FT-IR AND UV-VIS SPECTROSCOPY PHOTOCHEMICAL ANALYSIS OF DRAGON FRUIT

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ABSTRACT

Dragon fruit or *Hylocereus polyrhizus* was extracted using ethanol and distilled water (DI) for the purpose as sensitizer for Dye sensitized solar cell (DSSC). Ultrasonic extraction method was employed to extract these dyes at temperature, time and frequency settings of 30 ºC, 30 minutes and 37 Hz, respectively. Different extracting solvent from ethanol and distilled water were used to observe the absorption spectra by using UV-Vis absorption spectroscopy. Fourier transforms infrared (FT-IR) were used to characterize the dye's active components. Result of FT-IR shows that dye extracted from dragon fruit contained C=O stretching vibrations at the peak of 1667 cm^{-1} and at the peak at 3407 cm^{-1}, represents the O-H stretching vibration. From the FT-IR result, the CO=OH which corresponds to the carboxylic group in Betalain's pigment for Dragon fruit's dye is observed. From UV-Vis absorbance, dragon fruit under distilled water treatment has the highest absorbance rate comparing to ethanol with the peak of 510 nm and bandgap of 2.26 eV while the absorption coefficient is at 2.12 k m^{-1}. From the result obtained, it is found that dragon fruit which was treated with DI has the potential as natural sensitizer in developing a high efficiency of DSSC.

Keywords: dragon fruit, solvent, stretching vibration, distilled water, ethanol.

INTRODUCTION

Brian O'Regan and Micheal Gratzel are the inventers of Dye-Sensitized Solar Cell (DSSC) in 1991 that is novel compare to their counterpart which has an advantage such as clean to environment, non-tedious fabrication method and promises a low cost in manufacturing (Chang *et al.* 2010 and Polo *et al.* 2006). DSSC converts visible light into electricity based on sensitization of wide band gap semiconductors (Wongcharee *et al.*2007). Basic structures of a DSSC consist of a pair of conductive transparent glass substrate, oxide semiconductor as photo anode, dye sensitizer, electrolyte and counter electrode material which is usually platinum (Pt) or carbon (C). In DSSC, the dyes works as a sensitizer that is responsible in absorbing sunlight and triggering electrical conversion mechanism. Commercial DSSC uses dyes from Ruthenium (II) polypyridinic complexes such as those from N719 and N3dyes which are available in companies such as Sigma Aldrich, Soloronix, Dyesol. Rutheniumcontains heavy metal complex which is hard to synthesize and not to mention the cost. Due to this, nature based dyes extracted from fruits, plants and flower were introduced. It is stated that most natural dye contained pigments such as betalains, chlorophyll and anthocyanins which can help the energy conversion in DSSC. Natural dyes from fruits and flowers contains colored pigments which are usually anthocyanin pigments.

In this paper the dragon fruit extract was proposed as dye sensitizer. The dragon fruit shown in Figure-1 grows on a veining epiphytic cactus (Hylocereus sp.) in the tropical forest regions of Mexico and South America (Merten, 2003).Dragon fruit is also known to have betalain pigment and has an active carboxyl group.

Figure-1. Dragon fruit.

This paper studies the potential in dragon fruit as dye-sensitizer from the optical point of view. Dragon fruit was extracted by using different extraction solvents which are from distilled water (DI) and ethanol to investigate the effect of solvents in the performance of DSSC. The fruit extract was characterized by UV-Vis spectrophotometer to observe on the absorption spectra and determine the band gap of the dye. FT-IR spectral analysis was used to determine the functional group in the nature dye.

Structure of DSSC

The typical configuration of DSSC is shown in Figure-2. Dyes should fulfill certain requirement such as having an intense absorption in the visible light spectrum and also possess the =O (conjugated oxide) or OH (hydroxyl) stretching vibrations that helps in bonding with the Ti(IV) sites (Narayan, 2012).

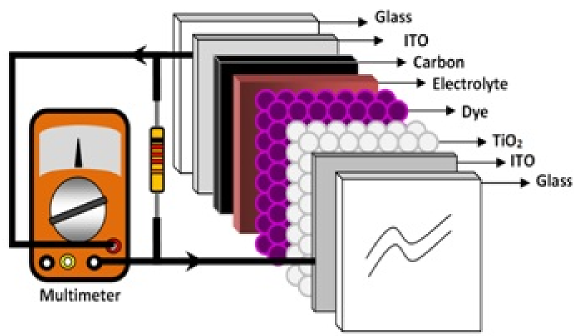

Figure-2. Cross section of DSSC.

Natural dye

The existence of betalains pigments in dragon fruit together with the present of –COOH functional group ligands with TiO_2 surface. The betalains pigment shown in Figure-3 includes the red-purple betacyanins, betanin (I) and betanidin (II), which present the maximum absorptivity λ_{max} about 535 nm, and the yellow betaxanthins with λ_{max} near 480 nm (Zhang *et al.* 2008).

Betalains has favorable light absorbing and antioxidant properties which are capable of complexing metal ions and exist in nature in association with various co-pigments which modify their light absorption properties.

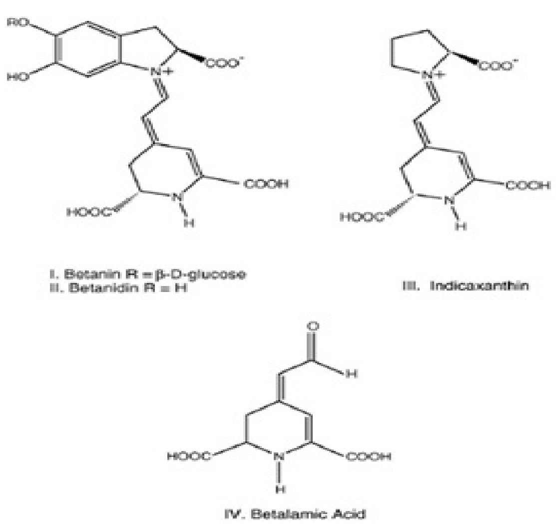

Figure-3. Betalain pigments (Zhang *et al.* 2008).

Reviews on Natural Dye

Based on Oviri *et al.* the transmittance and band gap energy level of the dye can be characterized by using the calculation (Oviri and Ekpunobi, 2013).B. K. S. Perera et al. testified that by using natural pigment extracted from Nilkatarolu Flowers yields a conversion efficiency of 0.06% (Perera *et al.* 2011). M. I. Kimpa et al. discovered in their experiment that by using Pawpaw Leaf and Flame Tree Flower as sensitizer, the conversion efficiency obtained is 0.20% for both natural dyes (Kimpa *et al.* 2012). Hee-Je Kim et al uses Curcumin Dye as natural sensitizer in which the conversion efficiency is achieved to 0.36% (Kim *et al.* 2013). G.R.A Kumara et al. found by using Shisho leaf pigments, an energy conversion efficiency of 1.3% was obtained (Kumara *et al.* 2006). M. S. Roy et al. reported that the Rose Bengal dye results in a conversion efficiency of 2.09 (Roy *et al.* 2008). H. Chang et al. discovered that by using pomegranate leaves and mulberry fruit as natural dyes, the conversion efficiencies are 0.597% and 0.548% (Chang *et al.* 2010). K. V. Hemalatha et al. reported carotenoid and anthocyanin were extracted from Kerria japonica and Rosa chinensis which showed the conversion efficiency are about 0.22% and 0.29% (Hemalatha *et al.* 2012).

MATERIALS AND METHOD

Preparation of natural dye sensitizers

10 g of dragon fruit is mixed into 15 ml pair which consist of distilled water (DI) and ethanolat room temperature as the extract solvent. Dragon fruit is mashed using a mortar into a liquefied paste. The mashed samples are placed into the ultrasonic cleaner as shown in Figure-4 for 15 minutes with frequency of 37 Hz by using 'degas' mode at the temperature of 30 ^{O}C to further extract the colored pigment. Next, the solvents is centrifuged for 25 minutes at 2500 rpm to obtain a homogenous dye solution with the debris collected at the bottom of the tube. The detail procedures are as shown in Figure-5 and Figure-6 and the final dye product are shown in Figure-7 which consist of (a) dragon fruit extract by Di-water solvent(D-Di) and (b) ethanol solvent (D-Etha).

Figure-4. Ultrasonic Cleaner.

Figure-5. Preparation of natural dye sensitizer.

Figure-6. Preparation of natural dye sensitizer.

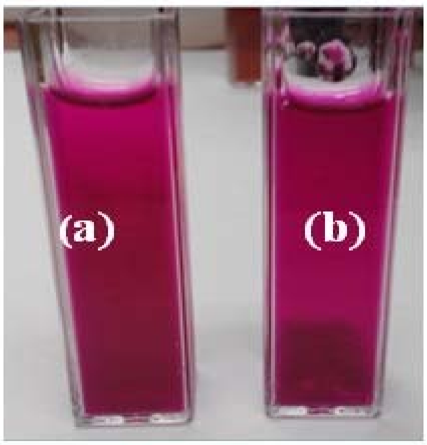

Figure-7. Liquid Dye from (a) D-DI and (b) D-Etha.

Characterization and measurements

The absorption spectra of the dyes were performed using Evolution 201 UV-Vis Spectrophotometeras shown in Figure-8. UV-Vis spectrophotometer is used to measure the absorbance rate in visible light spectrum. Detailed procedure on UV-Vis Measurement can be obtained in Gomesh *et al.* 2014. The photon energy absorbed into the dye in the TiO_2 is calculated by using formula as in Eq. (1).

$$E = \frac{hc}{\lambda} \quad (1)$$

Where h is the planck's constant, λ is the wavelength and c is the speed of light. The numerical values of the symbols are; $h = 6.63 \times 10^{-34}$ Js, $c = 3.0 \times 10^{8}$ m/s, 1eV = 1.60 $\times 10^{-19}$ J. The absorption coefficient determines how far into a material, light of a particular wavelength can penetrate before it is absorbed. The absorption coefficient (α) of the respective wavelengths is obtained by the division of the absorbance with the wavelength shown in Eq. (2);

$$Absorption\ coefficient = \frac{4\pi K}{wavelength\ (\lambda)} \quad (2)$$

Where λ (nm) is taken from the cutoff wavelength of the dyes and K is the Boltzman constant with the value of 8.617×10^{-5}eV.

Figure-8. Evolution 201 UV-Vis Spectrophotometer.

FT-IR Spectra

Figure-9 shows FT-IR spectra of dragon fruit diluted with ethanol (D-Etha) and distilled water (D-DI). For FT-IR spectra of dragon fruit, diluted with ethanol (D-Etha), the peak at 1048 cm^{-1} represents C-O stretching vibration. The peak of 1435 cm^{-1} corresponds to aromatic group contained C-C stretch. The peak at 1667 cm^{-1}corresponds to the C=O stretching vibrations which represented the carbonyl group for ketone structure. The peak at 3031 cm^{-1} also contains O-H group which is the hydroxyl group in dragon fruit dye. The broad peak at 3400 cm^{-1}also corresponds to the O-H stretch. Fordragon fruit diluted with distilled water(D-DI), the peak at 1666 $cm^{-1}$is represented with C=O vibrations and at the peak of 3407 cm^{-1}, correspond to O-H stretching vibrations which is also shown in Coates, 2000.

For Dragon fruit dye, most of the active components such as C=O (which are attributed to carbonyl) and O-H (corresponds to the hydroxyl group) usually in carboxylic acid. The presence of Carboxyl group contained in Betalains pigment (Figure-10) promotes strong hydrogen bonding, towards high characteristic and observes a large shift to lower frequencies. The presence of COOH stretching vibration confirms the carboxyl group in Betalains derivatives and is well matched with UV-Vis absorption spectra. The range of absorption in the visible light spectrum of betalains pigment in between 476 nm and 600 nm are corresponding to the betacyanins and betaxanthins in betalains pigment which promotes a stronger electron coupling bond (Al-Alwani *et al.* 2015).

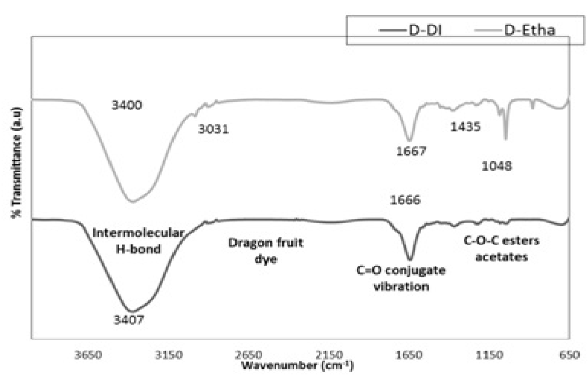

Figure-9. FTIR spectrum of Dragon fruit natural dye extracted by Di-water (D-DI) and Ethanol (D-Etha).

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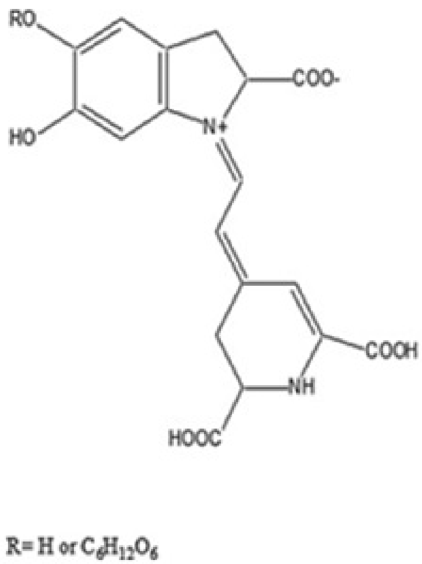

Figure-10. Structure of Betalain's Pigment (Calogero *et al.* 2012).

Absorption spectra

Dragon fruit's dye which is extracted using ethanol is resulted in deep colored solutions. Figure-11 shows the absorption spectra of D-Etha and D-DI and the dye's ability to absorb photons from visible light spectrum. Maximum absorption of wavelength obtained by D-DI is about 550 nm and slightly red shifted compared to D-Etha with the peak wavelength of 510 nm. This absorption range of 470-600 nm resulted of the existing of betalains pigments in dragon fruit's dye.Betalains have antioxidant properties which favourable light absorbing which capable of complexing metal ions and can modify their light absorbing properties because that pigments existed in nature in association with various copigments (Zhang *et al.* 2008).

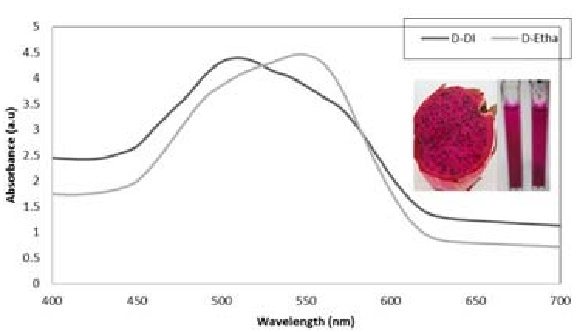

Figure-11. Absorption spectra of Dragon fruit extracted by using Di-water (D-DI) and Ethanol (D-Eth).

Optical Characteristic Nature Dyes

Table-1 show the photon energy and absorption coefficient (α) of the dyes with different extract solvent from DI water and ethanol. From the table, the photon energy and higher absorption coefficient (α) is when extracted the Dragon fruit with distilled water which is about 2.44 eV and 2.12 k m^{-1}.Fig.12 shows the dependence of absorption coefficient on the wavelength of dye

Table-1. Photon energy and absorption coefficient (α) of the dyes.

Dyes	Extract solvent	Structure or structural class	Peak Absorbance (nm)	Absorption range (nm)	Photon energy (eV)	Absorption coefficient (α) k m^{-1}
Dragon fruit	Ethanol	Betalain pigment	550	450-600	2.26	1.97
	Distilled water		510		2.44	2.12

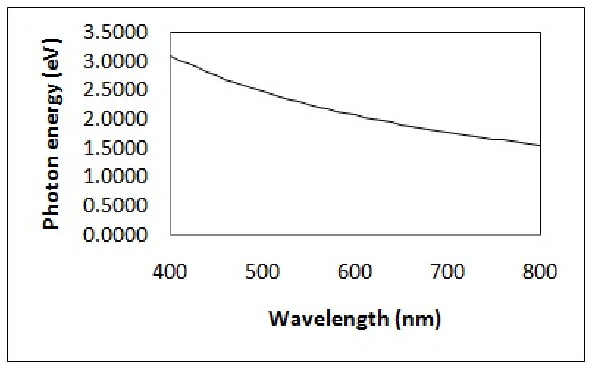

Figure-12. Dependence of absorption coefficient on the wavelength of dye.

CONCLUSIONS

Natural dyes from Dragon fruit, in the spectral response to visible light have been accomplished. The broad absorption peak for the dye in the visible light (400-700 nm) indicates the ability of absorption of dye molecules to bind with TiO_2 surface. Result of FT-IR shows that dye extracted from Dragon fruit contained C=O stretching vibrations at the peak at 1667 cm^{-1} and the peak at 3407 cm^{-1} represents the O-H stretching vibration. From the FT-IR result, the existing of CO=OH corresponds to the carboxylic group in Betalain's pigment for Dragon fruit's dye. The use of natural dye sensitizer offered simple preparation and purification and clean to environment and provide a low cost DSSC.

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