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Krokot Extract (*Portulaca Oleracea*. L) As Natural Light-harvesting pigments for Dye-Sensitized Solar Cells (DSSCs): Influence of Dye Acidity

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Abstract

Dye-sensitized solar cells (DSSCs) was fabricated using natural dyes extracted from krokot (Portulaca Oleracea. L). The effect of dye acidity was investigated on natural pH extract, 5.00, 4.00 and 3.00 of pH. The efficiency and stability DSSCs as a function of the dye acidity was studied. The result of the UV-Vis shows that the absorption of wave-length from dye extract of krokot is located in the visible region with the absorbance peak in 410.5 nm and 664.5 nm which are the peak of chlorophyll. The efficiency of extract krokot dye sensitized solar cells was decreasing 6.88 x 10-3 % to 0.42 x 10-3 % when pH of the dye was adjusted from 6.27 to 3.00. DSSCs stability was also decreased look for efficiency loss from 5.27% to 97.49% in the same conditions.

Keywords: Dye Sensitized Solar Cell (DSSCs), chlorophyll, efficiency

Introduction

Portulaca oleracea L. is a warm-climate, herbaceous succulent annual plant with a cosmopolitan distribution belonging to the Portulacaceae family (Xi Zhou et al., 2015). Many constituents of Portulaca oleracea have been isolated, including alkaloids, beta-carotene, beta-sitosterol, caffeic acid, catechol, chlorophyll, coumarins, DHA, EPA, ferulic acid, flavanoids, saponins and tannin (Esiyok et al., 2004), (Palaniswamy et al., 2001), (Mohamed and Hussein, 1994).

The green pigmented chlorophyll has the desirable photovoltaic properties that are utilized in today's organic photosynthetic solar cells.

Figure 1. The *Portulaca oleracea* L plants.

Chlorophyll is a light harvesting pigment that absorbs light in the visible spectrum of solar radiation which promotes electron transfer. Carotenoids are also an important part of the photosynthetic process. They aid in energy transfer to the chlorophyll molecule,and serve to supplement the light gathering properties of chlorophyll (Diarra et al., 1986). Appropriate plant species for use in photosynthetic solar cell applications are those with high concentrations of chlorophyll alpha and chlorophyll beta. Krokot or Purslane (*Portulaca oleracea*) have been found to contain high concentrations of chlorophyll alpha and beta (Griffin et al., 2004).

The idea of using the reactions of photosynthesis to convert light into electrical power appeared already Melvin Calvin before 1974 (Hug et al., 2013). Sun light excited the electrons of pigment into higher energy level then transfered to the conduction band of the wide band gap semiconductor. The model based on a synthetic membrane where carotenoids were used as a wire inside the membrane. After absorption of a light by a sensitizer molecule at one side of the membrane, the electron is transfered to a carotenoid and then diffuse through the membrane the the other side where it is captured by ellectron acceptor. Dye-sensitized solar cells (DSSCs) are belonging to the third generation photovoltaics concept where used natural dyes as light harvesting pigment (Kalyanasundaram and Graetzel, 2010; Hagfeldt et al., 2010). They are also called Graetzel cells (O'regan and Graetzel, 1991)

The advantages of natural dyes as photosensitizer are large adsorption coefficients, high light-harvesting efficiency, no resource limitations, low cost, easy prepared and no harm to the environment (Luo et al., 2009). Chlorophyll is the principal pigments in natural photosynthetic system. It is a green pigment found in the leaves of most green plant, algae and cyanobacteria. Six different types of chlorophyll pigment exist and the most occuring types is chlorophyll α. The molecular structure include a chlorine ring with Mg center, along with different side chains and a hydrocarbon trail depending on the chlorophyll type (Ludin et al., 2014). Their function include harvesting sunlight, converting solar energy to chemical enery and tranferring electrons. Chlorohyll and their derivatives are inserted into DSSCs as dye sensitizer because of their beneficial light absorption tendency modes. Chlorophyll has an absorption maximum at 670 nm because of an attractive compound that acts as an photosensitizer the visible light range (Wang *et al.* 2010)

A DSSC consists of a pair of coated glass TCO substrate (Transparent Conducting Oxide) as the electrode and the counter electrode, the redox electrolyte that contains iodide and triiodide ion (I - /I_3^-) carbon layer as the catalyst, porous TiO2 nanocrystal as fotoanoda, and a dye photosensitizer. All components are arranged in front of the sandwich structure where the top layer is the working electrode as the initial layer in receiving photons and the lower layer is the counter electrode and the middle is electrolyte to regenerate electron. Dye criteria that can be used as a dye sensitizer is adsorption intensity at visible wavelengths, strong adsorption on the surface of the semiconductor, has the ability to inject electrons to the band conduction of the semiconductor, and has a group = O or -H to bind to the surface of TiO2 which can increase the reaction rate of the electron transfer.

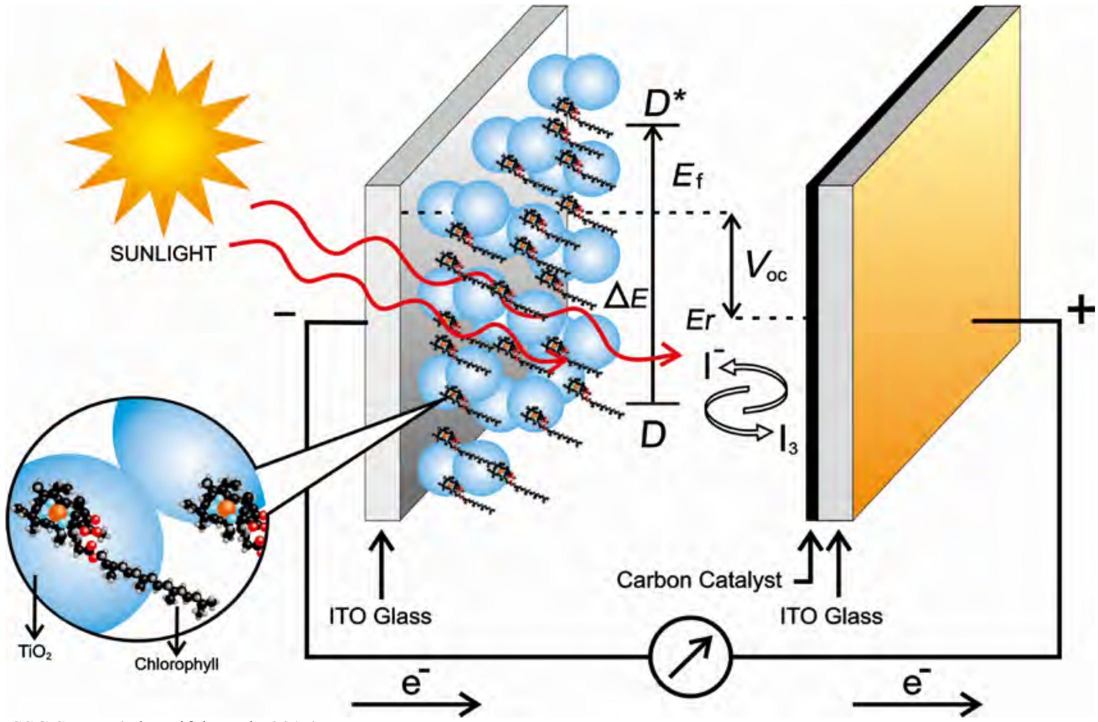

Figure 2. DSSC Sceme (Khuzaifah et al., 2015).

Therefore, this study will utilize the potential of the natural dye that derived from extracts of krokot which are expected to fulfill the requirement as a natural sensitizer. Optical and electrical test are done in order to determine the compliance of the requirement and can be used in DSSC system. To further understand the effect of dye acidity was used to investigate the electron transport characteristics of the fabricated cells. This study shows the correlation between efficiency and stability as a function of the dye acidity.

Experiment

Chemicals and instrumentation

Chemicals used for research are krokot, Indium Transparent Oxide (ITO), TiO2 (degusa), KI, I2, polyethylene glycol, ethanol 96%, Polyvinyl alcohol (PVA), aquades, graphite pencil 8B and detergent. Instrumentation applied for research are Sonikator, ultrasonic cleaner, hotplate, glassware, aluminium foil, paper clips, scothlite, screen proyektor (gasket) and cutter. spektrofotometer UV-Vis single beam, UV-Vis spekular reflektansi UV 1700 Pharmaspec, Fourier Transformation Infra-Red (FT-IR) Shimadzu and I-V meter Keithley 2400 Source Meter.

Preparation of dye-sensitizer

Ten grams of krokot powder are macerated with 120 mL of 96% ethanol for 24 hours. Then, it is filtered by using vacuum filtration and before it is used for further processing, it should be analyzed first using UV-Vis spectrophotometer in the wavelength range 400-700 nm. The effect of pH of dye solution was studied by adjusting pH from the original pH of 6.27 using 0.1 M HCl solution to three different pHs (3.0, 4.0 and 5.0).

Preparation of electrodes

TiO2 powder was weighed as much as 1.5 grams and then inserted into erlenmeyer and added with 3 mL of aquades. Then, it is stirred with a magnetite stirring spoon and sonicated with 20 kHz frequency for 2 hours. The next solution was then added with polyvinyl alcohol solution which previously has been made from 0.5 grams PVA added with 6 mL of aquades by heating at a temperature of 150oC until all of PVA are dissolved. The mixing is followed by stirring for 10 minutes until it is formed a homogeneous paste.. Then, it is performed TiO2 paste deposition on surfaces glass of Transparent Indium Oxide (ITO) with Doctor Blanding technique. But before it, ITO should be washed with detergent and followed by aquades using ultrasonic cleaner for 10 minutes and rinsed with ethanol. Before TiO2 paste is dropped on ITO glass, the conductive part should be found and then each of it is given a scotchlite restraint and it is made a rectangular pattern by leaving a 1.8 x 1.3 cm room. Furthermore, in above of that fields, the TiO2 paste is distributed evenly with a glass rod and then dried in the air and the scotchlite is opened, then it is heated at 80 ° C for 1 hour.

TiO2 film is inserted into the krokot extract, the container is covered with aluminum foil and then it is saved for an hour. The film which has been soaked then removed and rinsed with ethanol to clean the edge of the layer. Then,it is dried at room temperature and analyzed by UV-Vis reflectance spectrometer and FT-IR. The graphite of a 8B pencil is spread into the surface of ITO on the conductive layer with the shading manner to average carbon layer. Then, it is heated at temperature of 300oC for 1 Hour.

Preparation of electrolytes

Potassium iodide (KI) is weighed as much as 0.815 grams and then dissolved in 10 mL of polyethylene glycol (PEG) 400 and stirred until dissolved then added with 0.128 grams of I2 and stirred again until completely mixed. The finished Electrolyte solution then stored in the dark bottles and also sealed.

Assembly of Dye-Sensitized Solar Cells (DSSCs)

DSSC fabrication which is used is a sandwich construction with a composition such as: glass-ITO working electrode (TiO2 layer) that has been coated with dye-screen projector-counter electrode (carbon layer) – ITO glass. The use of screen proyector is intended to prevent the short on DSSC system. At the ends of the glass that does not stick together is spilled with the electrolyte solution and allowed to seep between the two layers after it is clamped with paperclip (binder clips) on two opposite sides are not coated.

Measurements

DSSC prototype was tested by measuring the I-V characteristic curve using a digital multimeter Keithley 2400, in the light of a xenon lamp at an intensity of 1000 W / m2.The result of the I-V characteristic curves test were then analyzed Voc, Isc, fill factor, and the efficiency of solar cells [6] by the equation:

$$F = \frac{V_m \cdot I_m}{V_o \cdot I_s} \quad (1)$$

$$\eta = \frac{V_o\,(V).I_s\,(A).F}{F_i \cdot \left(\frac{W}{c^{2}}\right).A(c^{2})} \quad (2)$$

Result and Discussion

The effect of dye pH on the absorption spectra

The result of characterization of Krokot extract color absorption spectrum in Figure. 3 shows the Krokot extract absorbs the blue spectrum (400-450 nm) and red (650-700 nm) with peak absorbance is absorbed at λ = 410.5 with a absorbance value of 0.91 Abs, λ = 536.5 with a absorbance value of 0.567 Abs, λ = 608 with a absorbance value of 0.473 Abs and λ = 664.5 with absorbance values of 0.30 Abs so that from the great absorbance at a wavelength of 410.5 nm and 664.5 nm can be known that the more dominant krokot extract contains the pigment chlorophyll.

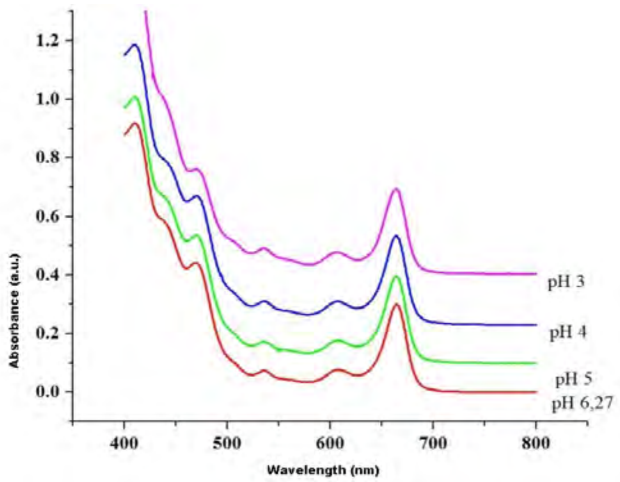

Figure 3. Absorbance of krokot extract.

The effect of pH was also investigated in absorbance of krokot extract as a dye sensitizer. As shown in Table 1, the pH extract solution has not a significant effect on the absorbance. The absorbance was found the chlorophyll pigment in different pH extract solution of krokot dye. The variation of pH extract did not effect the absorption peak, two maximum peak were detected in 410.5 nm and 664.5 nm.

Table 1. Absorbance of dye sensitizer.

pH	λ maximum (nm)	Absorbance (a.u.)
6.27	664.50	0.30
	410.50	0.91
5.00	664.00	0.29
	410.50	0.90
4.00	664.00	0.30
	410.50	0.95
3.00	663.50	0.29
	412.00	1.02

Figure. 4 showed the absorbance graphic of plot toward different pH of krokot extract as TiO2-dye system. The absorbance indicated that TiO2-dye system of extract krokot dye had a wide electronic absorbance in visible light region. Extract absorbance was shifted into higher wave length or red shift that indicated dye was absorb into TiO2 surfaces than the TiO2-dye had lower exited state energy. The red shift showed an electron injection from dyes into semiconductor surfaces.

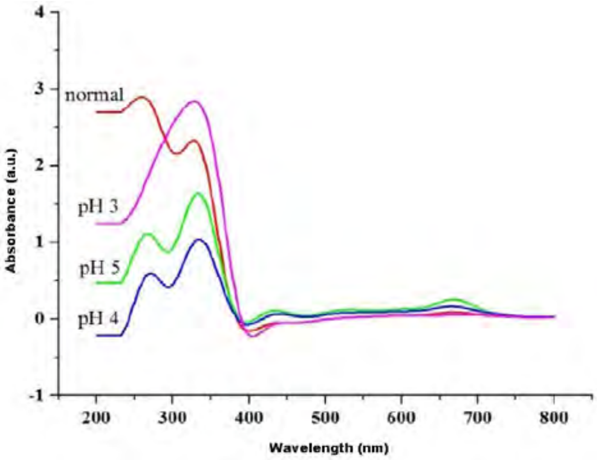

Figure 4. The graph of absorbance to wavelength of thin layer TiO2 – dye in different pH extract dye.

Table 2. Absorbance shift of extract dye.

pH	λ dye	λ TiO_2-dye	shift
6.27	664.50	670.00	5.50
5.00	664.00	669.00	5.00
4.00	664.00	666.00	2.00
3.00	663.50	684.00	20.50

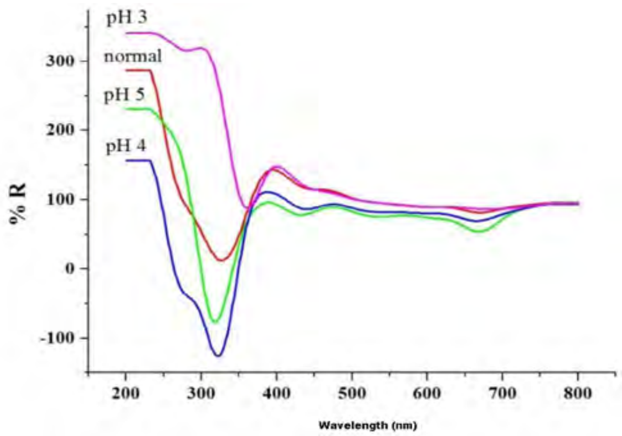

Figure 5. The graph of reflectance to wavelength of thin layer TiO2 – dye in different pH extract dye

Absorbance is used to calculate the band gap energy (Eg) in the TiO2-dye film by tauc plot method. Figure 6 showed that dyes acidity increased from 3.28, 3.61, 3.42 and 3.38 eV when the pH of the dyes was adjusted from 6.24, 5.00, 4.00 and 3.00. The band gap was influence the semiconductor performance when apllied into dye sensitized solar cells (DSSCs) system. The wide band gap (more than 3.00 eV) absorb high foton energy from sunlight.

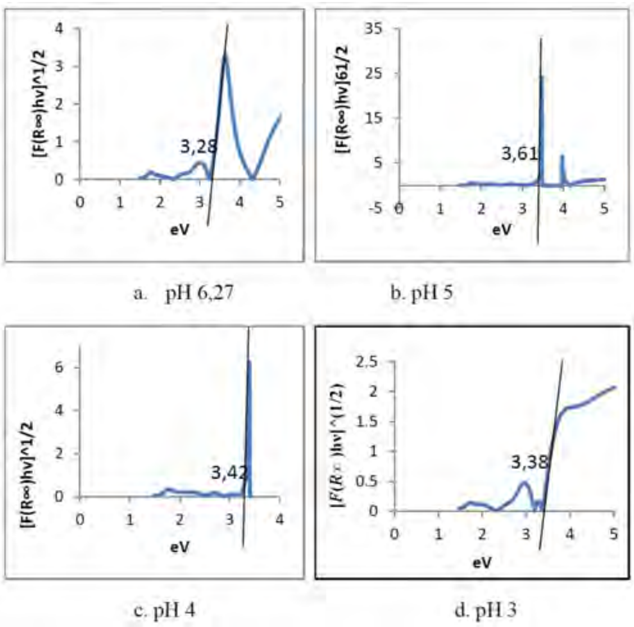

Figure 6. *Energy gap* thin layer TiO2-dye.

The effect of dye pH on the FTIR spectrum

Infrared absorption spectrum of a material has a distinctive pattern so that it possible to identify the material and also shows the existence of the major functional groups in the identified structure. The bond can be estimated if the IR spectra of TiO2-dye system shows the appearance of a significant new peak or functional groups shift if it is compared with the spectra of dye and spectra of TiO2 film. Krokot extract used in this study contains carboxyl and carbonyl because in the analysis that uses UV-Vis is identified to contain chlorophyll so it is possible there is efficient sensitization through the formation of a bond between the dye and TiO2.

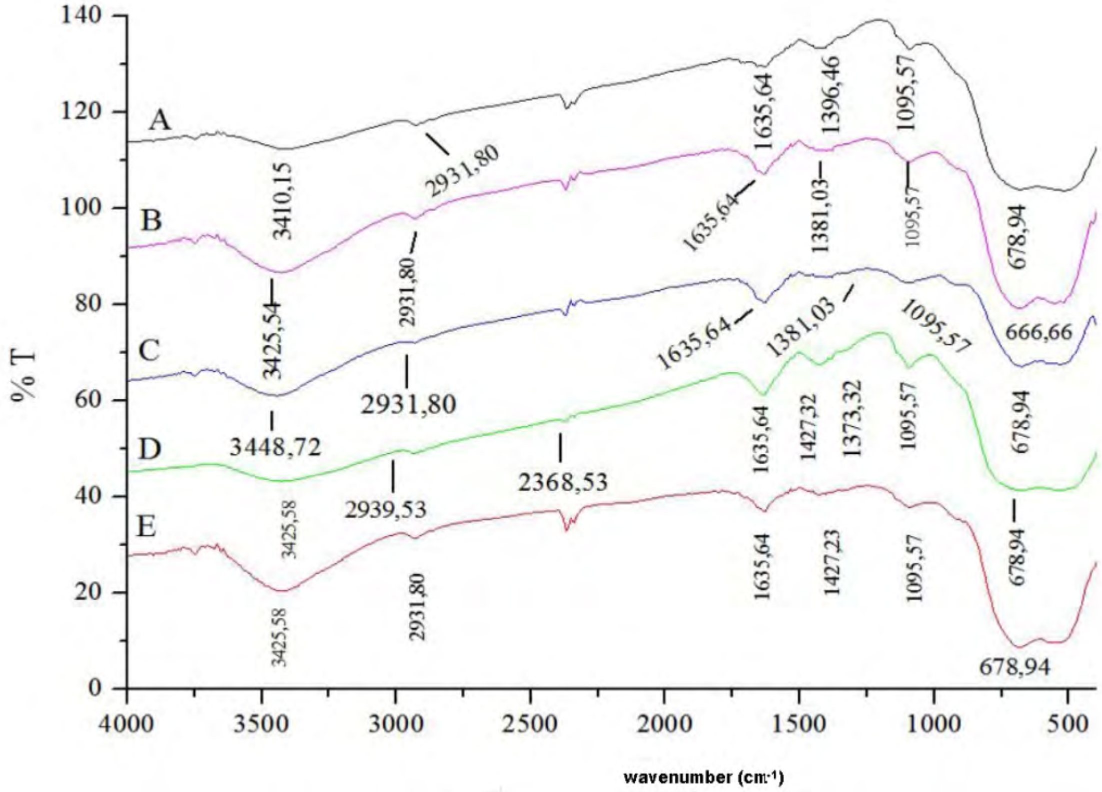

Figure 7. Infrared spectra (A) Thin layer TiO2, (B) Thin layer TiO2-*dye* pH 6.27 (C) Thin layer TiO2-*dye* pH 5.00 (D) Thin layer TiO2-*dye* pH 4.00 and (E) Thin layer TiO2-dye pH 3.00.

The results of FTIR analysis for TiO2 film, and TiO2-dye film of Krokot extract is shown in the Figure. 4 which shows the existence of the carbonyl absorption at wave number 1635.64 cm-1 and there is absorption at 3410.15 cm-1 region which is the absorption area of hydroxyl groups. Carbonyl and hydroxyl group that is owned by krokot extract that can bind to the group of Ti (IV) on TiO2 (Kuzaifah et al 2015).

Table 3. Infrared spectra Thin layer TiO2-*dye*.

Wavenumber (cm^{-1})					groups
TiO_2	TiO_2-dye				
	pH 6.27	pH 5.00	pH 4.00	pH 3.00	
3425.58	3425.58	3448.72	3425.50	3410.00	-OH
2931.80	2931.80	2939.53	2931.80	2932.00	C-H
1635.64	1635.64	1635.64	1635.60	1636.00	C=O
1427.23	1427.57	1381.03	1381.00	1396.00	C-C
1095.57	1095.57	1095.57	1095.60	1096.00	C-O
678.94	678.94	678.94	666.66	678.90	Ti-O

From FTIR analysis is not seen the significant difference from treatment with variation of extract solution acidity. It is only seen the carbonyl absorption shift of in TiO2 film is at a wavelength of 1635.64 cm-1 for natural pH shifted to a wave number 1636.00 cm-1 for 3.00 pH of extract krokot dye. This shows that Krokot extract does not bind yet optimally with a film of TiO2 or the interaction possibility that occurs only physical interaction.

The effect of dye pH on the DSSCs efficiency

A DSSCs efficiency can be characterized with an IV-diagram where the corresponding current (I) at rising voltage (V) is plotted. At a bias of 0 V the short circuit current (I_{SC}) is measured and when the current 0 V the open circuit voltage (V_{OC}) is defined. The maximum power output (P_{MAX}) generated by DSSCs is reached when the product of the current and the voltage is maximal. How efficient a solar cell can convert the power of the incident light into electricity described by electricity conversion efficiency (η) (Hug et al., 2013). An IV-diagram of DSSCs with different dye solution pH was showed in figure 8.

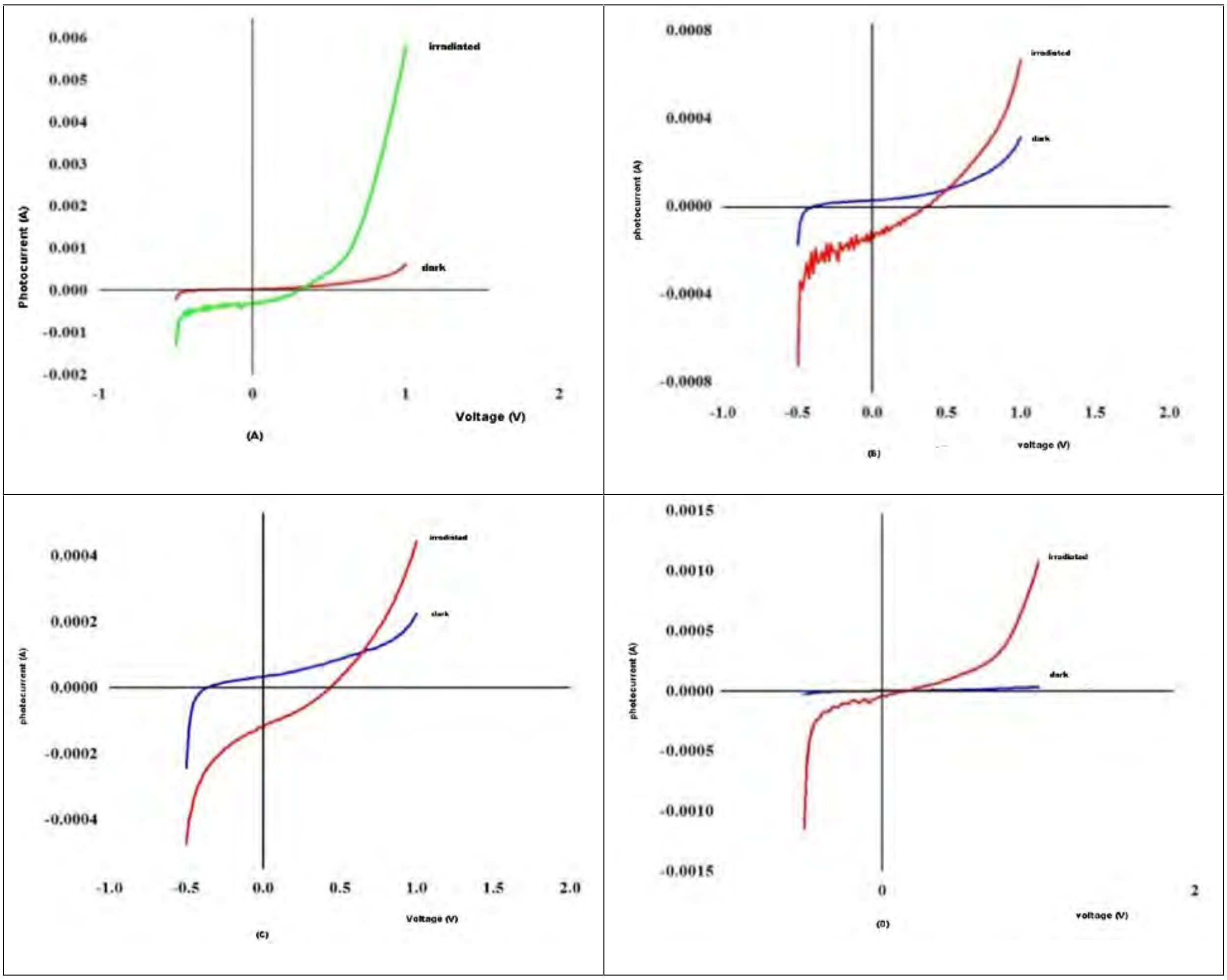

Figure 8. Current-voltage curve for krokot extract dye sensitized solar cell in pH 6.27 (A), 5.00 (B), 4.00 (C) and 3.00 (D).

Table 4 present the performance of DSSCs in the term of short-circuit photocurrent (I_{SC}) , open circuit voltage (V_{OC}), fill factor (FF) and energy convertion efficency (η) (Wongcharee et al 2007). The efficiency was found to decrease with decreased pH and had maximum at the natural solution pH. The photoanode made from the krokot extract can absorb more light from chlorophyll pigment. As another pigment, chlorophyll was easy to degradation with heat, light, oxidator and pH (Gross et al., 1991). *Pheophytin,* a *degradation* product of *chlorophyll*, which represents *chlorophyll* that has lost the central Mg ion replace with H+ in acidic solution that was colorless breakdown products.

Table 4. Photoelectrochemical parameter of the cells sensitized by krokot extract dye.

pH	I_{sc} (m.A.cm^{-2}) . 10^{-5}	V_{oc} (mV)	FF	η (%) . 10^{-3}
6.27	31.00	0.28	0.32	6.88
5.00	12.50	0.36	0.33	3.62
4.00	11.50	0.44	0.33	4.08
3.00	35.00	0.14	0.34	0.42

In this study, the little DSSC efficiency which is produced can be caused by the performance of the natural dye used is still low due to the effect of the extract used still contains a lot of pigment with the long structure R which lead steric hindrance of the pigment to the surface band structure so as to prevent oxidation of TiO2 molecules bind with TiO2 in effective to cause the transfer of electrons from the conduction band to the dye molecule is reduced (Khuzaifah et al., 2015).

The effect of dye pH on the DSSCs stability

Dye sensitized solar cells with krokot extract stability was also decrease by adjusting the pH of the extract from 6.27 to 3.00. As can be seen from figure 10 efficiency loss of dye sensitized solar cells increased with decreasing pH from 5.27% to 97.49% after irradiated for 2 hours.

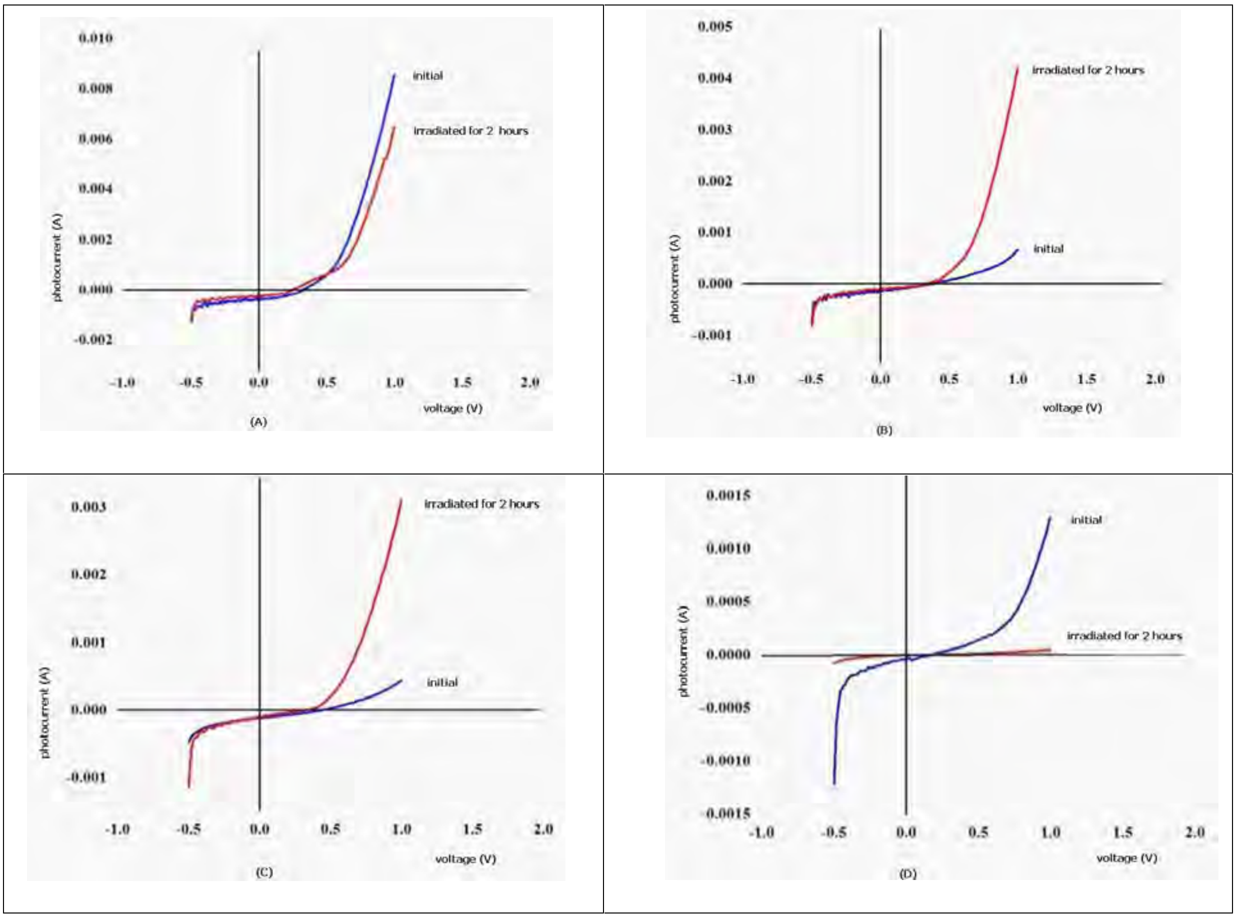

Figure 9. Current-voltage curve for krokot extract dye sensitized solar cell in pH 6.27 (A), 5.00 (B), 4.00 (C) and 3.00 (D) after irradiated.

Table 5. Photoelectrochemical parameter of the cells sensitized by krokot extract dye after irradiated.

pH	I_{sc} (m.A.cm^{-2}) . 10^{-5}	V_{oc} (mV)	FF	η (%) . 10^{-3}
6.27	28.00	0.26	0.37	6.52
5.00	8.90	0.31	0.45	3.02
4.00	11.00	0.31	0.29	2.41
3.00	0.09	0.06	0.70	0.01

A reason for the worse stability is that, at natural krokot extract acidity the chlorophyll was existed. The pigment are labile and can transformed into the colorless coumpound with decreasing pH. Chlorophyll that has lost the central Mg ion replace with H+ in acidic solution was degradation into *Pheophytin.*

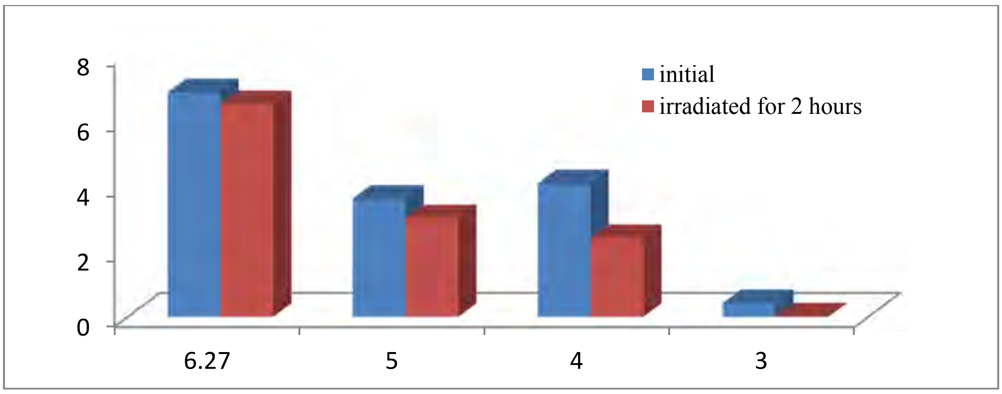

Figure 10. Stability cells sensitized krokot extract.

Conclusion

The results shows that the absorbance spectrum of the krokot extract dye is stretched in the range of visible light to the maximum absorbance peak at a wavelength of 410.5 nm and 664.5 nm so that can be known that krokot extract dye contains chlorophyll. The efficiency of extract krokot dye sensitized solar cells was decreasing 6.88 x 10-3 % to 0.42 x 10-3 % when pH of the dye was adjusted from 6.27 to 3.00. DSSCs stability was also decreased look for efficiency loss from 5.27% to 97.49% in the same conditions.

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