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Preparation of Dye-Sensitized Solar Cell (DSSC) Using TiO_2 and Mahkota Dewa Fruit (*Phaleria Macrocarpa (Scheff) Boerl.*) Extract

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Abstract

A dye sensitized solar cell (DSSC) is a low-cost solar cell with attractive features. DSCC contains of photo electrode, dye, electrolyte, and counter electrode with photo electrochemical system. The aim of this research is to determine the percent efficiency produced by DSSC from the Mahkota Dewa extract. This was carried out in various stages, namely sample preparation and extraction, DSSC assembly, TiO_2 characterization using Scanning Electron Microscopy (SEM), and testing its current and voltage. The results showed that the maximum wavelength of the Mahkota Dewa extract dye test using a UV-Vis spectrophotometer was 554 nm with an absorbance of 0.163, which was believed to be the wavelength of flavonoid and anthocyanin compounds. Based on the characterization results, surface morphology was spherical and agglomerated. However, after being soaked in the dye, the surface morphology of the TiO_2 layer did not appear spherical on the surface that was expected to have been covered by the dye. The measurement using sunlight sources showed that the maximum current and voltage of DSSC with a concentration of 30% w/v was $21.8x10^{-4}$A and 58.86 V with an efficiency of $22.43x10^{-3}$ %. In addition, there was a 0.482% decrease in DSSC efficiency based on the storage time which lasted for a period of 6 days.

INTRODUCTION

The use of fuel in conventional power plants in the long term depletes oil, natural gas, and coal resources and also causes environmental pollution. Furthermore, previous researches have showed that obtaining fossil energy sources such as petroleum, natural gas, and coal is estimated to take 40, 60, and 200 years, respectively. Therefore, these resources need to be conserved by using other methods, such as sunlight (Anh, 2006). Indonesia is a tropical region with enormous potential for solar energy which may be used to produce renewable alternative energy. Geographically, this country is located at the equator, which enables it to receive more solar heat than other countries by 4800 watts/m^2/day (Manan, 2009). However, solar energy has not been used optimally, hence, it is necessary to apply the use of sunlight into an energy that may be utilized in the future.

One of the innovations that involve converting solar energy into an alternative form, such as electrical energy to be used as a substitute fuel, is the use of solar cells. However, due to the fact that the price is relatively more expensive, people still prefer using fossil energy which costs less. (Maysha, 2013).

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One of the interesting developments in solar cell technology is the one developed by Gratzel which is commonly referred to as Dye-Sensitized Solar Cell. This is a photoelectrochemical solar cell that uses an electrolyte as a charge transport medium. Furthermore, its working principle is based on converting light energy into electricity in the form of electron transfer reactions on a molecular scale (Smestad, 1998). The DSSC has great potential to be developed in the next generation of solar cells because it does not require high purity materials, hence, the production costs are relatively low.

Dye-Sensitized Solar Cells are divided into several parts, namely TiO_2 nanopores which are used as charge separation sites, catalysts adsorbed on the TiO_2 surface, and dye molecules which are used as light absorbers in the form of synthetic or natural dyes containing chlorophyll, carotene, or anthocyanins (Bashir, 2016). Furthermore, one of the fruits that may be used as a dye is Mahkota Dewa (*Phaleria macrocarpa (Scheff) Boerl.*) because it has a distinctive red color which indicates that it contains a lot of anthocyanins that may be utilized in DSSC. (Sunaryo, 2014).

According to the working mechanism of the DSSC, the current is generated from electrons in the dye due to photons emitted by sunlight. Furthermore, electrons would flow to the TiO_2 conduction band and then to the reference or carbon electrode. The triiodide from the electrolyte would capture electrons from the outer circuit with the help of carbon as a catalyst. The excited electrons then re-enter the cell and react with the electrolyte to the oxidized dye. Furthermore, the electrolyte provides a replacement electron for the dye to be oxidized, hence, it returns to the original equation.

Several factors affect the DSSC performance, include substrate, dye, electrolyte solution, TiO_2, and storage time. One of the most influential factors is dye concentration, hence, the higher the concentration, the more compounds needed to absorb light and the greater the efficiency of the DSSC obtained (Lashmin, 2016). Furthermore, another influential factor is the storage duration, and this is because the longer the storage duration, the lower the efficiency obtained. (Alfidharisti, 2018).

Based on these descriptions, this research aims to produce DSSC using Mahkota Dewa (*Phaleria macrocarpa (Scheff) Boerl.*) extract and a semiconductor in the form of TiO_2. This was carried out based on the effect of time and storage duration to produce high efficiency.

MATERIALS AND METHODS

Equipment and Materials

The materials also include ITO (Indium Tin Oxide) glass, TiO_2 powder, Mahkota Dewa fruit, KI solid, iodine solution, 96% ethanol, 1% HCl solution, distilled water, filter paper, 8B carbon pencil, Polyvinyl Alcohol (PVA), chloroform, Mg band, HCl(p) solution, 2M NaOH solution, 2M HCl solution, and Polyethylene glycol.

The equipment used in this research, include Scanning Electron Microscope (SEM), Fourier Transformed Infra-Red (FTIR), UV-Vis Evolution 201 spectrophotometer, Heles UX-78 multimeter, lux meter, analytical balance, blender, 100 mL volumetric flask, glass chemical, mortar and pestle, furnace, hot plate with a magnetic stirrer, spray bottle, spatula, stirring rod, paper clip, tape, connecting cable, dropper, and rotary evaporator.

Extraction of Mahkota Dewa Fruit (*Phaleria macrocarpa (Scheff) Boerl.*)

A total of 500 grams of Mahkota Dewa sample was washed, cleaned, and then cut into 1 to 2 cm small pieces and dried. Furthermore, after drying, the sample was mashed using a blender until it was in the powdered form and then placed into a dark glass bottle. It was macerated using 96% ethanol as the solvent with the addition of 1% HCl in a ratio of 9:1 until it submerged and then left for 1x24 hours at room temperature. The macerate was filtered using filter paper and the filtrate was concentrated using a rotary evaporator to obtain a thick extract. Subsequently, the extract was diluted by taking 10 gr, 20 gr, 30 gr, respectively. The resulting extract was tested using UV-Vis to determine the absorbance and wavelength as well as using FTIR to detect the functional groups of the Mahkota Dewa extract.

Phytochemical Test

In the flavonoid test, the crude ethanolic extract of Mahkota Dewa (*Phaleria macrocarpa (Scheff) Boerl.*) fruit was dissolved in a suitable solvent. 1 mL of the extract solution was added with 2 mg of Mg powder and 3 drops of $HCl_{(P)}$. Furthermore, a positive test for flavonoids is indicated by the formation of a yellow, orange or red color.

In the anthocyanin test, the crude ethanol extract was dissolved using a suitable solvent. Furthermore, 1 mL of the extract solution was added to 2M HCl, heated and observed, before adding 2M of NaOH. A positive test for anthocyanin is seen when the color changes to green and fades slowly.

Preparation of TiO_2 Coating on ITO glass (Working Electrode)

50 grams of TiO_2 was calcined at 500°C for 1 hour, and the PVA solution was made by dissolving 1.5 grams of PVA powder into 13.5 mL of distilled water with a stirrer for 30 minutes at 60˚C. Furthermore, 0.5 grams of calcined TiO_2 powder was put into the mortar and 15 drops of PVA solution were added and then crushed to form a paste. The paste was deposited on the ITO glass using the doctor blade method. This involved using the conductive side of the 2 X 1.5 cm ITO glass, measuring the resistance on one plane of the glass. Furthermore, a TiO_2 deposition area of size 2 X 1.5 cm above the surface was formed, and the paste was deposited and leveled using a spatula. The layer was left for 10 minutes and then calcined using a furnace for 30 minutes at a temperature of 450°C. Subsequently, the ITO glass coated with TiO_2 was immersed in the Mahkota Dewa extract dye with various concentrations, namely 10, 20, and 30% (w/v) inside a petri dish for 24 hours in a dark room. The surface morphology characterization of the TiO_2 thin layer semiconductor before and after calcination was carried out using Scanning Electron Microscopy (SEM) in order to view the surface phenomena.

Preparation of Reference Electrode

The ITO glass was scratched using an 8B pencil on an area of 2 cm x 1.5 cm.

Preparation of Electrolyte Solution

3 grams of KI solids and 3 mL of iodine were weighed and added to the solution. Afterward, 3 grams of PEG solids were dissolved in 3 mL of chloroform and then stirred using a hotplate with a magnetic stirrer for 30 minutes. The electrolyte solution was then mixed with the PEG solution and stirred for 60 minutes.

Preparation of DSSC Sandwich Layer

The working and reference electrodes were arranged in opposite positions, and their two sides were clamped using a paperclip. Furthermore, the two sides of the electrodes were opened and dripped with 2 drops of electrolyte solution on their sidelines and then clamped again.

Testing of DSSC Current and Voltage

The DSSC voltage which has been treated with different variations in dye concentration using a Heles UX-78 multimeter was exposed to sunlight as a light source for 1 hour at 11:00 to 12:00 am. Furthermore, to determine the durability/storage time of the DSSC, current and voltage measurements were carried out periodically (every day) for 6 days, and the efficiency was also calculated. While the lux meter was used for measuring the power of sunlight.

RESULTS AND DISCUSSION

Phytochemical Test Results of Mahkota Dewa Fruit Extract

The tests for secondary metabolites of flavonoids and anthocyanins were carried out on the Mahkota Dewa fruit extract *(Phaleria macrocarpa (Scheff) Boerl.)* in order to determine the feasibility of the sample to be applied on the DSSC. The results of these tests are shown in Table 1.

These results showed that the group of compounds in the Mahkota Dewa *(Phaleria macrocarpa (Scheff) Boerl)* extracts are flavonoids and anthocyanins. Furthermore, the test results on extracts containing flavonoids showed color changes when adding concentrated Mg and HCl powder. This is because of the polarity of the compound which is attracted by polar ethanol solvents and its stability in acidic conditions. Furthermore, the phytochemical test results on the extract containing anthocyanin compounds showed color changes when adding concentrated NaOH and HCL. This was indicated by the appearance of blue color when adding 2M of NaOH which gradually disappeared. It is due to the change in pH of anthocyanins from acid to base, resulting in the addition of the –OH group which causes an unstable blue color. In addition, the color degradation of this compound was caused by the change of red flavilium cations to blue carbinol bases.

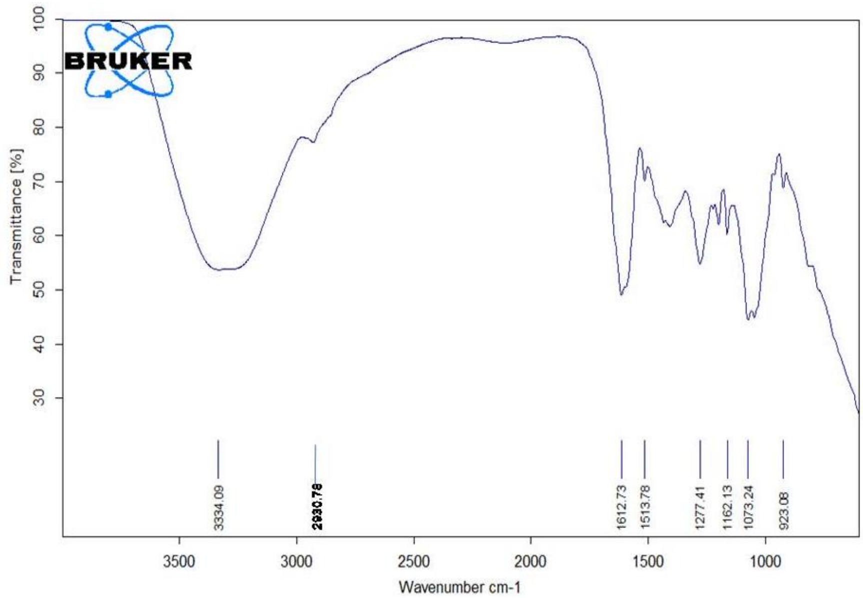

Figure 1. The results of FTIR dye extract of Mahkota Dewa.

Table 1. Phytochemical Test Results of Mahkota Dewa Extract (*Phaleria macrocarpa (Scheff) Boerl*).

Compound Group	Test Result
Flavonoid	+
Anthocyanins	+

Description:

(+) = indicates positive containing secondary metabolites

(-) = indicates negative containing secondary metabolites

UV-Vis Test Results

The Vis spectrophotometer was used in the Mahkota Dewa *(Phaleria macrocarpa (Scheff) Boerl.)* dye sample test to determine the maximum wavelength absorption within the range of 400 to 700 nm which is the wavelength of visible light. Table 2 shows the result of the test using a Vis spectrophotometer on Mahkota Dewa dye.

Table 2. Measurement of dye maximum wavelength.

Sample	Wavelength (nm)	Absorbance
Mahkota Dewa Extract Dye	554	0.163

In this spectrum, the maximum absorption was detected at a wavelength of 554 nm with an absorbance value of 0.163 which indicated the alleged absorption of anthocyanin compounds. The results showed that complementary colors in the dye changed from purple to red while the absorbed color was green. Furthermore, the characteristic of anthocyanins is the change from red to purple color, which indicates the dye contains this compound.

Fourier Transformed Infra-Red (FTIR) Test Results

The Mahkota Dewa *(Phaleria macrocarpa (Scheff) Boerl.)* extract was tested using Fourier Transformed Infra-Red (FTIR) to determine the functional groups present within the wave range of 4000 to 600 cm-1. Figure 1 shows the result of the FTIR dye test for the Mahkota Dewa extract.

Figure 1 and Table 3 show a wide absorption at wavenumber 3334.09 cm-1 which indicates the presence of hydrogen bonds between the –OH group. This was supported by a sharp absorption at 1073.24 cm^{-1}, which is the wavenumber of the -CO group in alcohol. Furthermore, there was a sharp absorption at 2930.78 cm-1, 1612.73 cm^{-1}, and 923.08 cm^{-1}which are the wavenumbers of the aliphatic C-H, C=C alkene, and -CH groups in the form of an aromatic ring. These results are in accordance with the research of Damayanti et al. (2014) which had absorption wavenumbers at 3348.88 cm^{-1}, 1641.17 cm^{-1}, 1015.10 cm^{-1} and 675.43 cm^{-1} indicating the presence of anthocyanin. In addition, the results from the research by Ondagau et al. (2018) showed that this compound was also present in the alcohol O-H functional group, CO alcohol bonding,

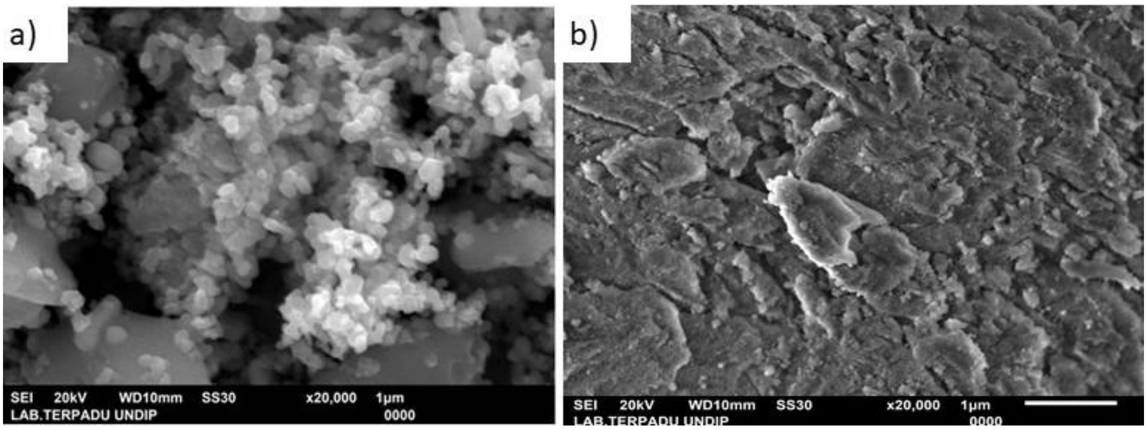

Figure 2. Differences in surface morphology of the TiO_2 layer on ITO glass (a) before and (b) after immersion in Mahkota Dewa extract dye with a magnification of 20,000x.

aromatic C=C double bond, aliphatic –CH group, and aromatic CH at wavenumbers 3359 cm-1 1055 cm^{-1}, 1617 cm^{-1} and 1523 cm^{-1}, 2936 cm^{-1}, and 867 cm^{-1}.

Table 3. FTIR Interpretation Results of Mahkota Dewa Extract.

No	Wavelength (cm^{-1}) On Spectra	Wavelength (cm^{-1}) In Library	Ribbon Shape	Functional groups
1.	3334.09	3500-3000	Widen	-OH
2.	2930.78	2850-2970	Moderate	-C-H *Aliphatic*
3.	1612.73	1650-1450	Sharp	-C=C aromatic
4.	1073.24	1230-1000	Sharp	-C-O alcohol
5.	923.08	995-675	Moderate	-C-H bend

Scanning Electron Microscope (SEM) Analysis Results

The SEM characterization was to see the morphological differences of TiO_2 deposited on ITO glass which had been calcined at a temperature of 450 °C before and after immersion in the Mahkota Dewa extract dye, as shown in Figure 2.

Figure 2 (a) shows the surface morphology of the TiO_2 layer which is spherical in shape and has many agglomerations. It was shown that the solid is porous, and there was a cavity on the surface for the adsorption of the dye molecules into the electrode layer. Furthermore, it was found that the number and area of cavities on the surface affect the effectiveness of dye adsorption into the surface, and also facilitate the spread of the electrolyte solution on the working electrodes of the cell system. Figure 2 (a) and (b) also shows that there are differences in the surface morphology of the TiO_2 layer on ITO glass that has been soaked in the Mahkota Dewa extract dye. This was in the area that does not show a spherical shape, but tends to be covered by other compounds that are believed to be the fruit extract dye.

Current and Voltage Test

The results of current and voltage measurements showed the maximum current and voltage values for each DSSC with different variations in dye concentration on the DSSC. Furthermore, Figure 3 shows the curve of the relationship between current and voltage with different variations in dye concentration by measuring DSSC daily for 6 days.

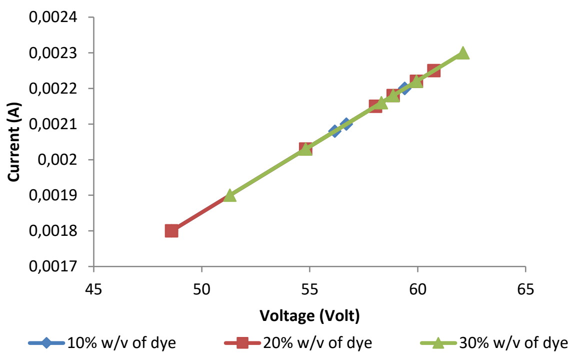

Figure 3. Current and voltage curve of DSSC TiO_2 and dye concentration of 10%.

The graph shows the relationship between current and voltage in which the higher the current, the greater the voltage. This is in accordance with Ohm's law which states that the amount of electric current flowing in a conductor is directly proportional to the magnitude of the voltage and inversely proportional to the resistance value. Based on the graph, it is found that the DSSC with a dye

Table 4. DSSC Efficiency Value Data.

Dye concentration	Efficiency (10-3%) Day-					
	1	2	3	4	5	6
10%	2.04	1.83	1.74	1.66	1.59	1.06
20%	2.18	1.84	1.80	1.66	1.59	1.00
30%	2.24	1.87	1.85	1.68	1.63	1.16

concentration of 30% w/v has more current and voltage compared to the ones with 20% w/v and 10% w/v. This is because the greater the concentration of the dye, the more anthocyanins and electrons are involved in the electron conversion process, and the larger the value of the resulting current.

Efficiency Value

The DSSC efficiency value was measured using a series of tools consisting of a multimeter which measures the current (I) and voltage (V), and a lux meter to measure the intensity of sunlight. The results of the efficiency values of the DSSC using variations in the dye concentration of Mahkota Dewa extract include 10, 20, and 30% (w/v), as shown in Table 4. In addition, the determination of the efficiency value was carried out for 6 days to determine the performance of the DSSC.

Based on Table 4, the highest efficiency was obtained at a dye concentration of 30% w/v on the first day, which was 2.24 x 10-3 % of the substance compared to the 10% w/v and 20% w/v which had an efficiency of 2.04 x 10-3 % and 2.18 x 10-3 %, respectively. This indicates that the concentration affects the efficiency value of the DSSC, whereby the greater the dye concentration, the more efficient the DSSC. As a result of the increased level of dye concentrations, more electrons were excited by sunlight and more compounds flowed through the TiO_2 pores, thereby producing a larger electric current. On the other hand, Figure 4 it also shown the decreasing of efficiency value with the length storage, maybe because the electrolyte solution undergoes an oxidation process due to exposure to sunlight for several days so that the electron cycle in the DSSC becomes blocked (Handayani et al., 2013). Moreover, the direct sunlight exposure will make that the electrons generated from the excitation process are reduced. According Hardani (2017), increase the absorption of the quantity of sunlight will influence the effectivity of DSSC because organic dyes will easily decay. Sasongko et al. (2019) report the solar light will increase the temperature, then greatly affects the stability of the anthocyanin structure, the more unstable the anthocyanin compound which causes damage to the anthocyanin structure. Furthermore, according to Mulyawanti et al. (2018), the concentration of anthocyanins will decrease due to sunlight will occurred Maillard's reaction and resulting the degradation of the anthocyanin become another compound such us furfural compounds.

CONCLUSION

The measurement and analysis of the absorption spectra of natural dye extract of Mahkota Dewa fruit shown the dye was content anthocyanin, with an absorption spectrum similar to that of anthocyanin at wavelength 554 nm with absorbance at 0,163. The FTIR result shown the peak was similar with anthocyanin. After immersion with natural dye, the surface morphology of the TiO_2 is covered by dye with reduced spherical shape. The maximum efficiency value of DSSC with a concentration variation is DSSC 30% w/v with the efficiency value of 2.24 x 10-3%. After six days, the efficiency was decrease (1.16 x 10-3%). Electrical current measurements produced by Mahkota Dewa fruit extracts necessary for further investigation as a DSSC sensitizer.

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