrication because it uses silicon as a raw material, where silicon is a single crystal with high purity, so it requires expensive and limited production costs. In the third generation, organic materials containing carbon are used, known as Dye-Sensitized Solar Cells (DSSC).

DSSC is a solar cell technology with the advantage of not requiring silicon material which has a high purity level so that the production cost is relatively lower compared to previous generations of solar cells. The main components of a DSSC consist of transparent/ conductive glass which is used as a cathode and anode. The cathode is a TCO (Transparent Conducting Oxide) glass coated with carbon as a catalyst in the redox reaction. The anode is a TCO glass coated with TiO_2 which is soaked in a dye or dye containing anthocyanin as a sensitizer [4].

Anthocyanin is a pigment responsible for the blue, red, or purple colors found in plants, both in the flowers, stems, and fruits, which are included in the flavonoid class [5]. One of the plants that contains anthocyanin compounds is parijoto. Parijoto (*Medinilla speciosa*) is one of the typical

plants that can grow in the Colo, Kudus, and Central Java areas. In parijoto fruit there are several chemicals and flavonoids such as saponins, cardeolin, flavonoids [6]. Chemically, anthocyanins are included in the flavonoid group and are polar compounds so they can be obtained by extraction using polar solvents. The acidic conditions of the solvent in the extraction process can affect the extraction results [7].

One of the methods of extracting anthocyanin compounds that can be done simply is maceration. In the extraction process using the maceration method, the material is soaked in a solvent with the same conditions as the active compound to be obtained, namely the anthocyanin compound. The advantage of using the maceration method is that the anthocyanin extract will not be damaged, due to the difference in pressure between the inside and outside of the cell membrane, causing the cell wall to rupture and the secondary metabolites contained in the cytoplasm will dissolve in the organic solvent used [8]. Therefore, anthocyanin extraction was carried out from parijoto fruit with variations of solvents used, namely ethanol, methanol, citric acid to determine the performance of Dye Sensitized Solar Cell (DSSC) in various types of solvents used.

2 Method

This study aims to determine how much power is produced from anthocyanin compounds as sensitizers in DSSC using variations of ethanol, methanol, ethanol-citric acid (50:50), methanol-citric acid (50:50) solvents through the maceration method for 48 hours. The parijoto fruit used came from Kudus Regency, Central Java. This study was conducted using parijoto fruit samples from the laboratory. DSSC testing consists of Indium Thin Oxide (ITO) glass, TiO_2 paste, electrolyte, and 2B pencil.

Treatment and Experimental Testing

The sorted parijoto fruit is separated from the fruit. Then macerated by adding each solvent with a ratio of 1:10 with a mass of 20 grams of parijoto and a solvent added as much as 200 ml for 2 days. The resulting macerate is evaporated to form an extract. Identification of anthocyanins in two ways, namely, a few drops of each extract are dripped with 0.25 M NaOH if the resulting color change changes from red to green-blue, it states that the results obtained are positive and the ethanol fruit extract is dripped with 0.25 M HCl during heating at a temperature of 100 ^oC, if there is no color change, it indicates a positive result. The resulting extract is characterized using FTIR (Fourier Transform Infrared), UV-Vis Spectrophotometer, and GCMS (Gas Chromatography Mass Spectrometry).

This DSSC application refers to research conducted by [9] with minor modifications. Deposition begins with resistance testing on ITO glass. On the anode, ITO glass is coated with TiO_2 paste, the layer is heated on a hotplate at a temperature of 250 C for 20 minutes. The TiO_2 layer is immersed in the extract and left for 30 minutes. On the cathode, the ITO glass is lightly shaded using a 2B pencil. DSSC assembly is carried out by clamping the two ITO glasses using paper clips on both sides of the glass, then dripping electrolyte solution through the gaps in the ITO glass until a sandwich layer is formed. Then the DSSC current and voltage measurements are carried out using a multimeter (**Fig. 1**).

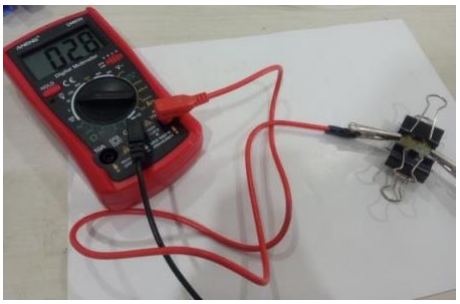


Figure 1. Instrument of DSSC Circuit.

3 Result and Discussion

Extraction of anthocyanins from whole fruit and skin using the maceration method aims to extract more compounds contained in the fruit using the solvent entering the cell membrane and then heading to the cell cavity containing the active substance. Anthocyanin compounds (**Fig. 2**) are polar due to the presence of polar groups such as hydroxyl groups and carbonyl groups, so the solvent used must have the ability to dissolve the anthocyanin compound. This is also known as the term dissolve where polar compounds can be dissolved in polar solvents [10]. The extract results indicate that the effect of adding acid increases the acidic conditions so that the ruptured vacuole cell walls are greater and the extracted anthocyanin compounds are greater [11]. From the maceration results, a reddish-brown extract was obtained with a different extract weight for each solvent.

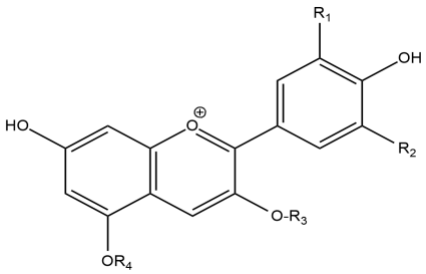
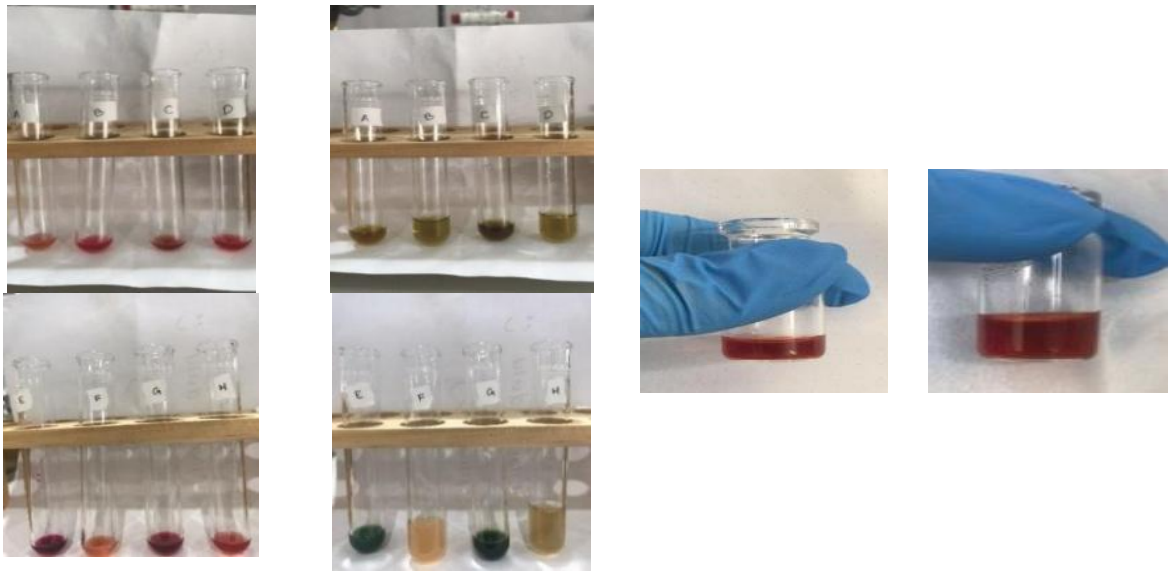


Figure 2. Anthocyanin Structure.

The extract yield results showed that the use of a methanol-citric acid solvent (50:50) produced the highest yield. The extract yield with the use of solvents added with citric acid was higher than the use of solvents not added with citric acid. This is because, in acidic conditions, anthocyanins are more stable so that they can break down the cell walls of plant vacuoles and more anthocyanins are extracted [12]. The yield results can also be influenced by the solvent used; this is due to the absorption capacity of each solvent against the content of the extracted material [13].

Referring to Widyastutik's research (2022), to ensure the presence of anthocyanins in a material, qualitative testing can be carried out by adding 0.25 M NaOH and 0.25 M HCl. Factors that can affect the color of anthocyanins are pH. Acidic conditions in anthocyanins will cause a color change to red and alkaline conditions cause a color change to green blue. The color that appears from anthocyanins depends on the acidity level (pH). Other factors that can affect the color of anthocyanins are the pigment content, position, and number of substituted hydroxy and methoxy groups [14]. The color changes resulting from anthocyanin analysis on the addition of NaOH are shown in **Fig. 3**.



(a) (b) (c) (d)

Figure 3. Color Changes of Anthocyanin Analysis (a) Before Addition of 0.25 M NaOH, (b) After Addition of 0.25 M NaOH, (c) Before Addition of 0.25 M HCl, and (d) After Addition of 0.25 M HCl. Codes in Figure (a) and (b): A = Fruit (Ethanol); B = Skin of Fruit (Ethanol); C= Fruit (Ethanol-Citric Acid); D=Skin of Fruit (Ethanol-Citric Acid); E= Fruit (Methanol); F= Skin of Fruit (Methanol); G= Fruit (Methanol-Citric Acid); H = Skin of Fruit (Methanol-Citric Acid).

This color change condition is caused by the presence of a more influential hydroxyl group so that the color is more bluish and relatively less stable, whereas if the more influential condition is the methoxy group in the anthocyanin structure, it will cause the color to tend to be reddish [12]. There are four main structures of anthocyanins in their equilibrium form, namely the red flavylium cation, the green blue quinoidal base, the colorless carbinol, and chalcone [15]. Structural changes caused by differences in pH are shown in Figure 4.

When adding HCl, most of the flavylium cations are present in the anthocyanin framework. In acidic conditions, anthocyanins are protonated and form positive ions or cations [13]. So that anthocyanins are more stable and the flavylium cations contained will be very soluble in water. The addition of NaOH results in a decrease in water concentration so that it can increase the rate

of deprotonation of flavylium cations and reduce color stability and a color change to green blue occurs. In acidic conditions, it will cause the chalcone carbinol structure to form and the formation of quinoidal due to competition between kinetics and thermodynamics in the hydration reaction of flavylium ions [16].

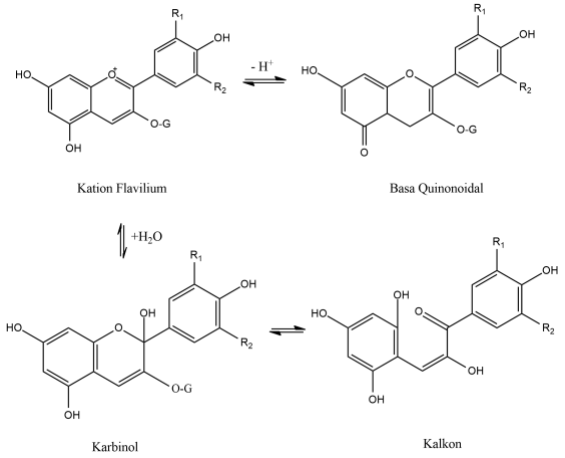


Figure 4. Changes in the structure of anthocyanin compounds at acidic pH.

The maximum wavelength and absorbance of parijoto fruit extract with methanol, ethanol, methanol-citric acid (50:50), and ethanol-citric acid (50:50) solvents were 301 nm, 309 nm, 301 nm, and 301 nm, respectively as shown in **Fig. 5**. Based on previous experiments, the typical UV-Vis spectrum of anthocyanins is indicated in two peak groups, namely in the UV region (260-280 nm) and the UV-Vis visible region (490-550 nm). However, from the results of this study, there was only a maximum spectrum in the wavelength region of around 300 nm. This indicates the sugar group contained in the acylated anthocyanin structure [17].

In general, the number of substituted hydroxyl groups will cause a shift in bathochromic absorption. This is supported by research produced on pelargonidin-type anthocyanins that do not have substitutions, a maximum wavelength of 494 nm was obtained, while in cyanidin-type anthocyanins substituted with one hydroxyl group, a maximum wavelength of 506 nm was obtained [17]. From other references, the maximum absorption value produced in this study indicates the presence of a chromophore group contained in the parijoto fruit extract. Where the chromophore group indicates that there is an aromatic framework bound to the auxochrome group, which indicates that the parijoto fruit extract contains anthocyanin compounds [18].

The results of FTIR (Fourier Transform Infrared) characterization were carried out using the ATR (Attenuated Total Reflectance) method to determine the functional groups contained in the compound. **Fig. 6** showed the results of FTIR-ATR analysis obtained from parijoto fruit extract with ethanol, methanol, ethanol-citric acid (50:50), and methanol-citric acid solvents.

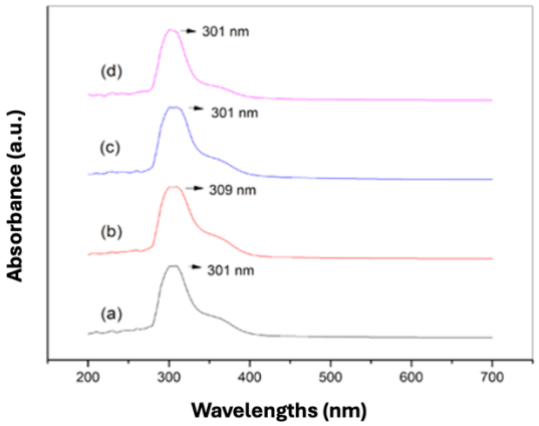


Figure 5. UV-Vis spectrum of fruit extract with solvents (a) Methanol, (b) Ethanol, (c) Methanol-Citric Acid, (d) Ethanol-Citric Acid.

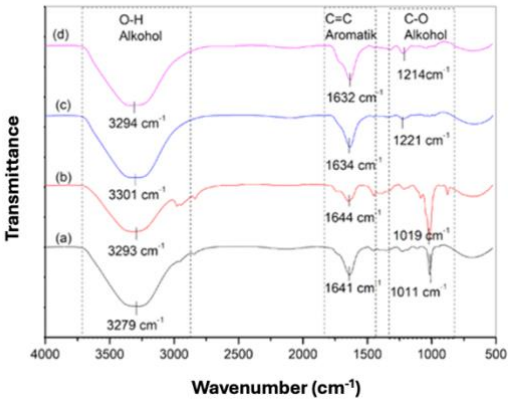


Figure 6. FTIR-ATR spectrum of parijoto fruit extract with solvents (a) Methanol, (b) Ethanol, (c) Methanol-Citric Acid, (d) Ethanol-Citric Acid.

The results of the FTIR-ATR spectrum of parijoto fruit extract showed the presence of a sharp -OH functional group in the range of 3500-3000 cm^{-1} wide absorption of all extracts, namely 3279 cm^{-1} from methanol solvent, 3293 cm^{-1} from methanol solvent, 3301 cm^{-1} from methanol-citric acid solvent, and 3294 cm^{-1} from ethanol-citric acid solvent. Absorption in the range of 1650-1450 cm^{-1} indicating the presence of aromatic C = C bonds produced from methanol solvent extracts is 1641 cm^{-1}, ethanol is 1644 cm^{-1}, methanol-citric acid is 1634 cm^{-1}, and ethanol-citric acid is 1632

cm^{-1}. The absorption of the CO bond is indicated in the range of 1230-1000 cm^{-1} but when citric acid is added to the solvent there is a shift in absorption from before the addition of citric acid caused by degradation. In the methanol extract, there is absorption at 1011 cm^{-1}, ethanol extract at 1019 cm^{-1}, methanol-citric acid extract at 1221 cm^{-1}, and ethanol-citric acid extract at 1214 cm^{-1}, but the absorption of the extract with the addition of citric acid is still within the range.

The characteristic absorption of sharp -OH indicates the detection of auxochrome groups or bound saturated functional groups. Where this group is responsible for giving color to a compound [18]. Through all the absorption data obtained from FTIR characterization, it is shown that each extract contains hydroxyl groups and aromatic groups which are by the typical absorption of anthocyanins [18].

The presence of anthocyanin compounds was characterized using GCMS (Gas Chromatography Mass Spectrometry) and the GC results shown in **Fig. 7**.

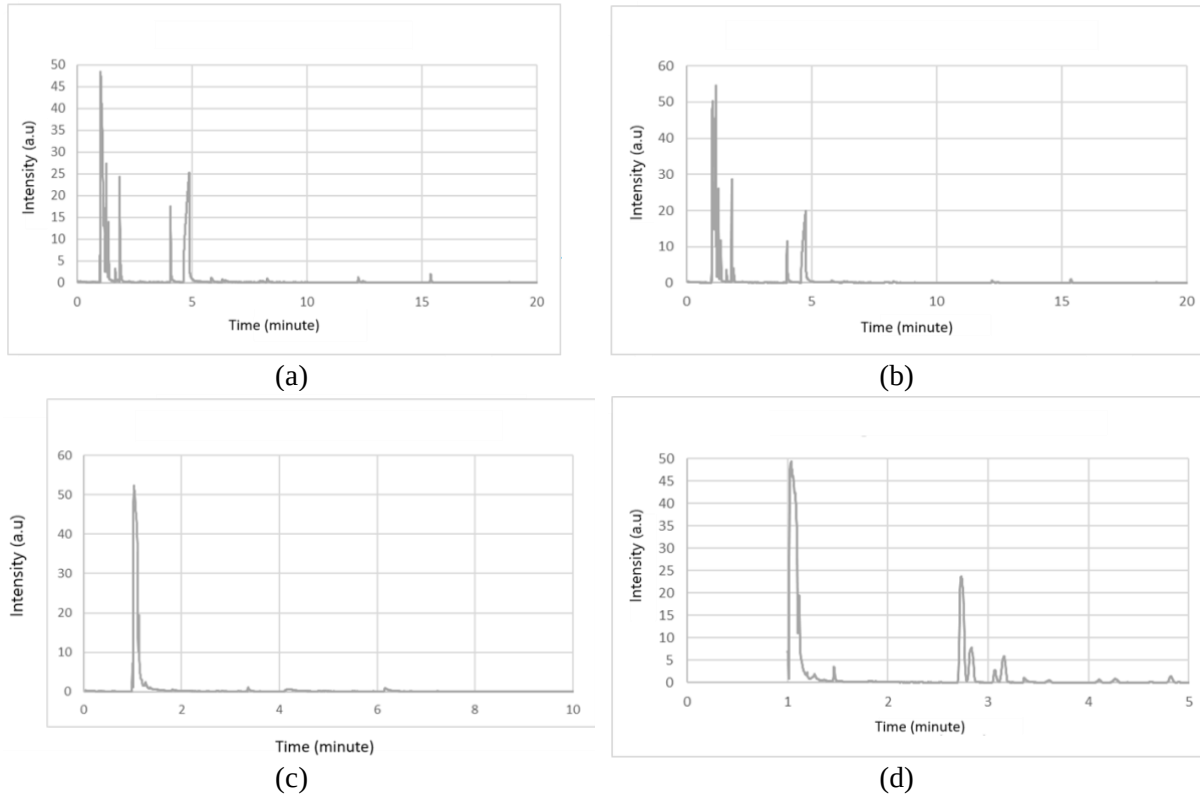


Figure 7. Chromatogram of Anthocyanin Extract from (a) Fruit Ethanol, (b) Fruit Ethanol-Citric Acid [50:50], (c) Fruit Methanol-Citric Acid [50:50], (d) Fruit Methanol

Based on the chromatogram of anthocyanin extract from fruit ethanol, it produces a mass spectrum with a retention time of 12.45 min with a main peak at 243 m/z. This molecular weight is like one of the molecular weights of anthocyanin compounds, namely cyanidin. In the results of the chromatogram of the ethanol-citric acid fruit extract, there is a mass spectrum with a retention time of 12.21 min with a main peak at 243 m/z. The molecular weight that appears is the same as the results of the mass spectrum of the ethanol fruit extract, so the type of anthocyanin contained in the parijoto fruit is cyanidin [20]. However, in the methanol extract both in methanol before and after the addition of acid, the same mass spectrum was not detected as the ethanol solvent, namely the absence of a typical mass spectrum at a retention time of around 12 min. So, it is estimated that the type of anthocyanin detected is not the cyanidin type anthocyanin. **Fig. 8** showed the structure of cyanidin molecule.

The Dye-Sensitized Solar Cell (DSSC) circuit was tested to determine the current and voltage obtained from the anthocyanin extract of parijoto fruit using a multimeter using a 60-watt LED lamp as a light source. The anode coated with a semiconductor plays a role in the formation of holes as a temporary place to store electrons. Testing on ethanol and ethanol-citric acid fruit extracts tested for 90 minutes with a checking duration every 5 minutes produced a current and voltage output that increased slightly along with

the increase in the duration of irradiation. However, there was also a decrease that was possibly due to the intensity of the less stable light caused by battery storage from the light source. This is by the theory which states that the current and voltage output values are directly proportional to the intensity of the light obtained.

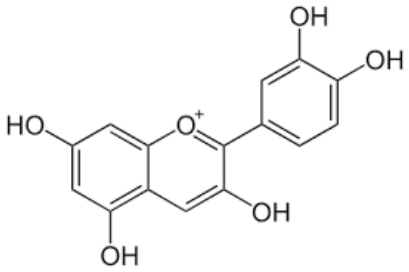


Figure 8. Chemical structure of cyanidin

From the results of obtaining current and voltage values through a multimeter, the ethanol extract produced a maximum power of 0.17416 mW, while the ethanol-citric acid fruit extract produced a maximum power of 0.0312 mW. This result is slightly larger when compared to previous studies that used LED lights as a light source with a size of 19 watts producing a power of 0.166213 mW. The performance of solar panels is directly proportional to the maximum power. To obtain maximum panel performance, it requires a minimum cross-sectional area [21].

4 Conclusion

Based on the research results, it can be concluded that anthocyanin compounds derived from parijoto fruit using the maceration method can produce a power of 0.1516 mW in ethanol extract, and 0.023 mW in ethanol-citric acid extract (50:50). This shows that anthocyanin extract from parijoto fruit can be used as a sensitizer in Dye-Sensitized Solar Cell (DSSC).

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