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Conversion of Anthocyanin From Dragon Fruit (*Hylocereus Costaricencis*) To Metal Complexes: Prospects For Sensitizer In Solar Cells

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Abstract: *The anthocyanin from nature compounds containing colour or chromophore groups biochemically and effectively absorbs sunlight in the visible spectrum because it has more than one benzene ring with a conjugated double bond. Super dragon fruit (Hylocereus costaricencis) is one of the plants with the highest anthocyanin content with 1.1 mg / 100 mL of anthocyanin solution. In this research, 400 gr of dragon fruit skin extracted with 300 mL CH_3OH for 24 hours in dark room at room temperature. And followed by liquid-liquid extraction using n-hexane and ethyl acetate. Each of 50 mL filtrate from extraction was synthesized with 0,5 gr $FeCl_3.6H_2O$, and 0,5 gr $CoCl_2.6H_2O$ for 5 hours and get well mixture, then identified using UV-Vis Spectrophotometer and FTIR. Spectra data's show the different profile before and after conversion, further characterization to determine the energy gab (Eg) and stability of the compound compared to natural sensitizers and others. The Eg found from synthesized $FeCl_3.6H2O$ is 0.33 eV and synthesized $CoCl_2.6H_2O$ 0.185 eV. The energy gab identification and analyzation from metal complexes give much better performance photoelectric conversion than using natural photosensitizers.*

Keywords: *Solar Cell, Anthocyanin, Dragon Fruit, Sensitizer*

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I. Introduction

The high number of world population growth shows a linear correlation with the need for energy. However, it is known that reserves of oil and mineral resources belonging to non-renewable resources that have been used are decreasing with the length of exploration and high consumption. More than 81% of the world's energy consumption depends on fossil fuels (Jager, 2014). Therefore, a number of studies that utilize renewable natural resources continue to be developed to address the high demand for these energy needs so as not to continue to depend on fossil fuel energy sources, such as research on solar energy or known as solar energy. Approximately 4 million masses per second of the sun's constituent material is converted to energy, with a theoretical estimate of the 275 W / m matahari sun center (Jager, 2014). Recognizing the abundance of these energy sources, the development of solar cells is a highly potential study developed as an alternative to starting a reduction in energy use with fossil fuels.

The first silicon solar cell (SiO2) developed shows high efficiency performance of about 17-25% (Hardeli, 2013). However, a number of facts mention that the use of silicon is dangerous in its manufacturing process and costly. This is because silicon is a raw material that is widely used as a tool in the technology industry (Mehmood, 2014). As a competitive alternative then Michel Gratzel in 1991 developed DSSC (Dye Sensitized Solar Cell). Important components in DSSC devices are electrolytes, sensitizers, sunlight, semiconductor materials and so on. Currently, the development of these components is an ongoing challenge to improve the results of high energy conversion efficiency. The type of sensitizer (dye) is divided into two types, namely the dye obtained naturally and the second by synthesis. This natural organic dye is advantageous because the source of the material can be obtained anytime, practically and can be obtained in large quantities and from some references indicates a low assembly cost. Natural dye sources are often used as a natural sensitizer such as anthocyanin. The highest anthocyanin content is found in super red dragon fruit skin (Hylocereus costaricencis). The content of anthocyanin on super red dragon fruit (Hylocereus costaricencis) of 1.1 mg / 100 mL of anthocyanin solution (Hidayah, 2013) and (Wahyuni, 2011), 45.15 ± 0.5117 gr / 100 gr Dry skin dragon fruit Hylocerius undatus (Vargas et al., 2013). But has a deficiency of low 1-7% efficiency, cannot survive at high temperatures or less stable, and interacts with TiO2 (Narayan, 2012).

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process and costly. As a competitive alternative, Michel Gratzel in 1991 developed DSSC (Dye Sensitized Solar Cell) with components are electrolytes, sensitizers, sunlight, semiconductor materials and so on. Currently, the development of these components is an ongoing challenge to improve the results of high energy conversion efficiency. The type of sensitizer (dye) is divided into two types, namely the dye obtained naturally and the second by synthesis. This natural organic dye is advantageous because the source of the ingredients can be obtained anytime, is practical and can be obtained in large quantities and from some references indicates low assembly costs, but has a deficiency of low 1-7% efficiency performance, unable to survive at high temperatures or less stable, and interacting with TiO2 (Narayan, 2012).

Compared to natural dye, synthetic dye has been shown high energy conversion value due to MLCT (metal to ligand charge transfer) interaction between central metals and binding ligands such as N3, N719, YE05 compounds (Nazeeruddin et al., 2011). The presence of MLCT interactions causes the electrons in the upper state position or the state of excitation (exited state) more, so the number of electrons to be transferred becomes more. The number of electrons transferred to the electron collecting electrode produces PCE (power conversion energy) or a high percent efficiency (η) as well. However, the complex synthesis sensitizer has constraints in the form of expensive and highly complex synthesis processes (Suhaimi et al., 2013). Answering these challenges, research on sensitizers continues, including by utilizing complex compounds as sensitizers by reacting to ligands from natural dyes with transition metals.

This study aims to obtain complex compounds with anthocyanins as natural organic ligands which are reacted with iron salts trichloride hexahydrate (FeCl3.6H2O), cobalt dichloride hexahydrate (CoCl2.6H2O) and form complex compounds (Housecrofy and Sharpe, 2005). The complex compounds of the synthesized product were further identified using UV-Vis spectrophotometer and then the data obtained were analyzed to determine the value of energy gap (Eg) of the organometallic compound compared to the natural sensitizer.

II. Experimental Details

This research was conducted at 3 stages including: anthocyanin isolation, organometallic reaction, spectra data analysis. Isolation of anthocyanin from super red dragon fruit skin (Hylocereus costaricencis).This anthocyanin isolation stage begins by preparing the red dragon fruit skin sample, including cleaning equipment and materials to be used. As many as 400 grams of super red dragon fruit skin (Hylocereus costaricencis) cut small and blend puree. Dry the sample using the freeze drying tool Alpha 1-2 LD plus Christ for 24 hours, to reduce the water content. Then dried samples were soaked (macerated) in 300 ml of methanol solvent for 24 hours. Use a shaker to increase the surface area of the sample contact with the solvent and store it in the dark room. Strain the extractants obtained using filter paper whatmann no. 42. Further filtrate / dye is evaporated using a rotary evaporator.

After that, the anthocyanin content was tested in filtrate with thin layer chromatography (TLC). The isolation step is carried out by using liquid-liquid extraction method using n-hexane (nonpolar) solvent, ethyl acetate (semipolar) and others. Finally, identification was done using UV-Vis spectrophotometer. Synthesis of organometallic compounds with iron salts trichloride hexahydrate (FeCl3.6H2O), cobalt dichloride hexahydrate (CoCl2.6H2O)

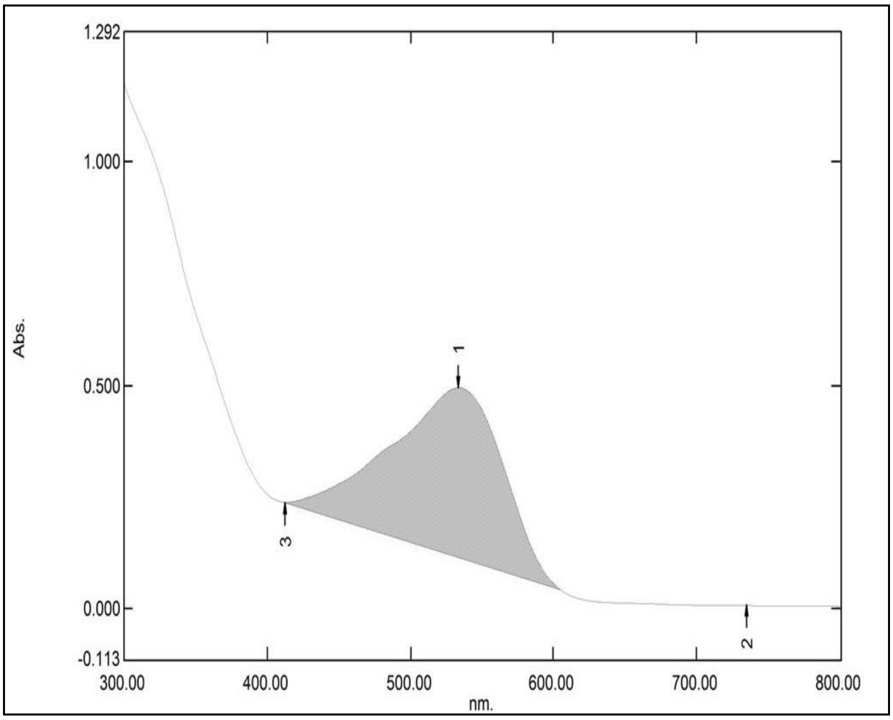
This second stage begins by weighing 0.5 grams of each of the FeCl3.6H2O salt compounds, CoCl2.6H2O. Samples of each weighed salt were placed into a beaker and 50 mL of each anthocyanin filtrate were added each. Then the solution was stirred using a stirrer stirrer in the tatas of the electric stove for 5 hours. After that the solution was filtered and identified by UV-Vis spectrophotometer and FTIR.

Energy Gap Analysis (Eg), the result of the UV-Vis spectral data before and after the reaction of the organometallic analyzed using Microcal Origin program to get the value of the energy gap (Eg) of natural photosensitizer (filtrate before organometallic reactions) and organometallic photosensitizer (filtrate after organometallic reactions).

III. Result And Discussion

In this study, the synthesis of complex compounds using anthocyanin from super red dragon fruit skin (Hylocereus costaricencis) ligand. Super red dragon fruit skin is known to have a very high antosianin. Anthocyanin is one of the natural pigments of the flavonoid group that is easily found in large quantities in the vicinity. Based on a literature review, the price of the PCE (power conversion energy) of a complex compound of Ru has a high value because it can mengabsopsi enough spectrum width, forming interaction MLCT (metal to ligand charge transfer) so that the electrons are in a position exitasi easier and more as well as having good stability. However, to synthesize complex Ru through reactions with synthetic organic ligands is very complex and uses high cost. Therefore, this study used the mechanism of the synthesis of complex compounds by reacting Ru anthocyanins (natural organic pigments) with salts of iron trichloride hexahydrate (FeCl3.6H2O), cobalt dichloride hexahydrate (CoCl2.6H2O). in this section the energy gap (Eg) values are obtained through UV-VIS spectra analysis.

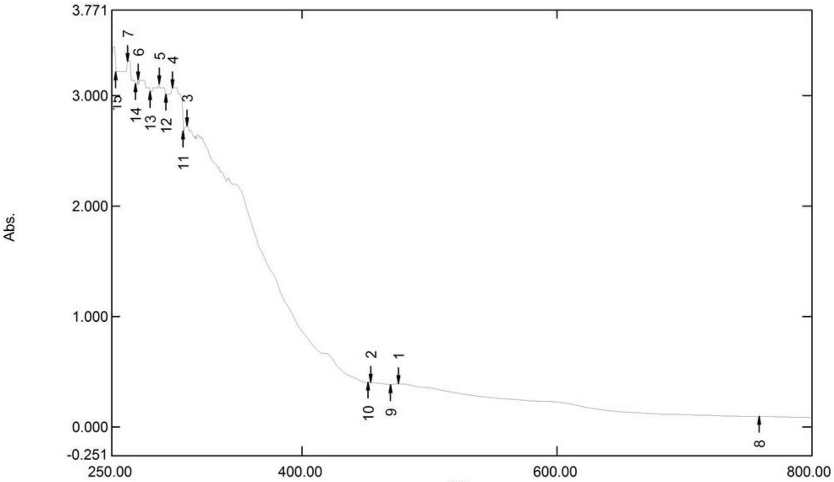
The preliminary study carried out by the process of maceration and liquid-liquid extraction using a nonpolar solvent (n-hexane) and semipoar (ethyl acetate), which aims to reduce the other components in the filtrate was isolated. Thus, the main component of the obtained filtrate is anthocyanin (polar). Furthermore, the anthocyanin filtrate was measured for absorbance using a spectrophotometer in the range 400-700 nm with a methanol solvent with a ratio of 1: 8. The following is the result of characterization of anthocyanin UV-VIS absorbance.



Picture 1. Dye Antosianin Absorbance

The results of identification of anthocyanin dye absorbance of red dragon fruit skin extract showed spectrum absorbance range from 412-734 nm. The magnitude of the wavelength indicates the red sueron dragon skin absorbs the purple light to the red on the visible spectrum and absorbs a little infrared spectrum. A fairly wide range of absorbances in the anthocyanin spectra results show that it can absorb photons well on a wider spectrum of light. Therefore, anthocyanin dye can also be utilized as a sensitizer on DSSC devices.

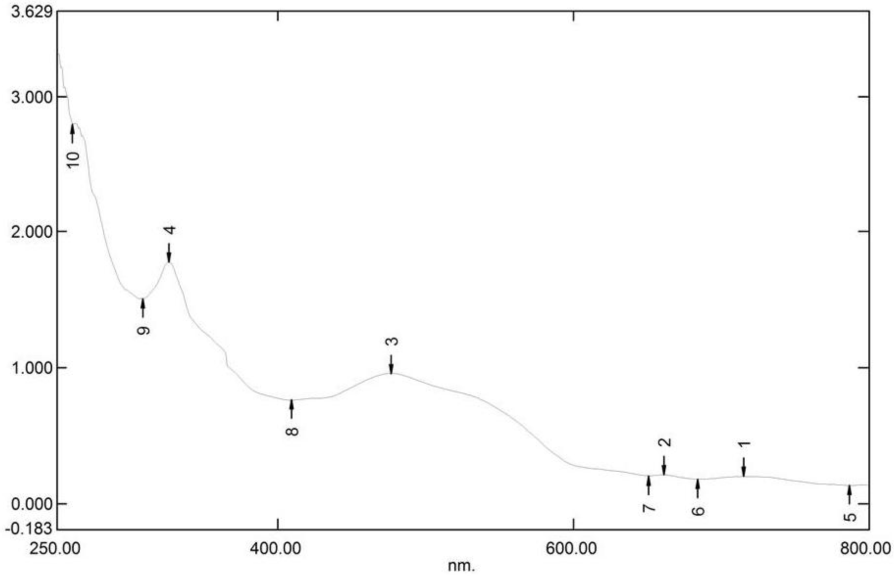
In the UV-VIS spectra for the identification of the result of iron complex compounds obtained a wider absorbance range that is at the wavelength of 253-759 nm. The absorption range obtained is wider than the absorbance of the anthocyanin dye.



Picture 2. Iron complex Absorbance

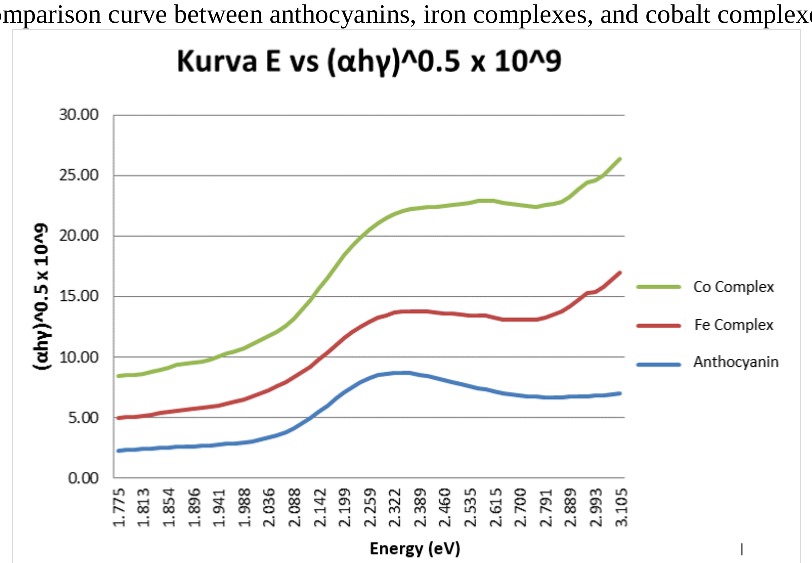
The extent of absorbance produced by iron complexes suggests that the light or energy of photons that can be absorbed by iron complexes can be wider than anthocyanin dye. The resulting absorbance of the iron complex is in the ultraviolet spectrum up to infrared spectrum. The wider / wider area of photon absorption produces a better sensitizer character, as it will absorb more of the photon energy. The amount of energy absorbed photons can be used as energy that can make the electron in the dye excited more there is a state of upper state. Thus the electrons that can be transferred to the semiconductor and electron collecting electrode more also to produce high PCE.

The UV-VIS spectra of the cobalt complex also exhibit a wider range of absorbances than anthocyanins, which are at wavelengths of 260-787 nm. The uptake of photons produced by the cobalt complex is highest compared to anthocyanin and iron complexes. The absorption of the cobalt complex photon spectrum is similar to that given to the iron complexes, ie, from the ultraviolet to infrared spectrum.



Picture 3. Cobalt Complex Absorbance

An analysis of the anthocyanin absorbance ratio curve, iron complex, and cobalt complex is performed to obtain an energy gap (Eg) value that can be a theoretical source whether the sensitizer has a good character as one of the photosystem devices. Energy gap is known as the amount of energy needed by electrons to excite from down state / HOMO to upper state / LUMO. Eg is therefore a reduction value between LUMO-HOMO. The greater the Eg, the less electron will be in the upper state / LUMO state, because if Eg is generated then the electron needs big energy to reach the excitation state. The UV-VIS spectra data obtained were processed and analyzed using the SPSS program and Tauc Plot method. A good sensitizer is expressed when it has a low Eg value. Here is a comparison curve between anthocyanins, iron complexes, and cobalt complexes:



Picture 4. Curva $(\alpha h\gamma)^{1/2}$ versus hγ for Cobalt Complex, Iron Complex and Anthocyanin

A comparison curva $(\alpha h\gamma)^{1/2}$ versus $h\gamma$ for cobalt complex, iron complex and anthocyanin for energy gap analysis above show that complex of iron and cobalt have higher energy than anthocyanin. Eg for cobalt complex is 0.185 eV, for iron complex is 0.33 eV while Eg for anthocyanin is 1.35 eV.

IV. Conclusion

Based on the results of research that has been done can be seen that the complex sensitizer obtained from iron complex and cobalt complex has a better character as a sensitizer. This is because the two complexes can absorb photons in a wider range of spectrums in the ultraviolet to infrared region, rather than the uptake of anthosinin which only absorbs photons in the visible spectrum to slightly infrared. The result of energy gap analysis showed that the value of Eg produced by the two complexes is lower than the value of Eg produced by anthocyanin.

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References

[1]. Abodunrin, T, Boyo, T, Obafemi, O, and Timothy, A. 2015. Characterization of Dye Sensitized Cells Using Natural Dye from Oil Bean Leaf (Pentaclethra macrophylla): The Effect of dye pH on the Photoelectric Parameters. *Materials sciences and Applications*. Vol 6, 656-655.

[2]. Abdel-Latif, M., Abuiriban, M Taher M. El-Agez, and Sofyan A. Taya. 2015. Dye- Sensitized Solar Cells Using Dyes Extracted From Flowers, Leaves, Parks, and Roots of Three Trees, *International Journal of Renewable Energy Research*. Vol 5, 1.

[3]. Abdel-Latif, M., El-Agez, T, Taya, S, Amal Y. Batniji, and El-Ghamri. H. 2013. Plant Seeds-Based Dye-Sensitized Solar Cells, *Materials Sciences and Applications*. Vol 4, 516-520.

[4]. Amadi, L, Jenny, S, Ahmed, A, Brown, N, Yadav, S, Destiny, B, Ghann, W, Gayrama, A, Jiru, M, Jamaluddin. 2015. Creation of Natural Dye Sensitized Solar Cell by Using Nanostructured Titanium Oxide. *Nanoscience and Nanoengineering*. Vol 3, 25- 32.

[5]. Ayalew, W and Delele W. 2016. Dye-sensitized solar cells using natural dye as light- harvesting materials extracted from Acanthus sennii chiovenda flower and Euphorbia cotinifolia leaf. *Advanced Materials and Devices*. Vol 1, 488-494.

[6]. Brian, H, Snaith, H and McGehee, M. 2012. The Renaissance of Dye-Sensitized Solar Cells. *Nature photonics*. Vol 3, 406-411.

[7]. Calogero, G, Yum, J, Sinopoli, A, Marco, D, Gra¨tzel, M and Nazeeruddin, M. 2012. Anthocyanins and betalains as light-harvesting pigments for dye-sensitized solar cells. *Solar Energy*. Vol 86, 1563–1575.

[8]. Castaneda, O, Hernandez, A, Rodriguez, E, Carlos, J, Galan, V. 2009. Chemical Study of Anthocyanin. *Food Chemistry*. Vol 113, 859-871.

[9]. Chang, H, Wu, T, Chen, K, Huang, C, Jwo, Y, Loa, J. 2010. Dye-sensitized Solar Cell Using Natural Dyes Extracted from Spinach and Ipomoea. *Journal of Alloys and Compounds*. Vol 495, 606–610.

[10]. Chermat, F, Vian, M and Cravotto, G. 2012. Green Extraction of Natural Products: Concept and Principles. *Molecular Sciences*. Vol 13, 8615-8627.

[11]. El-Agez, T, Taya, S, Elrefi, K and Abdel, M. 2014. Dye Sensitized Solar Cells Using Some Organis Dyes as Photosensitizers. *Optica Applicata*. Vol 24, 2.

[12]. El-Ghamri, Taya, S, Taher M, El-Agez, T, Al-Kahlout, A, Al Dahoudi, N, Abdel-Latif, M. 2015. Natural Dyes as Photosensitizers for Dye-sensitized Solar Cells. *Journal of Nano and Electronic Physics*. Vol 7, 3001.

[13]. Fran, R, Govindasamy, G, Yan, F, and Abu Bakar, H. 2014. Hibiscus Flower Extract as a Natural Dye Sensitizer for a Dye-sensitized Solar Cell. *Physical Science*. Vol 25, 85-96.

[14]. Gratzel, M. 2003. Review: Dye-sensitized Solar Cells. *Photochemistry and Photobiology*. Vol 4, 145-153.

[15]. Harbone, J. 1996. *Metode Fitokimia Penentuan Cara Modern Menganalisis Tumbuhan. Bandung*. ITB- Press.

[16]. Hardeli, Suwardani, Riky, Fernando T, Maulidis, Ridwan, S. 2013. *Dye Sensitized Solar Cells (DSSC) Berbasis Nanopori TiO2 Menggunakan Antosianin dari Berbagai Sumber Alami.* Makalah disampaikan pada Semirata FMIPA Universitas Lampung.

[17]. Housecrofy, C and Sharpe, A. 2005. *Inorganic Chemistry*. London. The Ashford Colour Press, Ltd.

[18]. Hidayah, T. 2013. Uji Stabilitas Pigmen dan Antioksidan Hasil Ekstraksi Zat Warna Alami dari Kulit Buah Naga (Hylocereus undatus). FMIPA, UNS.

[19]. Hug, H, Bader, M, Mair, P and Glatzel, T. 2014. Biophotovoltaics: Natural Pigments in dye-sensitized Solar Cells. *Applied Energy*. Vol 115, 216-225.

[20]. Ingrath, W, Nugroho, W, dan Yulianingsih, R. 2015. Ekstraksi Pigmen Antosianin Dari Kulit Buah Naga Merah (Hylocereus costaricensis) Sebagai Pewarna Alami Makanan Dengan Menggunakan Microwave (Kajian Waktu Pemanasan Dengan Microwave Dan Penambahan Rasio Pelarut Akuades dan Asam Sitrat). Jurnal *Bioproses Komoditas Tropis*. Vol 3, 3.

[21]. Inggrid, M, dan Iskandar, R. 2016. *Pengaruh pH dan Temperatur pada Ekstraksi Antioksidan dan Zat Warna Buah Stroberi.* Makalah disajikan pada Seminar Nasional Pengembangan Teknologi Kimia untuk Pengolahan Sumber Daya Alam Indonesia, 16 Maret, Yogyakarta.

[22]. Jäger, K, Isabella, O, Smets, A, Van Swaaij, R, Zeman, M. 2014. *Solar Energy. Fundamentals, Technology, and Systems.* Delf: Copyright Delf University of Technology.

[23]. Jinchu I, Sreekala, O, b, and Sreelatha, K. 2014. Review: Dye Sensitized Solar Cell using Natural Dyes as Chromophores. Material Science Forum. Vol 771, 39-51.

[24]. Kong, F, Dai, S and Wang, K. 2007. Review of Recent Progress in Dye-Sensitized Solar Cells. *Advances in OptoElectronics*. Vol 18, 1409-1424.

[25]. Maddu, A, Zuhri, M dan Irmansyah. 2007. Penggunaan Ekstrak Antosianin Kol Merah Sebagai Fotosensitizer pada Sel Turya TiO 2 Nanokristal Tersensitisasi Dye. *Makara, Teknologi*, Vol 11, 78-84.

[26]. Mathew, S, Yella, G, Humphry, B, Curchod, B, Ashari, N, Tavernelli, I, Nazeeruddin, M and Gratzel, M. 2014. Dye-sensitized Solar Cells with 13% Efficiency Achieved Through the Molecular Engineering of Porphyrin Sensitizers. *Nature Chemistry*. Vol 115, 14415-14424.

[27]. Martin, K. 2011. *Design, Synthesis and Properties of Organic Sensitizers for Dye Sensitized Solar Cell*. Doctoral Thesis. Royal Institude of technology.

[28]. Mehmood, U, Rahman, S, Harrabi, K, Waleed, A, Hussein and Reddy. 2014. Review: Recent Advances in Dye Sensitized Solar Cells. *Advances in Materials Science and Engineering.* Vol 2014, 12.

[29]. Narayan, M. 2012. Review: Dye Sensitized Solar Cells Based on Natural Photosensitizers. *Renewable and Sustainable Energy Reviews.* Vol 16, 208–215.

[30]. Nazeeruddin, M, Baranoff, E, and Gratzel, M. 2011. Dye-sensitized solar cells: A Brief Overview. *Solar Energy*. Vol 85, 1172–1178.

[31]. Ola, O, Mercedes, M, and Valer, M. 2015. Review of Material Design and Reactor Engineering on TiO_2 Photocatalysis for CO_2 Reduction. *Journal of Photochemistry and Photobiology*. Vol 24, 16-42.

[32]. Robinson, T. 1995. *Kandungan Organik Tumbuhan Tinggi*. Bandung. ITB- Press.

[33]. Rosana, M, Joshua, A, Joseph, V, Suresh, S. Anandan, G, Saritha. 2014. Natural Sensitizers for Dye Sensitized Solar Cell Applications. *International Journal of Scientific & Engineering Research*. Vol 5, 340- 344.

[34]. Ryuzi, K, Annemarie H, Kohjiro, H, Tom, J and Laurens, D. 2007. Effect of the Particle Size on the Electron Injection Efficiency in Dye-Sensitized Nanocrystalline TiO 2 Films Studied by Time-Resolved Microwave Conductivity (TRMC) Measurements. *J. Phys. Chem*. Vol 111, 10741-10746.

[35]. Saito, Taro. 2008. *Inorganic Chemistry.* Tokyo. Iwanami Shoten Publishing Company.

[36]. Santoni, A, Darwis, D dan Syahri, S. 2013. *Isolasi Antosianin dari Buah Pucuk Merah (Syzygium campanulatum korth) Serta Pengujian Antioksidan dan Aplikasi Sebagai Pewarna Alami.* Makalah disajikan pada Semirata FMIPA Universitas Lampung.

[37]. Suhaimi, S, Shahimin, M, Mohammad, S and Norizan, N. 2013. Comparative Study of Natural Anthocyanins Compund as Photovoltaic Sensitizer. *Advances in Environmental Biology*. Vol 12, 3617-3620.

[38]. Vargas, M, Cortez, J, Duch, E, Lizama, A and Mendez, C. 2013. Extraction and Stability of Anthocyanins Present in the Skin of the Dragon Fruit (*Hylocereus undatus*). *Food and Nutrition Sciences*. Vol 4, 1221-1228.

[39]. Wahyuni, R. 2011. Pemanfaatan Kulit Buah Naga Super Merah *(Hylocereus costaricencis*) Sebagai Sumber Antioksidan dan Pewarna Alami pada Pembuatan Jelly. *Jurnal Teknologi Pangan*. Vol 1, 68-85.

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