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INFLUENCE OF CONCENTRATION OF RIND EXTRACT OF RED DRAGON FRUIT (HYLOCEREUS COSTARICENSIS) AGAINST THE DSSC EFFECIENCY

PENGARUH KONSENTRASI EKSTRAK KULIT BUAH NAGA MERAH (HYLOCEREUS COSTARICENSIS) TERHADAP EFISIENSI DSSC

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ABSTRAK

Penelitian mengenai pemanfaatan ekstrak kulit buah naga merah (hylocereus costaricensis) sebagai penyensitif pada dye sensitized solar cell (DSSC) telah dilakukan dengan meninjau pengaruh konsentrasi ekstrak terhadap efisiensi DSSC. Terhadap dye berupa ekstrak kulit H. Costaricencis dilakukan pengujian serapan optik pada berbagai konsentrasi dan identifikasi gugus fungsi, masing-masing menggunakan spektrometer UV-Vis dan fourier transform infra red (FTIR). Hasil pengujian dye pada konsentrasi 100 %, 50 %, 33,33 %, 25%, dan 20% menunjukan serapan optik yang terjadi pada panjang gelombang 320-760 nm, memiliki puncak yang cenderung semakin tinggi seiring dengan peningkatan konsentrasi. Dye yang berasal dari ekstrak kulit H. Costaricensis ini mampu berperan sebagai sunlight absorber. Sementara itu, spektrum serapan infra red yang diperoleh dari hasil FTIR mengindikasikan adanya gugus fungsi O-H, C=O, C=C, C-O, dan C-H aromatik. Hasil karakterisasi arus-tegangan dari DSSC menunjukkan adanya peningkatan nilai daya maksimum dan efisiensi seiring peningkatan konsentrasi.

ABSTRACT

Research on utilization of rind extracts of red dragon fruit (hylocereus costaricensis) as sensitizer for dye sensitized solar cell (DSSC) has been conducted by reviewing influence of the concentration against the DSSC efficiency. Characterization on optical absorption at various concentrations and identification of functional groups, each using an UV-Vis spectrometer and Fourier transform infra red (FTIR), have done to the dye in the form of the extracts. The dye characterization result on optical absorption at various concentration shows that the optical absorption at range of wavelength 320-760 nm has the peak of absorbance tend to increase with increasing the concentration. Therefore the dye is capable to role as a sunlight absorber. Meanwhile, infra red absorption spectrum obtained from FTIR results indicate the presence of functional groups O-H, C=O, C=C, C-O, and C-H aromatic. Results of current-voltage characterization of DSSC show an increase in maximum power and efficiency with increasing concentration.

Keywords: absorbance, DSSC efficiency, dye concentration, rind of red dragon fruit (H. Costaricensis).

INTRODUCTION

The conversion of solar energy into electrical energy can be done by using solar cells. Electronic semiconductor technology development is very rapid, among other produce solar cells based on silicon technology which is still widely used today. In the development of solar cell research, has now present solar cells using organic materials which include dye-sensitized solar cell (DSSC). DSSC is one

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of the potential candidates of future generation solar cell, this is because it is environmentally friendly, cheap to produced, dye available in large quantities, easy to extract and easily decompose in the environment but is not required process further purification (Zhou et al., 2011; Singh et al., 2013).

DSSC introduced by Prof. Grätzel (O'Regan, and Grätzel, 1991) which generally consists of three parts, i.e. a transparent photoanode (working electrode), an electrolyte solution, and a counter electrode. In contrast whit conventional solar cells in which all procces involves silicon material, light absorption and separation of electrical charge on DSSC occur in a separate process. Absorption of light is carried by the dye molecules and separation of charge by inorganic semiconductor nanocrystal that having a wide band gap. The conversion of sunlight into electrical energy in DSSC is very dependent on the dye as a photosensitizer (Alhamed et al., 2012).

One of the semiconductor has a wide band gap is Titanium dioxide (TiO_2). Usually, researchers using TiO2 because of a number of advantages including; stable used as electrodes in photoelectrochemical system that works in extreme conditions (high temperature), cheap, non-toxic, and has good optical characteristics thus supporting electron injection from the excited dye to the semiconductor (Narayan, 2012).

Dye used in DSSC can be sourced from synthetic organic materials of *ruthenium complex* type, and can also be derived from natural organic materials obtained from extraction result of the plant parts such as leaves, flowers, fruit or rind. Although it can generate good efficiency, *ruthenium complex* has its limitations such as the expensive production costs, complexity in the synthesis, is not environmentally friendly and prone to degradation when interacting with water (Yusoff et al., 2014). This led to the thrive research the use of natural organic matter as sensitizer on DSSC, because of low production cost in addition insulation process that much easier.

Natural organic matter used as sensitizer in DSSC must have the ability to absorb a wide spectrum of light and match the energy bands of inorganic semiconductors, in this case is TiO_2. In this study, be chosen rind of red dragon fruit (*hylocereus costaricensis* or written as *H. Costaricencis*) as a source of dye, which from its color is predicted to have appropriate optical absorption.

Utilization the rind of *H. costaricensis* as a source of dye in this study, in addition to its potential in optical absorption, also taking into environmental aspects, i.e. the usage of organic waste in an effort to reduce waste production. To obtain the dye, rind of *H. Costaricencis* be destroyed, and then extracted by maceration.

In this article is presented the results of research on the effect of the rind extract concentration of *H. Costaricencis* against the efficiency of DSSC. In the discussion described the optical absorption (absorbance) at various rind extract concentrations of *H. Costaricencis* in order to examine the consistency of the optical absorption of the dye extracted, including absorbance at TiO_2 before and after immersion in the dye. In addition, it is discussed the identification result on functional groups, as well as the tendency both of values of the maximum output power and the DSSC efficiency associated with the rind extract concentration of *H. Costaricencis* which is used, based on the characterization results of the current-voltage (I-V).

METHODS

Extraction rind of *H. Costaricencis* was done by maceration process. Rind have been separated from the meat, sliced up into small pieces, then crushed using a blender machine. Rind that has been smoothed weighed as much as 20 grams, then soaked in a solution (which is a mixture of 25 ml of distilled water, 24 ml of ethanol and 4 ml of acetic acid), stored in a container covered aluminum foil. After being stored for 24 hours in the dark condition, the extraction result is filtered using flannel.

Preparation of the working electrode is conducted by adding 1.18 grams of technical TiO_2 into 5 ml of ethanol. This mixture is stirred using a magnetic stirrer for 1 hour to form a paste. Afterwards, the pasta TiO_2 superimposed into glass coated-FTO (Fluorine doped Tin Oxide), before heated at temperature of 450 ^{0}C.

TiO_2 layers soaked in dye rind extract of *H. Costaricensis* for 24 hours. TiO_2 layers soaked in dye at concentrations vary, i.e. 100%, 50%, 33.33%, 25% and 20%. The dye with varying concentrations obtained through the process of dilution. This concentration value is the ratio of the volume of dye as result of rind extraction against the total volume in the same solvent that used in the process of maceration.

Pairing redox of iodide/triiodide is used as electrolyte. Synthesis of electrolytes is done by mixing 0.8 grams of KI 0.5 M (Potassium Iodide) with 10 ml of acetonitrile, then stirred until evenly, followed by the addition of 0.127 grams of I_2 (Iodine) into the mixture.

Counter electrode prepared from glass coated-FTO that given layer of graphite. Graphite layer is made by shading the glass coated-FTO using a pencil 6B.

Both electrodes are stacked with give an offset of about 0.5 cm, and clamped using a paperclip. Electrolyte solution which has been prepared dripped on the both ends of the electrodes on the offset.

Characterization of optical absorption of the dye at each concentration was performed using a UV-Vis spectrometer Hewlett Packard 8453 Agilent Technologies. Besides, characterization of TiO_2 layers that have been soaked for 24 hours in the rind extract of *H. Costaricencis* also be done. From this characterization was obtained pattern of absorbance in the wavelength range of 300 nm to 800 nm.

Identification of functional groups using Fourier Transform Infrared (FTIR) performed on rind extract of *H. Costaricencis*, and the TiO_2 layer before and after soaked in dye. Characterization carried out on the wave number range of 500 cm^{-1} to 4500 cm^{-1}. Analysis is performed by looking at the shape of the spectrum and the specific peaks that show the bonding of the functional groups contained in the extract.

Testing of DSSC conducted through the current-voltage characterization (*I-V*) at five different prototypes has been made by varying the concentration of dye. The equipment used is a multi meter for measure both of voltage and current, as well as external potentiometers are used as resistor (external load) during the current and voltage measurements. The solar cell be connected to the multi meter to the positive pole on the counter electrode, while the negative pole at the working electrode. Measurements were made using a source of sunlight. Light intensity during the test was measured using a light meter.

RESULTS AND DISCUSSION

The effectiveness of the dye to absorb sunlight spectrum is one of the things that greatly affect the efficiency of DSSC. Results of characterization absorbance (at the wavelength range of 300-800 nm) of the rind extract of *H. Costaricencis* at various concentrations can be seen in Figure 1.

Spectrum in Figure 1 shows that the dye from the rind extract of *H. Costaricensis* can absorb light, in the range between 320 nm to 760 nm (visible light) and high light absorption at a wavelength of 420-580 nm. Absorption peaks in these wavelength range indicates that there are anthocyanin content in the dye, which is usually identified in the wavelength range of 500-600 nm (Hao et al., 2006; Hemalata et al., 2012; Yusoff et al., 2014).

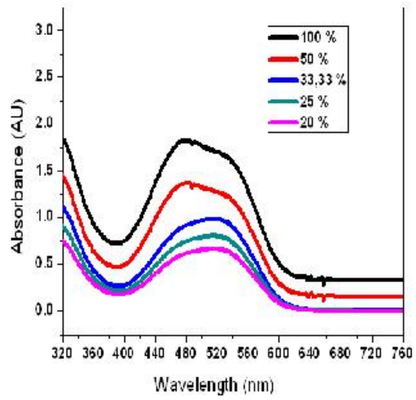

Figure 1. The pattern of the absorbance of the rind extract of red dragon fruit (*H. costaricensis*) to the wavelength at various concentrations.

Optical absorptions are consistently declines with a reduction in the concentration of dye. The lower the concentration, the smaller the pigment compound contained in the dye, and therefore the optical absorption peak is decreases. Thus the dye derived from the rind extract of *H. Costaricensis* is capable of acting as a sunlight absorber. This suggests chance or oppurtunity for using this dye as sensitizer in DSSC.

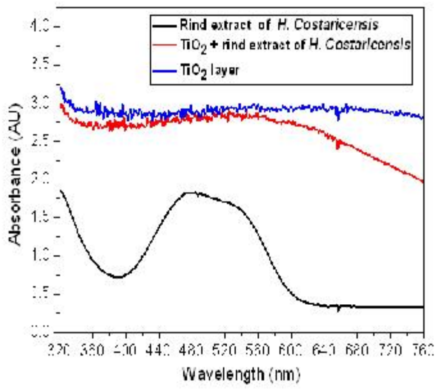

Figure 2. The both absorbance pattern of rind extract of *H. Costaricensis* and TiO_2 layer before and after immersion.

Figure 2 shows the absorbance pattern of the rind extract of *H. Costaricensis* and TiO_2 layer before and after immersion. On this picture it appears that in the wavelength range 320-760 nm occur optical absorption by the TiO_2. Absorbance of TiO_2 that has been soaked is similar in pattern with the absorbance of TiO_2 that has not been soaked. Dye effect is not so apparent in the absorbance pattern. This is because the compounds contained in the pigment dye very less than TiO_2.

After immersion, we can observe that there is a color change of the dye that absorbs in the TiO_2 layer. This color change can occur as a result of the formation of the bond between the chromophore of the dye anthocyanin with Ti (IV) of TiO_2. An ion OH^- from pasta of TiO_2 can bind to an ion H^+ from anthocyanin of dye to form one molecule of H_2O. Absorption of light on the surface of the TiO_2 form a quinoidal that causes the surface of TiO_2 looks to be purple and a little contains flavilium form (as a cause red) (Maddu et al., 2007).

The characterization results of infrared (IR) absorption spectra using FTIR is shown in Figure 3. Absorption peaks in the infrared spectrum shows absorption associated with functional groups contained in the dye. Based on Figure 3 we can identify the presence of anthocyanin content in the dye indicated by the absorbance at the wave number range of 3200-3500 cm^{-1}. Functional groups of -OH identified in wave numbers of 3421, 3381 and 3346 cm^{-1}. Infrared absorption spectra at wave numbers of 1629 and 1598 cm^{-1} corresponding to the functional groups of C=O. Functional groups of C=C identified by their absorption at wave number of 1408 cm^{-1}. Meanwhile, the absorption spectrum at wave numbers of 1101.35, 1078.21, 1049.28 cm^{-1} corresponds with the functional groups of C-O, and the absorption spectrum at wave numbers of 773.46, 705.95, 640.37 cm^{-1} corresponds to functional groups of CH aromatic.

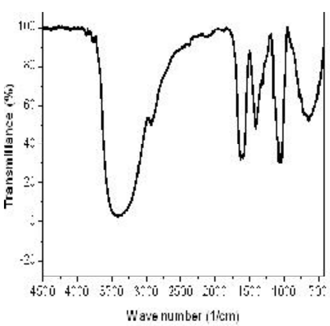

Figure 3. The transmittance pattern against wave number FTIR characterization results of the rind extract of *H. Costaricensis*.

Functional groups of -OH are a hydroxyl group making up the structure of anthocyanin. The hydroxyl group is useful as an adhesive between the layers of TiO_2 pigment compounds on the FTO (Wongcharee, K et.al., 2007)

Based on the infra red absorption spectrum of TiO2 that has been soaked in dye, the functional groups of -OH *stretching vibration* is identified from absorption peak at the wave number of 3348.72 cm-1, functional groups of -OH *bending vibration* at wave number of 1633.72 cm^{-1}, and functional groups of Ti=O at wave number of 687 cm^{-1}.

The performance of DSSC is affected by many factors. Once of the important factors that affect DSSC performance is the dye structure must possess several *carbonyl* (C=O) or *hydroxyl* (-OH) (Khalil, 2012). Thus, the rind extract of *H. Costaricensis* can be use as a good sensitizer in DSSC.

Table 1. Influence of dye concentration C against the maximum current I_m, and maximum voltage V_m.

C (%)	I_m (mA)	V_m (mV)
100	0,6	12,2
50	0,051	29,5
33,3	0,05	19,6
25	0,047	18,2
20	0,03	26,2

The influence of the dye concentration against the maximum current and voltage (I_m and V_m) generated by prototype of DSSC can be seen in Table 1. The maximum current is generated by DSSC tend to increase with increasing dye concentration. Thus the maximum power generated is also dependent on the concentration.

The influence of the dye concentration against the each values of short circuit current I_{sc} and open circuit voltage V_{oc} as well as efficiency of solar cells η can be seen in Table 2. Based on this table it can be seen that the open-circuit currents and the efficiency of solar cells is influenced by the dye concentration. Plot a graph of the dye concentration against the efficiency of the solar cell is shown in Figure 4.

The greater the concentration value, the higher the chances of the bond formation between both molecules of dye and TiO_2. The amount of the bond that is formed affects the efficiency of solar cells (Al-Alwani et al., 2014). Thus, there is influence of the dye concentration on the efficiency of DSSC.

Table 2. Influence of dye concentration *C* against short circuit current I_{sc}, open circuit voltage V_{oc}, and efficiency η of DSSC.

C (%)	I_{sc} (mA)	V_{oc} (mV)	η (%)
100	1,1	22,6	$1{,}03 \times 10^{-3}$
50	0,09	50,5	$2{,}75 \times 10^{-4}$
33,3	0,08	31,8	$1{,}28 \times 10^{-4}$
25	0,08	37,2	$9{,}78 \times 10^{-5}$
20	0,06	47,9	$7{,}5 \times 10^{-5}$

Energy of incident photon (sunlight) absorbed by the dye molecules resulting in excitation of the electrons. If the excitation energy level of electron is higher than the conduction band of TiO_2, there will be an injection of electrons to the conduction band accompanied the formation of positive ions of dye molecules. This injection process is influenced by amount of bonds between molecules of dye and TiO_2, so it will affect the performance of solar cells.

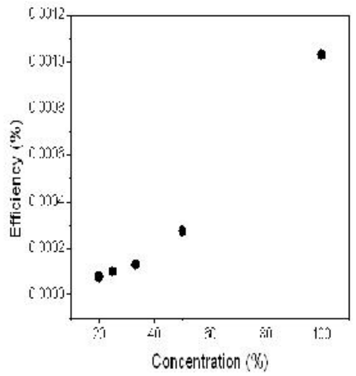

Figure 4. Concentration of the rind extract of *H. Costaricensis* against the DSSC efficiency.

The dye molecules that ionized into positive ions will capture electrons from iodide derived from the electrolyte, so that electrons that injected in the conduction band of TiO_2 will not undergo recombination. This recombination process must be prevented so the DSSC efficiency does not decrease. Injected electron in the conduction band of TiO_2 will be reach to FTO. These electrons will reach to the counter electrode through the external circuit. Graphite that superimposed on the counter electrode, acts as a catalyst to facilitate these electrons to react with tri-iodide of electrolyte to form iodide. This iodide would be a deterrent for recombination of subsequent injected electron, so cycle of electron transport can take place.

The results show the consistency of optical absorption of the dye, the maximum power and efficiency of DSSC. This is indicated by dependences of the efficiency on the dye concentration as shown in Figure 4. The emergence of currents in the circuit shows that electron injection from the dye skin extract of *H. Costaricensis* to the conduction band of TiO_2 is presence. Thus, the rind extract of *H. Ccostaricensis*, in principle, can be used as a sensitizer for DSSC.

Injection of electrons excited into the conduction band of TiO_2 can occur if energy conduction band of TiO_2 is slightly lower than the energy level of lowest unoccupied molecular orbital (LUMO) of the dye material. In order to support the regeneration of the oxidized dye, the energy level of highest occupied molecular orbital (HOMO) of the dye material should be lower than the redox potential energy of iodide/ triiodide.

The DSSC efficiency not only influenced by the dye material, but also influenced by inorganic semiconductor material on the work electrode, electrolyte, and catalyst at the counter electrode. Technically, the factors that can affect the performance DSSC is the design and drafting process, such as how to superimposing TiO_2, merging the two electrodes form a sandwich, electrolyte injection process, as well as problems of electrolyte leakage and permeation after injected.

The efficiency of DSSC with dye from the rind extract of *H. Costaricensis* can be improved among others by taking into account the size of the particles and the thickness of the layer of TiO_2, the immersion time in the dye, usage a liquid electrolyte, and material selection of the catalyst. The particle size and immersion time are related to the absorption of the dye. Layer thickness affects to the internal resistance (and the mobility of the charge passing through the cell). Electrolyte and catalyst effect on electron transport cycle. Thus, the research on the utilization rind extracts of *H. Costaricensis* to be exciting and challenging research to be continued, especially in increasing the performance.

CONCLUSION

Rind extract of red dragon fruit (H. costaricensis) absorbs sunlight spectrum in the range of visible light, with a high absorption in the range 420-580 nm. Consistently, the higher the rind extract concentration, the higher the absorbance. Concentration of dye used in DSSC affect the maximum current (maximum power) is generated and the effeciency of solar cells. In principle, the rind extract of red dragon fruit allow to be used as a sensitizer for DSSC. Thus, there are opportunities to do further research in an effort to improve the efficiency of DSSC that uses dye from the rind extract of red dragon fruit.

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