Preparation of dye sensitized solar cell (DSSC) using isolated anthocyanin from fruit sat (Melastomamalabathricum l) dicopimented with salicylic acid as dye

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Abstract—A study has been conducted on the use of anthocyanin extract from fruits (Melastomamalabthricum L), which was incubated by the addition of salicylic acid as photosensitizer in DSSC solar cells. The objective of this study was to determine the optimum condition of the extracts of copigmentation which resulted in the optimum efficiency of DSSC solar cells by increasing the absorption ability of anthocyanin pigment photons. The method used is the method of copigmentation. Copigmentation is an anthocyanin reaction with a copigment compound to form a more complex anthocyanin structure with a number of double bonds that can absorb more photons than the original anthocyanin. The results of dye characterization using UV-Vis and FTIR indicate a wider absorption spectrum and a more complex structure in antigianated anthocyanins when compared without copigmentation. Based on the results of the characterization of the prepared TiO₂ thin film, obtained crystal size of TiO₂ used ranged from 27.377 to 64.738 nm with a width of 200-950 nm photocathode spekrum absorption. Based on the results of the research, it is found that the antigianant extract can be increased by DSSC solar cell efficiency from 0.62% to 1.32% with 24 hours of copigmentation time and 1:2 concentration of concentration.

1. Introduction

Energy is a very important requirement for mankind. The use of fossil energy at this time is very high and consequently the longer fossil fuels will be depleted. Global demand for energy and environmental problems faced in recent years has also demanded researchers to develop energy that has good prospects and is environmentally friendly.

Solar energy is the most potential alternative to be developed especially in Indonesia. Dye Sensitized Solar Cell (DSSC) is a solar cell that converts solar energy into generation III electrical energy which was first developed by Professor Michael Gratzel in 1991 [1]. DSSCs are developed because they are easily updated, do not require high purity materials, low production costs, relatively stable and environmentally friendly production processes [2, 3].

Dye Sensitized Solar Cell (DSSC) has several important components that are intensively studied and developed, namely thin layers of titanium dioxide semiconductors and dyes [4]. The titanium dioxide semiconductor layer in this study was coated on Indium Thin Oxide (ITO) glass. Coating is done by spin coating method at 2500 rpm for 60 seconds with calcination to a temperature of 4500C.
The spin coating method was chosen because according to the Arista et al. [5] study the results obtained were better because the homogeneity of the anatase TiO$_2$ phase calcined well on the substrate.

Dyes will be the focus of this research. Dyes in DSSCs are very important components because thin layers of TiO$_2$ semiconductors can only absorb 5% of the sunlight spectrum. The spectrum of sunlight, 5% is the UV spectrum, 45% of the visible light spectrum and 50% is the IR spectrum. The dyes used in DSSCs must have good absorption in the visible light region in order to obtain optimal solar energy conversion from DSSC solar cells [4].

The synthetic dyes used such as Ruthenium-complex are still not ideal in DSSC although the efficiency obtained is more than 10% because their ability to absorb in the area appears near IR [6]. Ruthenium-complex dyes require high costs in their synthesis and also the need for toxicity tests before they can be used so they are less environmentally friendly if used [6].

The dyestuff that will be the focus of this research is natural dyes. Natural dyes are relatively affordable, easily available and environmentally friendly dyestuffs even though the efficiency obtained is still small [6]. Anthocyanin is one of the most widely used natural dyes. DSSC using natural dyes such as anthocyanin has been widely developed such as dyes from purple sweet potato efficiency 0.11%, dragon fruit efficiency 0.240%, rosella flowers with efficiency of 0.30%, spinach leaves with efficiency of 0.304%, black glutinous rice with efficiency 0.405% [7] and others.

Anthocyanin is one of the natural dyes that has attracted attention to be developed as photosensitizer in DSSC. Anthocyanins have been known to form a more complex compound when interacting with other organic compounds through copigmentation reactions. Anthocyanin copigmentation is an anthocyanin interaction in the form of a flavillium cation with a copigment which can be a metal or an organic compound [8]. Anthocyanin copigmentation can be seen from the batochromic effect, namely the shift in absorption of maximum wavelengths to longer wavelength regions [8]. This study uses anthocyanin extract from seduduk fruit (Melastomamalabthricum L) as a dye (dye) used in DSSC. Seduduk fruit (Melastomamalabthricum L) is used as a dye because the fruit of senduduk besides containing high anthocyanin is also quite easy to obtain in tropical regions such as West Sumatra.

The senduduk fruit that will be used in this study will be extracted by ultrasonic bath and the subsequent miseration is copigmented by the addition of phenolic acids as copigmen. Phenolic acids such as salicylic acid are one of the phenolic acids which can be used as copigmen in extracanthanianin [9]. The interaction of anthocyanins with phenolic acids includes intramolecular copigmentation where copigmen become part of anthocyanin molecules or pigmented pigments. The bond that occurs between pigment and copigmen occurs bonded by covalent acylation as a result it is stronger than intermolecular copigmentation [10]. A more complex and stable structure formed between anthocyanin and copigmen is expected to increase the ability of photon absorption.

Copigmentation will be more efficient at lower pH, because of the main dominance of flavium cation (pH <2) however, the copigmentation reaction is less effective than at pH 2-5, ie when there is equilibrium with its quinoid form. Bimplas et al [11] have conducted a study of the copigmentation of anthocyanin in red wine with the addition of extracts of origanum vulgare and saturejathymbra. The observations showed an increase of copigmented anthocyanins which reached 30% during storage.

Research on the use of anthocyanin from the results of copigmentation as photosensitizer in DSSC was also conducted by Wahyuningsih et al [12], namely anthocyanin from mangis skin extract (Garcinia mangostana L.). The efficiency of DSSC solar cells obtained from the study was pure anthocyanin, with the addition of ascorbic acid and malic acid 0.1996%, 0.2922% and 0.3029%. The efficiency obtained is still small compared to synthetic dyes, but has shown the presence of copigmentation effects on the efficiency obtained.

Salicylic acid is a phenolic acid group that can be used as a pigment. Salicylic acid was chosen because it is a phenolic acid that has a more complex structure with the presence of the ring piran. The more complex structure of the copigmen allows the formation of copigmented anthocyanins which have good light absorption ability if used as dyes in DSSC.
Based on this background the author was interested in examining the use of salicylic acid as a copigment in the copigmentation of anthocyanin concentrated extracts from senduduk fruit. Concentrated extracts from anthocyanin are used to obtain more optimal copigmentation results. The anthocyanin copigmentation in this study will determine the optimum conditions of the copigmentation reaction. The optimum conditions determined are the optimum amount of copigment added and the optimum time in order to obtain optimal DSSC efficiency.

2. Experimental Section

2.1. Tools and Materials
Equipment needed in this study are: beaker (10, 250, 500, 1000) ml, 10 ml volumetric flask, measuring cup (5, 10, 25 and 100 ml), dropper pipette, 10 ml measuring pipette, goiter dropper 1 and 25 ml, stirring rods, magnetic stirers, spatulas, petri dishes, pestle mortar, masking tape, separating funnels, furnaces, digital multimeters, rotary vacuum evaporators, 100 ml erlenmeyer, refrigerators, spin coating and black glass bottles, shekers, spronic spectrophotometers 21, analytical scales, ultrasonic bath, 30 watt UV lamp and centrifuge.

Fruit Senduduk (Melastomamalabthricum L), Salicylic acid, Hydrochloric acid pa, Aquades, Indium Thin Oxide glass (ITO), Titanium dioxide Degusa P-25, Ethanol 96%, Citric acid, Sodium citrate, n-hexane pa, Whatman paper No.42, Potassium iodide, Iodine, Acetonitrile pa, Polyethylene glycol (PEG), Pencil 2B, Aluminum foil, Potassium chloride.

2.2. Seduduk Fruit Extraction (MalabthricumMelastoma L)
A total of 100 seeds of root (Melastomamalabthricum L) were washed and crushed, the residue and filtrate were then put into a dark bottle, then added 250 mL 96% ethanol which had been immersed with 2.5 mL 1% HCl until mixed. The mixture was then extracted by ultrasonic bath for 30 minutes. The extract was then sliced for 24 hours in a dark room at room temperature and filtered using Whatman filter paper No.42 to separate the solids and liquids. The resulting filtrate was evaporated by using a rotary vacuum evaporator at 550C.

2.3. Determination of the number of Kopigmen
The extract was diluted with buffer pH 4.5 and 1. The extract was diluted by piping 1 mL of concentrated extract with a pipette volume of 1 mL and then put into a 10 mL volumetric flask and diluted to the limit mark. The diluted extract was then measured for absorbance at a wavelength of 535 nm and 700 nm. The measurement data obtained is then entered into the equation below.

\[ A = [(A_{535} - A_{700})_{pH1} - (A_{535} - A_{700})_{pH4.5}] \]  

\[ \text{total anthocyanin (mM)} = \frac{A \times Df \times 1000}{\epsilon \times 1} \]  

From the value of anthocyanin concentration can be determined the number of copigmen to be added by entering the anthocyanin concentration obtained in the equation below [13].

\[ \text{CopigmenCocentration} = \frac{C \times BM \times V}{1000 \times R} \]  

2.4. Anthocyanin Kopigmentation
The anthocyanin extract was dissolved in 96% ethanol. The sample is then put into an erlenmeyer which has previously been wrapped in aluminum foil. The sample added salicylic acid according to the amount obtained in the previous experimental calculation. The mixture was then closed and homogenized using a shaker at 100 rpm for 30 minutes until homogeneous and mixed with extract.
The mixture was then determined by Agilent 8435 UV-VIS spectrophotometer. The extract was then stored for 12, 24 and 36 hours to be tested periodically as photosensitizer [11].

2.5. ITO Substrate Preparation

The DSSC solar cell assembly begins by preparing the ITO substrate which will be deposited with the process of cutting and sanding. The process of cutting the ITO substrate using a glass cutter with a size (1.25 x 2.5) cm. The side of the substrate that has been cut, sanded with sandpaper. The ITO glass substrate is cleaned using a detergent solution. The glass is then cleaned using an ultrasonic cleaner for 10 minutes using 96% alcohol. The glass is then rinsed with 96% alcohol to remove the dirt and dust that sticks.

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2.6. Preparation of TiO$_2$ Pasta

TiO$_2$ paste is made from 1.5 grams of TiO$_2$ Degusa P-25 powder, then crushed, sifted, and put into 250 ml beaker. TiO$_2$ Degusa P-25 powder was then added with 15 ml ethanol and slightly CTAB. The mixture is then sterilized with a magnetic stirrer for 30 minutes.

2.6.1. Semi-Solid Electrolyte Preparation. Semi-solid electrolytes are made by making a homogeneous mixture of KI / I$_2$ with polyethylene glycol (PEG) and stirring until homogeneous.

2.6.2. Carbon Electrode Counter Preparation. As a carbon source graphite is used from a pencil. Graphite is coated onto the ITO to the conductive part and then calcined to a temperature of 450°C so that graphite forms good contact with the ITO substrate.

2.7. DSSC Assembly

Preparation of a thin layer of TiO$_2$ using the spin coating method is done first by flattening the TiO$_2$ paste over the conductive part of the ITO glass. The pasta is evenly spun and then spin coating at 2500 rpm for 1 minute. The layer formed is then calcined to a temperature of 450°C. After all the components of the DSSC were finished, then an ITO / TiO$_2$ thin layer was immersed in a dye solution for 24 hours. All components were then assembled to form a sandwich structure.

3. Results And Discussion

3.1. DSSC Preparation

DSSC preparation begins with the preparation of dyes used as photosensitizers. Preparation of dyes was extracted with ultrasonic bath followed by miseration and copigmentation. Before copigmentation, concentrated extracts of dyes from senduduk fruit were diluted with pH 1 and 4.5 buffers. The extract sample was then determined by absorbance with a spronic 21 spectrophotometer. The results of absorbance measurements were used to determine the sample anthocyanin concentration. The sample anthocyanin concentration can be used to determine the amount of copigment to be added in the copigmentation. The amount of copigment added to the copigmentation can be seen in Table 1.

| No | Comparison | Number of copigment (mg) |
|----|-------------|--------------------------|
| 1  | 1 : 0       | 0 mg                     |
| 2  | 1 : 1       | 32,656 mg                |
Copigmentation is carried out according to the method conducted by [12] where the salicylic acid copigment is weighed according to the comparison in Table 1 with analytical scales. Kopigmen then added 100 ml of anthocyanin concentrated extract and disheker for 30 minutes, which aims to mix anthocyanin and copigmen until homogeneous.

Subsequent preparation was carried out on a thin layer of TiO$_2$. Preparation of TiO$_2$ thin layer was carried out by coating TiO$_2$-Degusa P-25 paste with a spin coating method with a speed of 2500 rpm which was then calcined to a temperature of 450 °C. The result is a white thin layer that attaches to the ITO glass. The thin layer that has been calcined is soaked in the dye solution that has been prepared. Soaking is intended so that the dyes used are adsorbed on the surface of the layer. The soaked layer is dried at room temperature. Drying aims to remove existing solvents.

Assembling of solar cells DSSC is done by forming sandwich structures facing each other with carbon electrode counters. The two electrodes in the off set area are clamped with binder clips with the aim that the solar cell structure does not shift to each other, causing electrolyte leakage. The electrolyte used is pressed on the gap between the two electrodes. Testing the electrical properties of solar cells using 30 Watt UV lamp sources. Electrical properties such as the value of stresses and barriers produced can determine the efficiency produced by solar cells.

3.2. Characterization of Dyes in DSSC

3.2.1. Characterization of dyes with a UV – Vis spectrophotometer
Characterization was carried out on anthocyanin dye samples with various comparisons of the concentration of salicylic acid copigment namely 1: 0, 1: 1, 1: 2 and 1: 3 with a 24-hour storage period. The sample measured the absorbance spectrum in the wavelength range of 400–800 nm. The characterization with a UV-Vis spectrophotometer aims to see the effect of salicylic acid on the running of the copigmentation reaction. The characterization results can be seen in Figure 1.

![Figure 1. Spectra of UV –Vis from a dye sample.](image)

The maximum absorption length of the gelambang ($\lambda_{\text{max}}$) from the pure anthocyanin fruit extract of senduduk fruit and the addition of salicylic acid pigment with various comparisons can be seen in Table 2.
Table 2. Absorption value of maximum wavelength (\(\lambda_{\text{max}}\)) anthocyanin with various comparisons of copigmen.

| No | Comparison Anthocyanin : Salicylic acid | 528 nm | 535 nm | 540 nm | 550 nm |
|----|------------------------------------------|--------|--------|--------|--------|
| 1  | Anthocyanin (1:0)                        | 0.5012 | 0.48235| 0.42669| 0.35284|
| 2  | Anthocyanin (1:1)                        | 0.81907| 0.89083| 0.60669| 0.35139|
| 3  | Anthocyanin (1:2)                        | 0.71516| 0.80428| 0.81025| 0.82909|
| 4  | Anthocyanin (1:3)                        | 0.38092| 0.46940| 0.50441| 0.45935|

From Figure 1 it can be seen that the addition of copigmen to anthocyanin causes a batochromic effect. The batochromic effect is the effect of shifting the absorption of the maximum wavelength to a longer wavelength region caused by the substitution of the ring of an anthocyanin due to the bond formed between anthocyanin and salicylic acid as copigmen. This shift can be seen in pure anthocyanin with \(\lambda_{\text{max}} = 528 \text{ nm}\) to 535 nm, 540 nm and 550 nm when adding salicylic acid. The width of the largest absorption spectrum is obtained at the copigmentation 400-630 nm in the ratio 1:2.

The results of katakerisasi which showed the spectral absorbance of senduduk fruit extract with the addition of salicylic acid as copigmen was good enough to be used as a source of dyes in DSSC. This is better than the research conducted by wahyuningsih et al [12] which pigmented the dyes from mangosteen peel extract. The extracted absorption spectrum was 450 nm-520 nm with the maximum absorption spectrum width of 480-600 nm.

Better results were obtained because in the extraction stage of the senduduk fruit extract in addition to extraction by means of miseration, extraction was also carried out with the help of ultrasonic bath to obtain optimal results. Fractionation and copigmentation are also very influential in the preparation stage of the dye extract. Fractionation can increase the purity of extracts and copigmentation which can form a more complex structure to increase the absorption of dyes.

3.2.2. Characterization with FTIR
The next characterization is using FTIR instruments. This characterization was carried out on pure anthocyanin extract samples compared with anthocyanin extract with the addition of salicylic acid. This characterization is carried out to determine the functional groups contained in extracts of the dyes used as photosensitizers. Testing the wave number spectrum is carried out at wavelengths of 4000–600 cm\(^{-1}\). The results of the characterization of the anthocyanin wave number spectrum with the addition of salicylic acid can be seen in Figure 2.

![Figure 2. Spectrum of pure wave anthocyanin extracts and with the addition of salicylic acid.](image-url)
The results of FTIR spectrum interpretation can be seen in Table 3.

**Table 3. Interpretation of the FTIR spectrum [14].**

| No | Functional group                  | Sample Data  | Literature Data       |
|----|----------------------------------|--------------|-----------------------|
| 1  | C-H (Aromatic)                   | 813.8 cm$^{-1}$ | 900 – 670 cm$^{-1}$   |
| 2  | Benzene rings                    | 1328, 49 cm$^{-1}$ | 1500 – 1430 cm$^{-1}$ |
| 3  | O-H                             | 3319.82 cm$^{-1}$ | 3570 - 3200 cm$^{-1}$ |
| 4  | O-H carboxylic acid              | 2816.38 cm$^{-1}$ | 3300 – 2500 cm$^{-1}$ |
| 5  | C=O                             | 1626.42 cm$^{-1}$ | 1680 – 1600 cm$^{-1}$ |
| 6  |                                 | 735.14 cm$^{-1}$ | 735-770 cm$^{-1}$     |

From Table 3, it is known that there are several compounds found in senduduk fruit extract samples, as previously known, some antioxidant compounds belonging to the phenol, polyphenolic or flavonoid compounds are generally anthocyanin seen in the pure anthocyanin spectrum. The uniqueness of these phenol compounds, polyphenols and flavonoids is that they have an O-H group and some aromatic rings which are characterized by the C = C group.

On anthocyanin with the addition of salicylic acid there was an absorption of groups at 735.14 cm$^{-1}$ which showed the existence of ortho substitution of the wave number spectrum in the anthocyanin extract with the addition of salicylic acid. Ortho substitution shows intermolecular copigmentation interactions in the form of covalent acylation bonds between anthocyanin molecules and salicylic acid.

3.2.3. *Characterization of TiO$_2$ Thin Layer*

Analyze the structure and crystal size of thin TiO$_2$ layers using XRD

Objects characterized by XRD were calcined TiO$_2$ paste to a temperature of 450°C. Characterization with XRD aims to determine the structure and size of the crystals formed in the sample. The structure and size of the crystal from the sample is very influential on DSSC efficiency produced because it can affect the touch surface area. The results of XRD characterization in the form of diffraction pattern (diffractogram) consisting of characteristic peaks of TiO$_2$, can be seen in Figure 3.

![Figure 3. XRD pattern of TiO2 degusa P - 25.](image)

The results of XRD data interpretation can be seen in Table 4.

**Table 4. Results of Interpretation of XRD data**

| No | 2-Theta | Area | FWHM | d(A) | I % | D | Crystal Structure |
|----|---------|------|------|------|----|---|------------------|
| 1  | 25.2657 | 5640.46 | 0.1279 | 3.52504 | 100.00 | 64,738 | Anatase          |
| 2  | 37.7353 | 1377.86 | 0.1791 | 2.38397 | 24.43 | 46,326 | Anatase          |
| 3  | 47.9726 | 1818.27 | 0.1248 | 1.89487 | 32.24 | 27,377 | Anatase          |
| 4  | 48.1301 | 989.99  | 0.0624 | 1.89373 | 17.55 | 64,119 | Anatase          |
| 5  | 62.6243 | 819.99  | 0.1248 | 1.66831 | 18.73 | 47,461 | Anatase          |
| 6  | 62.6243 | 819.99  | 0.1248 | 1.48220 | 14.54 | 66,135 | Anatase          |
The crystal obtained has an anatase crystal structure. This can be seen at the peaks produced. Peak - peak d (A) for crystals in the form of 3.52504; 2.38397 and 1.89487. Based on the data interpretation card that shows the anatase shape which is closer to 3.5143; 2.3732; and 1.8935. The rutile form is not too dominant in the interpretation results in Table 4 where there is no d (A) value close to 3.2442; 1.6972 and 1.6887.

The diffractogram pattern obtained in this study was used to determine the structure and crystal size (crystallite size) of TiO$_2$ based on FWHM values (full width at half-maximum) at various peaks using the Scherrer equation.

$$D = \frac{k \times \lambda}{\beta \cos \theta}$$

With D being the size of the crystal, $\lambda = 0.154$ nm is the X-ray wavelength, $\beta$ is the FWHM value which is half of the highest peak width, $\theta$ is the diffraction angle and k is a constant. The results of the calculation of each peak obtained by TiO$_2$ crystal size ranged from 27,377-64,738 nm.

The nanometer-sized crystal of titanium dioxide obtained in this study is very good when used in DSSC. The size of the crystals in the nanometer can increase the surface area of the thin layer of TiO$_2$ used so that the amount of dye (dye) adsorbed on the surface of TiO$_2$ will increase.

**Measurement of absorption of TiO$_2$ / anthocyanin photocathode and salicylic acid (1: 2) with UV-DRS spectrophotometer**

Characterization was carried out on the photocathode of DSSC solar cells which produced optimum efficiency with a ratio of 1: 2 anthocyanin and salicylic acid at 24-hour storage compared to those without storage. This characterization aims to see the effect of copigmentation time on the width of the absorption spectrum of the resulting TiO$_2$ / dye photocathode. Samples with a ratio of 1: 2 are chosen because they have the widest absorption spectrum. The UV-DRS spectrum of the copigmented TiO$_2$ / anthocyanin photocathode (1: 2) can be seen in Figure 4.

![Figure 4](image-url)

**Figure 4.** UV-DRS absorption spectrum of a copigmented TiO$_2$ / anthocyanin photocathode (1: 2) (a) 200-950nm (b) 400 nm - 950 nm.

From Figure 4 (a) and (b) it can be seen that the copigmented TiO$_2$ / anthocyanin photocathode (1: 2) has absorption spectrum which is quite 200–950 nm wide. The wide absorption spectrum is caused by the presence of three absorption peaks, namely in the UV area 200-400 nm, visible light is 400-660
nm and Infrared is 800-950 nm. This very wide absorption spectrum allows optimal conversion of light energy to electricity, because the light spectrum consists of 5% of the UV spectrum, 45% of the visible spectrum and 55% of the IR spectrum [3]. From Figure 4 (b) it can be seen that the copigmentation time of the extract affects the value of photocathode absorption. The effect of this time occurs because the concentration of the copigmented anthocyanin increases. Increased absorption at the maximum wavelength (λmax) which is from 2.6782 A to 3.4547 A in the visible region and 2.0795 A to 2.3009 A in the IR region shows an increase in the concentration of anthocyanin pigments during storage. This increase in concentration causes an increase in the efficiency of DSSC solar cells because the amount of the copigmentation anthocyanin molecule adsorbed in the photocathode increases.

3.3. Calculation of efficiency

To find out DSSC efficiency, voltage and resistance measurements were carried out with the help of 30 watt UV lights. From the value of voltage and resistance can be calculated the current strength generated by the formula V = I x R. Where V is the voltage, I = strong current and R = resistance. Based on this equation, the value of current and voltage strength will be directly proportional, where the greater the voltage, the greater the current, this matches the results of the research that has been done.

DSSC which uses anthocyanin by the addition of salicylic acid successfully converts light energy into electrical energy as indicated by the value of voltage and current strength. The high voltage generated is strongly influenced by the concentration of copigment and the storage time of the extract, as in Table 5.

| Duration of Storage of Extract (Hours) | Comparison of Anthocyanin Concentration : Salicylic acid (w/v) |
|---------------------------------------|---------------------------------------------------------------|
|                                       | 1 : 0  | 1 : 1  | 1 : 2  | 1 : 3  |
| 0                                     | 351.7 mV | 379.4 mV | 431 mV | 390.4 mV |
| 12                                    | 350.1 mV | 390.0 mV | 433 mV | 390.5 mV |
| 24                                    | 348.2 mV | 430 mV   | 467 mV | 428 mV   |
| 36                                    | 334.1 mV | 389.1 mV | 434 mV | 390.2 mV |

From Table 5, it can be seen in the ratio of anthocyanins with salicylic acid 1: 2 and the storage time of 24-hour extracts, the maximum stress is 467 mV. The effect of copigment concentration and storage time of extracts on the stress produced by DSSC solar cells can be seen in Figure 5.

DSSC with the addition of salicylic acid as copigment in dyes produces better solar cell voltage compared to pure anthocyanin. The highest stress was produced by comparison of anthocyanin and 1: 2 salicylic acid with a 24-hour extract storage time of 467 mV. From Figure 5 it can be seen that at 24-hour storage for each anthocyanin extract with the addition of salicylic acid showed an increase in optimal efficiency of DSSC solar cells.

This condition also occurs in the current generated as shown in Table 6 and Figure 6, where the highest current strength is found in the ratio of 1: 2 with a 24-hour storage time of 0.106mA.
Table 6. Data on current strength from DSSC solar cells.

| Duration of Storage of Extract (Hours) | Comparison of Anthocyanin Concentration : Salicylic acid (w/v) | 1 : 0 | 1 : 1 | 1 : 2 | 1 : 3 |
|----------------------------------------|---------------------------------------------------------------|------|------|------|------|
| 0                                      |                                                               | 0.0666 mA | 0.0672 mA | 0.0887 mA | 0.0700 mA |
| 12                                     |                                                               | 0.0620 mA | 0.0852 mA | 0.0952 mA | 0.0730 mA |
| 24                                     |                                                               | 0.0611 mA | 0.0993 mA | 0.1057 mA | 0.0924 mA |
| 36                                     |                                                               | 0.0525 mA | 0.0861 mA | 0.0977 mA | 0.0790 mA |

From Table 6, it can be seen that the highest current strength is in the ratio of 1: 2 with the length of the copigmentation time or 24 hour storage. These results indicate that the optimum current strength is in the ratio of anthocyanin and salicylic acid 1: 2 with a storage time (copigmentation) of 24 hours. The effect of the concentration and storage time of the extract on the current strength of the solar cell DSSC can be seen in Figure 6.

![Figure 6](image)

Figure 6. Graph of the effect of concentration and storage time of extract on the strong current of DSSC solar cells.

The effect of concentration and storage time of extracts on the value of current and voltage can be seen in Figure 5 and Figure 6. Optimum voltage and current strength were obtained in the ratio of 1: 2 copigmenconcentration to the storage time of 24 hour extract.

The results of the efficiency of anthocyanin with the addition of salicylic acid can be seen that in the ratio of anthocyanin and salicylic acid 1: 1, 1: 2 and 1: 3 it produces 1.14%, 1.32% and 1.06% efficiency with a 24 hour storage time. In pure anthocyanin (1: 0) the price of efficiency is 0.62% at the beginning of the measurement. The measurements carried out later on pure anthocyanin showed a decrease in efficiency. The decrease in efficiency occurs due to the degradation of anthocyanin molecules that occur. In anthocyanin with the addition of salicylic acid the degradation of anthocyanin molecules runs slowly due to the occurrence of anthocyanin copigmentation reactions. This anthocyanin copigmentation reaction can form a complex anthocyanin structure so that the process of degradation of dyes is more difficult to occur. The more complex structure of the copigmented anthocyanin can also increase the efficiency of the DSSC solar cells produced.

Table 7. DSSC efficiency.

| Storage duration of extract (Hours) | Anthocyanin : Salicylic acid (w/v) | 1.0  | 1.1  | 1.2  | 1.3  |
|------------------------------------|------------------------------------|------|------|------|------|
| 0                                  |                                    | 0.62 % | 0.68 % | 1.02 % | 0.73 % |
| 12                                 |                                    | 0.58 % | 0.89 % | 1.10 % | 0.76 % |
| 24                                 |                                    | 0.57 % | 1.14 % | 1.32 % | 1.06 % |
| 36                                 |                                    | 0.47 % | 0.89 % | 1.13 % | 0.82 % |
From the DSSC solar cell efficiency data measured every week, it can be seen that the optimum condition of anthocyanin copigmentation is by comparing 1:2 anthocyanin and copigment concentration and 24-hour storage time. Graph of the effect of concentration and storage time of extracts on solar cell DSSC efficiency can be seen in Figure 7.

![Figure 7. Graph of the effect of concentration and storage time of extract on DSSC solar cell efficiency.](image)

From Figure 7 it can be seen that the optimum conditions of copigmentation are found in anthocyanin with a ratio of 1:2 concentration and 24-hour storage time. These results indicate that the optimum condition of the copigmentation is in the ratio of anthocyanin and copigment 1:2 concentrations with the 24-hour extract storage time.

Increased efficiency of solar cells DSSC in copigmentation treatment caused by the structure of anthocyanins that are more complex. This more complex structure causes the bond of the number of double bonds π from the dyestuff to increase so that the ability of the dyes to absorb photons increases. The increasing ability of photon absorption can cause an increase in DSSC efficiency because the number of electrons flowing through the outer circuit will increase.

4. Conclusion
Based on the results of research that has been done, it can be concluded:

a. The highest current, voltage, power and efficiency were obtained in the ratio of anthocyanin and 1:2 salicylic acid concentrations with 24-hour extract storage duration of 0.1057 mA, 467 mV, 395.2 Watt/m² and 1.32%.

b. The concentration and optimum time of anthocyanin copigmentation for application as photosensitizer was obtained at a concentration ratio of 1:2 and 24-hour storage time.

Reference
[1] O’regan dan Gratzel, M. 1991. A Low-Cost, High Efficiency Solar Cell Based on Dye Sensitized Colloidal TiO₂ Films. Nature. Vol. 353, 6346-737.
[2] Hara dan Arakawa. 2003. Dye-Sensitised Solar Cells. National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Jepang.
[3] Hardeli, H Sanjaya, R Resikarnila, 2018, Solar Cell Polymer Based Active Ingredients PPV and PCBM, IOP Conference Series: Materials Science and Engineering 335 (1), 012029.
[4] Sutrisno,H. 2010. Sel Fotovoltaik Generasi Ke-III: Pengembangan Sel Fotovoltaik Berbasis Titanium Dioksid. Yogyakarta. Universitas Negeri Yogyakarta.
[5] Arista, A. 2016. Sintesis Lapisan TiO₂ Pada Substrat ITO Menggunakan Metode Elektrodeposisi dan Spin Coating. Jurnal Ilmu Fisika (Jif).
[6] Ito, S. 2011. Investigation of Dyes for Dye-Sensitized Solar Cells: Ruthenium Complex Dyes, Metal-Free Dyes, Metal-Complex Porphyrin Dyes and Natural Dyes. Shanghai, In Tech.
[7] Hardeli,. Fernando, T., Maulidis,. Ridwan,. S,.Risky dan Suwardani. 2013. Dye Sensitized Solar Cells (DSSC) Berbasis Nanopori TiO₂ Menggunakan Antosianin dari berbagai Sumber
Alami. Jurnal Semirata FMIPA Universitas Lampung.

[8] Lestario dan Andini. 2016. Kopigmentasi Kuersetin Apel (Pyrus Malus) Terhadap Stabilitas Warna Ekstrak Buah Dawet (Syzygium Cumini). Prosiding Karya Ilmiah.

[9] Darias-Martin, J., Carrillo, M., Diaz, E., & Boulton, R. B. 2001. Enhancement of Red Wine Colour by pre-fermentation Addition of Copigments. Food Chemistry.

[10] Safitri, I. G. 2009. Pengaruh Kopigmentasi Pewarna Alami Brazilein Kayu Secang (Caesalpinia Sappan L.) dengan Sinapic Acid Terhadap Stabilitas Warna Pada Model Minuman. Institut Pertanian Bogor. Bogor.

[11] Bimplas A dan Oreopaulou V. 2016. Anthocyanin Copigmentation and Color of Wine: The Effect of Naturally Obtained Hydroxycinnamic Acids as Cofactors. Food Chemistry.

[12] Wahyuningsih., Fadilah., G, Hanif., Q.A., Hidayat., S., and Munawaroh, H. 2016. The Co-pigmentation of Anthocyanin Isolated from Mangosteen Pericarp (Garcinia Mangostana L.) as Natural Dye for Dye Sensitized Solar Cells (DSSC). Journal of Materials Science and Engineering.

[13] Wulandari. 2016. Pengaruh Kopigmen Katekol dan Tanin Terhadap Stabilitas Warna Antosianin Ekstrak Bekatul Beras Ketan Hitam (Oryza Sativa Glutinosa). Bandar Lampung, UNILAM.

[14] Coates, J. 2014. Interpretation of Infrared Spectra. Newtown, USA : John Wiley & Sons.