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The Photosensitizer from the Basic Dye Extract of the Skin Fruit Of Eggplant (*Solanum melongena* L.)

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Abstract: *The latest generation of solar cell that utilizes dye from plants as a photosensitizer is Dye - Sensitized Solar Cell (DSSC). The dye from Solanum melongena L. is one of the potential photosensitizers due to its chemical and physical characteristics. This study aims to determine these characteristics as well as its efficiency value in DSSC. The dye was obtained by ultrasonic extraction in 1% HCl methanol solution. The crude extract of dye was treated in acid and basic condition and then separated by vacuum gravitation chromatography in a way that the polarity was increased. The results were a variety of dyes according to their polarity. The dye then applied in DSSC as the photosensitizers. The highest conversion value was 0.0211%, performed by the dye in pH 8 solution. The characteristic of this extract was identified by UV-Vis, FTIR and GC-MS. All the spectral data indicated that the main component which responsible for this efficiency was pelargonidin.*
Keywords: *DSSC, efficiency, photosensitizer, Solanum melongena L, solar cell.*

1. INTRODUCTION

Electricity has been the important needs of human being since its invention decades ago. Nowadays, electricity mainly obtained from fossil energy which undoubtedly declines over time. According to the Geology Board of the Ministry of Energy and Mining Resource of Indonesia, in 2014, Indonesia's fuel natural storage will not be sustainable up to 23 years later (www.tribunnews.com). The similar condition was also found in other natural resources, for instance: natural gas and coal.

To this end, the government of Indonesia implements some regulations to overcome the future energy crisis. The regulations make sure that in 2025 the use of fossil is decreased and alternatively substituted by more sustainable, renewable and environmentally friendly energy resources. The best candidate for these criteria is solar energy. This energy has been widely studied in several developed and developing countries.

Stated in the equator line from west to east, Indonesia obviously has this potential energy. The sun shines through the year providing the opportunity to develop conversion technology from solar to electric energy. The conversion technology based on the photovoltaic effect in a panel of the solar cell (Goetzberger dan Hoffmann, 2005:1). In 1991, Gratzel and O'Regan for the very first time introduced Dye-Sensitized Solar Cell (DSSC) by utilizing dyes as the photosensitizer (Gratzel dan O'Regan, 1991: 739)

DSSC has benefits compared to the prior conventional solar cell. It is quite economical in terms of industrial stage and performs better efficiency value. Generally, DSSC is made out of several components, namely: TCO (transparent conductive oxide) plate, TiO2, electrolyte solution, counter electrode and dye (Gratzel dan O'Regan, 1991: 737-739). The dye could be synthetic or natural dyes from plants.

The natural dye usually obtained by extraction method from rich colored-parts of plants like the flowers, leaves, and fruits (Chang dan Lo, 2010: 1834). It is found that the dye with hydroxyl and carbonyl group bound easily in the TiO2 surface (Wongcharee, et al., 2006: 566). Therefore, the main components of photosensitizer for DSSC are mainly identified as chlorophyll, carotenoid, flavonoid, and anthocyanin.

Anthocyanin is water soluble and widely found in Angiospermae plants from the flower, fruit, leaves, root, tuber, and stem (Andersen dan Markham, 2006: 472). According to the color produced, anthocyanin can be in several compounds. They are pelargonidin, cyanidin, peonidin, delphinidin, petunidin dan malvidin (Alhamed, et al., 2012: 1371).

Several researchers have studied the application of anthocyanin as the photosensitizer in DSSC. A research group in China, Zhou, et al. (2011) investigated 20 dyes from Begonia, Citrus hystrix skin, Rhododendron, Fructus lycii, Marigold, Perilla, Herbal artemiseae scoriae, China lorepetai, Yellow rose, Flowery knotweed, Bauhinia tree, Petunia, Lithospermum, Violet flower, Chinese Rose, Lily, Coffee bean, Broadleaf holly leaf and Mangosteen skin. The highest efficiency value was 1.17% and was obtained from Mangosteen skin. In addition, Alhamed, et.al. (2012) reported that dye from the crude extract of raspberries can convert the photonic energy up to 1.50%. Hug, et al. (2014) also found similar efficiency value from C. odontophyllum + ixora sp after investigating 12 plants extract which contain anthocyanin. Later, Chien and Hsu (2013) studied anthocyanin based dye in a series acidity of pH 2, 4, 6, 8, 10 and 12. They reported that the highest efficiency value was 1.184±0.051%, obtained from pH 8.

Anthocyanin can be provided from the fruit skin of Solanum melongena L which is famously known as purple eggplant. The anthocyanin which is familiar with eggplant skin fruit is nasunin (Noda, et al., 2000: 120) and delphinidin-3-rutenoside (Sadilova, et al., 2006: 527). Therefore, the dye of eggplant peels is very potential to apply as a photosensitizer to DSSC.

2. MATERIALS AND METHOD

Materials

The IR and UV spectra were measured by Shimadzu IR-Prestige 21 and Shimadzu UV-2600 Spectrometer, respectively. Mass spectra were recorded using Shimadzu GC-MS Instrument (GC trace 1310 and MS ISQ *single quadrupole*). The morphology of the solar cells was analyzed by SEM Vega3 Tescan. The ultrasonic wave was performed by an ultrasonic device with a frequency of 47 KHz. The solar cell was made of Transparent Conductive Oxide glass plates and technical grade of TiO_2. Electrical kit used were including LX-103 light meter and DT-860B multimeter. Solvents were mostly in technical grade but previously distilled before utilization except for ethanol whereas HCl, NaOH, and KI/I_2 were by analytical grades. Vacuum Liquid Chromatography was carried out using Merck Silica Gel 60 GF254 (cat. No.7730 and 7733). The eggplant fruits were collected from Garentong, Gowa District, South Sulawesi, Indonesia.

Experimentals

Extraction and Separation of the Dye

The dried powdered skin of the eggplant fruit was made as much as 250 g and subsequently extracted by 1% HCl in methanol under a 47 kHz of ultrasonic wave for 15 minutes. Afterward, the extract was made in acid and basic methanol solution. The basic one was made by addition of appropriate 10% of NaOH.

The two extracts were then fractionated on a Silica gel and eluted with n-Hexane: ethyl acetate (8:2 and 5:5) and methanol: ethyl acetate (8:2) in order to increase polarity.

Preparation and Assembly of DSSC

TiO_2 was diluted in hot distilled water to remove impurities. The TiO_2 was then mixed with ethanol to form a white liquid paste. Meanwhile, the electrolyte solution (KI/I_2) was made by dissolving 0.83 g of KI into 0.13 g iodine in 10 mL of water. The electrode, TCO glass plates were prepared by applying the TiO_2 paste on to the plate surface which had been previously covered by a clear tape. Then, a sintering process was performed to obtain smooth and homogenous dried surface. A few drops of the dye extracts then were applied to the dried surface of TiO_2. Afterward, few drops of the electrolyte solution were applied to the good mixture of TiO_2 and the dye. The other TCO plates as the counter electrode were prepared by cleaning them in the ultrasonic device and dried. One side of these plates was introduced to the fire flame to form thin carbon layer. These plates then used to cover the electrode plates with dye. The overall construction was then connected to the electrical apparatus and irradiated by the sunshine. The electrical current and the voltage were recorded to measure the efficiency value of the DSSC cells.

Characterization

UV-Vis Analysis

The basic dye extract of eggplant skin fruit analyzed by spectrophotometer UV-2600 Shimadzu at wavelength 200-800 nm.

FTIR Analysis

The basic dye extract of eggplant skin fruit mixed with potassium bromide (KBr) known as KBr pellets then analyzed by Shimadzu IR-Prestige 21 to know the functional group and the bonding types in the dye.

GC-MS Analysis

The basic dye extract of eggplant skin fruit analyzed by GC-MS Shimadzu (GC trace 1310 and MS ISQ single quadropole) to know molecule structure based on fragment and molecular weight.

SEM Analysis

TCO glass plate size 0.5 x 0.5 cm were prepared by applying the TiO_2 paste on to the plate surface which had been previously covered by a clear tape. Then, a sintering process was performed to obtain smooth and homogenous dried surface. A few drops of the dye extracts then were applied to the dried surface of TiO_2 then analyzed by SEM.

3. RESULT AND DISCUSSION

Extraction and Separation of the Dye

The extract of the fruit's skin of eggplants was made in acid and basic condition. The acid one was in pH 1 and achieved by extracting the dye using 1% HCl in methanol while the basic one was in pH 8 and made by addition of 10% NaOH to the methanol extract. The extracts were then applied in DSSC. The efficiency value of the obtained DSSC can be seen in Table 1. It is obvious from the data that there is a significant difference in the values. The basic extract tends to be more efficient in converting the photon energy to be electricity.

Table 1. The Efficiency Value of the Acid and Basic Extract of Eggplant Skin Fruit

No	pH	V (mV)	I (mA)	P_{Max} (mW)	P_{In} (mW/cm^2)	η (%)
1	pH 1	105	1.6	0.000168	3.074820	0.0054
2	pH 8	170	16.0	0.002720	12.88496	0.0211

Several researchers conducted a study of dyes separated by vacuum gravitation chromatography using eluent methanol: n-Hexane by increasing the polarity which then the dye was applied as a photosensitizer on DSSC. Baharuddin, et al. (2015) reported that the highest efficiency from teak leaf was 0.05% that obtained by eluent ratio 5:5. Maming, et al. (2017) used dye from red pepper and the highest efficiency value was 0.03% with eluent ratio 4:1. Indeed, Wahab, et al. (2016) found that the highest efficiency from tomato extract with eluent ratio 1:1 was 0.02%. Based on table 1, the efficiency value obtained on the basic dye extract of eggplant skin fruit is lower than efficiency value from teak leaf and red pepper.

In addition, the crude methanol extract was also fractionated by vacuum gravitation chromatography eluting with n-Hexane: ethyl acetate (8:2 and 5:5) and methanol: ethyl acetate (8:2). Later the fractions were also applied into DSSC and hence the efficiency value was recorded. The results were shown in Table 2.

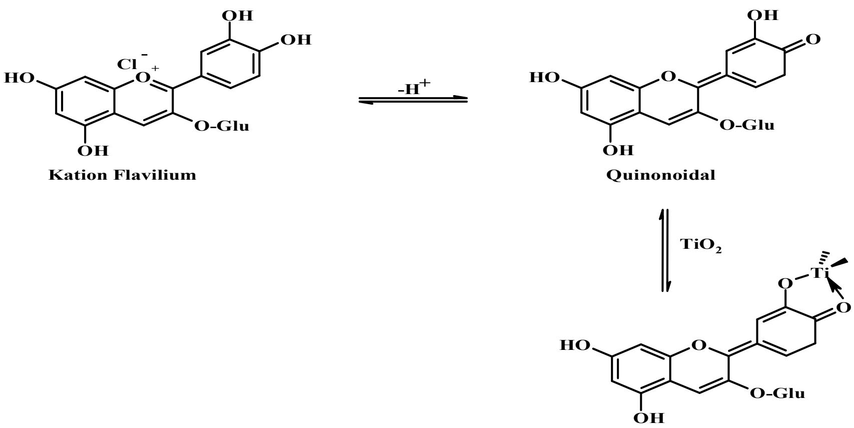
Table 2. The Efficiency Value of the Fractionated Extract of Eggplant Skin Fruit

No	Eluent	V (mV)	I (mA)	P_{Max} (mW)	P_{In} (mW/cm^2)	η (%)

1	n-Hexane:ethyl acetate (8:2)	104	12.0	0.0012480	12.870318	0.0097 %
2	n-Hexane:ethyl acetate (5:5)	61	1.6	0.0000918	7.833470	0.0011%
3	Methanol:ethyl acetate (8:2)	43	9.6	0.0004128	12.928886	0.0032%

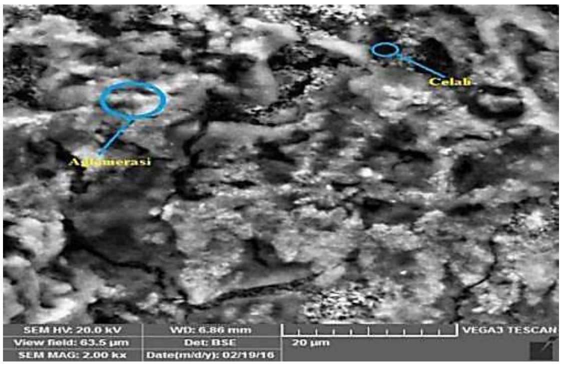
Based on Table 1 and 2, it is indicated that the highest efficiency value of DSSC was achieved by the basic extract in pH 8. It can be assumed that this value is a consequence of the ability of the main dye components in pH 8 to bind with TiO_2. As it is bound appropriately, the electron radiation from sun rays can be absorbed as much as possible to the TiO_2 before it is released to the counter electrode to generate electricity.

The ability of the dye components to bind to TiO_2 basically comes from its chemical structure. In basic condition, the main components which are flavilium turn to be basic quinoidal, something that is impossibly occurred in pH 1-2. This quinoidal binds easily to form a complex structure thanks to the carbonyl and the hydroxyl group of anthocyanin ring B (Chiang and Hsu, 2013: 205). The illustration of the binding site was given in Picture 1. Whereas, in pH 1-2, flavilium cation is perfectly stable so it cannot be bound to the TiO_2.



Picture 1. Antocyanin and TiO_2 Binding in Acid and Basic Solution (Cherepy, et al., 1997: 9343)

Nevertheless, this efficiency value of the basic extract is still rather lower than that of the previous findings. It is possibly caused by the imperfection of the TiO_2 to bind to the dye since the TiO_2 used was technical grade. It can be seen from the SEM image of the DSSC that there are several identified agglomerations of dye while some empty pores also found in the TiO_2 surface. This means that the dye was not homogeneously mixed with the TiO_2 so there were no sufficient dye molecules to absorb the electrons. As a consequence, the electricity produced will be lower and so will the efficiency values.



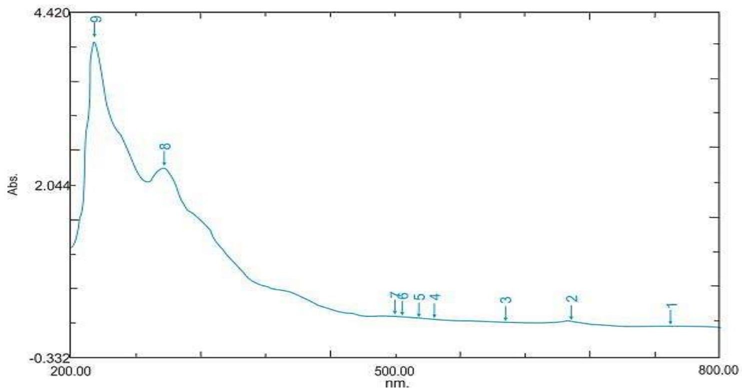
Picture 2. The Image of TiO_2-Dye Mixture by SEM (1: 10 µm)

Characterization of The Dye.

The basic extract then led in several spectral identifications to investigate its secondary metabolites.

UV-Vis Analysis

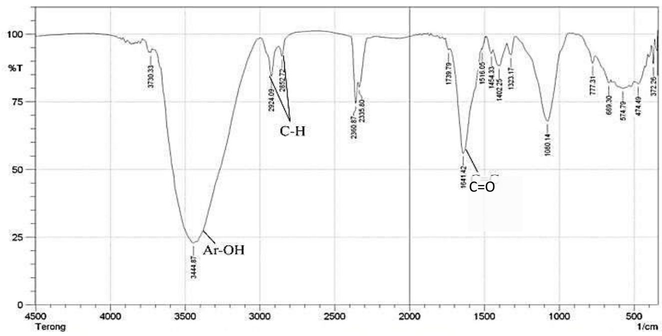
UV-Vis spectrum of the basic extract indicated the presence of anthocyanin components due to the appearance of maximum absorbance in 500-550 nm in visible area and in 280 nm in UV area. The components regarding this spectrum are pelargonidin and cyanidin (Harborne, 1987: 62). Several components were also identified as minor components.



Picture 3. The UV-Vis Spectrum of the Basic Extract of Eggplant Skin Fruit

FTIR Analysis

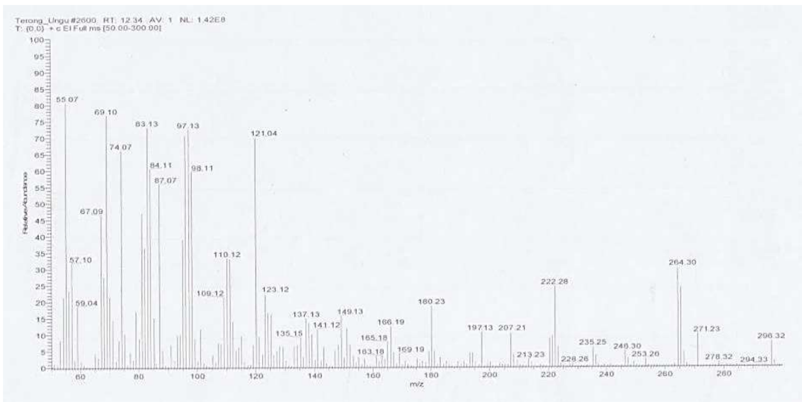
The IR spectrum exhibited the presence of hydroxyl (3445 cm^{-1}), aliphatic C-H (2852 and 2924 cm^{-1}) and conjugated carbonyl (1641 cm^{-1}) (Kosela, 2010: 181-188). These peaks in accordance with the UV-Vis spectrum that the main components are anthocyanin groups.



Picture 4. The FTIR Spectrum of the Basic Extract of Eggplant Skin Fruit

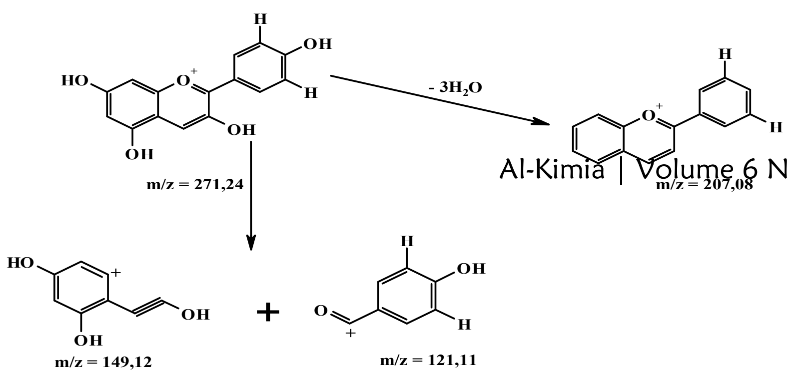
GC–MS Analysis

Further evidence was provided by GC-MS analysis. The fragmentation patterns of the basic extract were recorded as shown in Picture 5. It is seen from the mass abundance of molecule ion (m/z 271,23) that the main anthocyanin component was Pelargonidin. The fragmentation patterns were m/z 121, 149,197, 169.



Picture 5. The GC-MS Spectrum of the Basic Extract of Eggplant Skin Fruit

The fragments m/z 149 and 121 resulted from the cleavage of the pelargonidin as the molecule ion to the fragment of m/z 149 and 121 as depicted in Picture 6. The cleavage occurred in the C-O binding of the ring A and C which is initiated by the loss of one electron of the pelargonidin radical ion. It results in two fragments which are complementary to each other.



Picture 6. Fragmentation of Pelargonidin

4. CONCLUSION

The highest efficiency value of DSSC was 0.02% and achieved by the basic extract of the eggplant skin fruit. The spectral analysis, including UV-Vis, FTIR, and GCMS indicated that the main component of the basic extract was pelargonidin.

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