International Journal of Engineering & Technology, 7 (3.11) (2018) 126-128

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Comparison of Conductivity Performance of Dragon Fruit Dye Extracted Using Water and Ethanol for Dye Sensitized Solar Cells

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Abstract

Natural pigments such as anthocyanin, carotenoid, flavonoids, and chlorophyll can be considered as promising alternative sensitizer dyes for DSSC to replace synthetic dye such as N719 because of their simple preparation technique, low cost, complete biodegradation, availability, purity grade, environmental friendliness and most importantly ability to reduce noble metal. In this work, UV-Vis spectra is used to observe the absorption spectra of different extracting solvent of dragon fruit dye. Fourier Transform Infrared Spectroscopy (FTIR) identifies the functional components of the dye while impedance spectroscopy gives the conductivity data. Dragon fruit dye extracted with ethanol had a lower absorbance at 518 nm compared to dragon fruit dye extracted with distilled water at 521 nm. The presence of carboxyl group in Betalains pigment within the range of 400 - 700 nm wavenumber promotes strong hydrogen bonding while the presence of COOH stretching vibration further confirms the carboxyl group of Betalains derivatives in dragon fruit dye. The electrical conductivity measured at room temperature (27°C), boiling point (100°C) and 130°C recorded highest value of 183 Scm^{-1} at 100 °C for dragon fruit dye diluted with distilled water (D-DI) while for dragon fruit dye diluted with ethanol (D-Etha) the value is 9.56×10^{-1} Scm^{-1} at 130°C hence showing that distilled water is the best solvent for natural dye from dragon fruit.

Keywords: *absorption spectra, conductivity, carboxyl group, dragon fruit dye, solvent***.**

1. Introduction

Natural pigments have been considered as promising alternative sensitizer dyes for DSSC because of their simple preparation technique, low cost, complete biodegradation, availability, purity grade, environmental friendliness, and most importantly, high reduction of noble metal and chemical synthesis cost. Natural colorants are pigmentary molecules and dyes obtained mainly from plants such as chlorophyll, carotenoid, anthocyanin, flavonoid, cyanine, and tannin (Ludin *et al*., 2014).

Dragon fruit known as Hylocereus undatus is a tropical fruit popular in Southeast Asia, belonging to the climbing cacti (Cactaceae) family (Castro *et al*., 2017). Dragon fruit contains a lot of vitamin C and is said to aid in digestion. Dragon fruit, also known as pitaya or pitahaya grows on a veining epiphytic cactus (Hylocereus sp.) native to the tropical forest regions of Mexico and Central and South America (Syafinar R *et al* 2015). The flesh of the fruit is red-purple in color when ripened with minute black seeds interspersed and has gained a growing interest for cultivation in Malaysia (Hoa *et al*., 2006). This fruit has gained much interest in the society because of its exotic features, attractive colors, nutritional value and pleasant taste (Bellec *et al*., 2006).

Ultraviolet and visible spectrometers have been in general use for the last 35 years and over this period have become the most important analytical instrument nowadays which can indicate the presence of anthocyanins in the fruit (Mozaffari, Saeidi, & Rahmanian, 2015). However, the molecular fingerprint can be determined through Fourier Transform Infrared Spectroscopy (FTIR) characterization (Syafinar R *et al*, 2015). In the infrared spectroscopy technique, infrared radiation will pass through the sample where some of the infrared radiations were absorbed and some were transmitted. The absorption and transmission of the infrared radiation by the sample will create a molecular fingerprint EIS is a promising technique to measure the electrical impedance of a substance as a function of the frequency of an applied electrical current by using alternating current. It is also used to study the effects of interface modification on the electron transport and recombination kinetics of the dye-sensitized solar cell including chemical capacitance (C_μ) at the TiO_2/dye/electrolyte interface, recombination resistance (R_{rec}) and electron transport resistance (R_t) (Luo *et al*., 2016)

2. Methodology

Two samples were prepared. The first sample, D-DI is a mixture of 10 g of dragon fruit with 15 ml of distilled water as the solvent.

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The second sample, D-Etha is a mixture of 10 ml ethanol and 10 g of the dragon fruit. Both samples were centrifuged at 10000 rpm for 10 minutes. A dropper was used to collect dragon fruit dye pigment at the center of the test tube before undergoing Ultraviolet-visible Spectroscopy (UV-Vis) and Fourier Transform Infrared Spectroscopy (FTIR) analysis.

Meanwhile, ITO glass was sequentially cleaned in distilled water, acetone and ethanol using an ultrasonic bath. The ITO-coated glass was first dried in an oven at 44°C for 24 hours. It was covered with two parallel adhesive tapes 1 cm apart to control the thickness and the area of the TiO_2 film (1.8 cm X 1.0 cm). Before coating with TiO_2 paste, the ITO glass was tested with a multimeter to check the conductive side. Then, the TiO_2 paste was coated onto the ITO glass substrate using Doctor Blade technique. The TiO_2 coated films were heated at 450°C for 30 min and left to dry for 2 days at room temperature. Then, two ITO coated glasses were soaked for 24 hours in a dark environment in dragon fruit mixture, D-DI, and D-Etha separately. Lastly, the samples were washed away of any residue using ethanol and further dried at 60˚C before undergoing characterization by EIS.

3. Results and Discussion

3.1. Uv-Vis Absorption Spectra

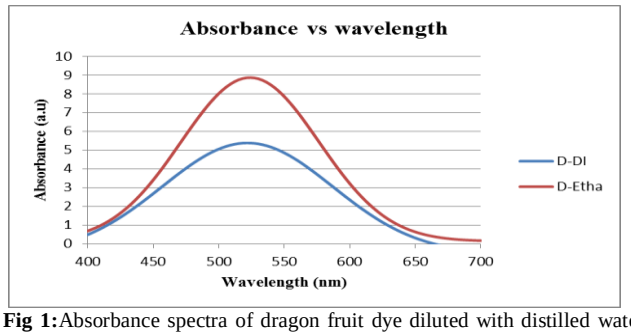


Fig 1: Absorbance spectra of dragon fruit dye diluted with distilled water (D-DI) and ethanol (D-Etha)

Fig. 1 shows the absorption spectra of D-DI and D-Etha which shows the ability of the dye solutions to absorb photon from visible light. The absorption range of 470 nm to 600 nm is attributed to the existence of betalains pigments in dragon fruit's dye. Betalains have antioxidant properties which favors to absorb light and capable of complexing with metal ions which can modify their light absorbing properties because that pigment exists in nature in association with various copigments (Zhang *et al.* 2014). Dragon fruit's dye extracted using ethanol have lower absorbance compared to dragon fruit that has been diluted with distilled water. Maximum absorption wavelength obtained by D-DI is 521 nm, which is slightly higher than that of D-Etha which has a peak wavelength at 518 nm.

3.1. Fourier Transform Infrared Spectroscopy (FTIR)

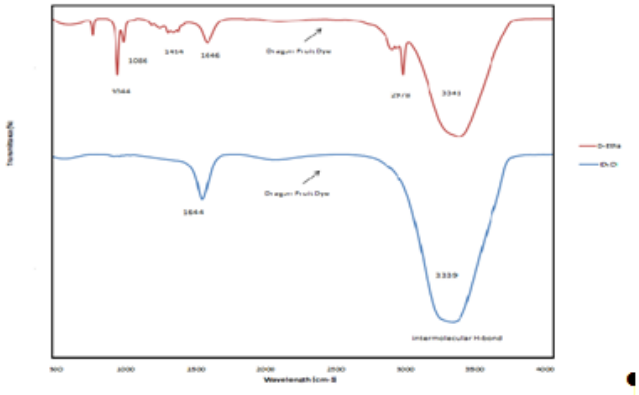


Fig 2: FTIR spectrum of D-DI and D-Etha

The dye solution for dragon fruit diluted with ethanol (D-Etha) showed a peak at 1044 cm^{-1} due to C-O stretching vibration. The peak at 1454 cm^{-1} corresponds to the aromatic group contained in C-C stretching. Besides that, the peak at 1646 cm^{-1} corresponds to C=O stretching vibration which represents the carbonyl group of ketone structure. The peak at 3341 cm^{-1} is due to hydroxyl O-H group in the dragon fruit dye. In the case of dragon fruit diluted with distilled water (D-DI), the peak at 1644 cm^{-1} represents C=O vibration and the peak of 3339 cm^{-1}, corresponds to O-H stretching vibrations.

These results are in agreement with the results presented by Ahmad *et al.*, (2010) who obtained a broad absorption range between 3200~3400 cm^{-1}, sharp adsorption between 1600~1700 cm^{-1} and a sharp peak between 1030~1060 cm^{-1} as observed in D-DI sample. Other than that ,D-Etha showed a peak at 3031 cm^{-1} attributed to O-H group which is the hydroxyl group in dragon fruit dye and a broad peak at 3400 cm^{-1} which corresponds to O-H stretching (Syafinar R *et al.*, 2015).

Hence, active components are present in the dragon fruit dye investigated in this work and these are C=O (attributed to carbonyl) and O-H (corresponds to the hydroxyl group) usually in a carboxylic acid form. The presence of Carboxyl group contained in betalains pigment promotes strong hydrogen bonding. The presence of COOH stretching vibration confirms the carboxyl group in Betalains derivatives and is well matched with the UV-Vis absorption spectra. The range of absorption in the visible light spectrum of betalains pigment is in the range between 400 nm and 700 nm which corresponds to the betacyanins and betaxanthins in betalains pigment which promotes a stronger electron coupling bond (Ahmad *et al*. 2010).

3.3. Electrochemical Impedance Spectroscopy (Eis)

Table 1: Conductivity measurement of dragon fruit dye with distilled water – D-DI

Temperature (°C)	Bulk resistance, R_b (Ω)	Conductivity, σ (Scm^{-1})
27	1.057×10^{3}	7.41×10^{-1}
100	0.416×10^{3}	1.83×10^{0}
130	0.423×10^{3}	1.80×10^{0}

Table 2: Conductivity measurement of dragon fruit dye with ethanol- D-Etha

Temperature (°C)	Bulk resistance, R_b (Ω)	Conductivity, σ (Scm^{-1})
27	4.384×10^{3}	1.724×10^{-1}
100	1.163×10^{3}	6.563×10^{-1}
130	0.834×10^{3}	9.556×10^{-1}

The conductivity was measured at room temperature, 27°C, boiling point, 100°C and 130°C. The conductivity for both sampleswas found to increase with increase in temperature. This happened because the samples absorbed heat which is converted to electrical energy (Laily *et al*., 2016).

The highest conductivity is 183 Scm^{-1} at 100°C obtained from the sample of dragon fruit dye extracted with distilled water. Overall, the conductivity of dragon fruit dye with distilled water, slightly decreased as the temperature increased to 130°C. The lowest conductivity obtained is 1.724×10^{-1} Scm^{-1} from the sample of dragon fruit dye extracted with ethanol at room temperature. Hence, the dragon fruit dye with distilled water shows higher conductivity compared to the dragon fruit dye with ethanol.

4. Conclusion

UV-Vis analysis showed that the dragon fruit dye with ethanol obtained lower absorbance at 518 nm compared to dragon fruit diluted with distilled water at 521 nm. The UV-Vis absorption spectra have measured the ability of the dye to absorb a photon in visible light spectrum.

Based on the results of FTIR spectra, the samples showed the presence of functional group of active components in extracting

dye. Besides that, a dye extracted from dragon fruit contained C=O stretching vibration peak at 1646 cm^{-1} and a peak at 3341cm^{-1} due to O-H stretching vibration. From the FT-IR results, the existence of CO=OH corresponding to carboxylic group in Betalain's pigment of Dragon fruit's dye is substantiated.

The conductivity of extracted dye was measured using impedance spectroscopy. The highest electrical conductivity belong to dragon fruit dye diluted with distilled water (D-DI), which is 183 Scm^{-1} at 100 °C and for dragon fruit dye diluted with ethanol (D-Etha) the value is 9.56×10^{-1} Scm^{-1} at 130°C. It showed that distilled water is the best solvent for the natural dye from dragon fruit.

However, natural dye can be easily degraded but could probably be improved by adding stabilizers like antioxidants, such as vitamin C or E (Hoa *et al*., 2006). Besides that, natural dye can be extracted from various parts of a plant such as the flower, fruit, leaf and root that contains strong color. Various types of extraction solvent can be used in dye extraction to maintain the color of natural dye.

Acknowledgement

The authors gratefully acknowledge the help of the Ministry of Higher Education (MOHE) of Malaysia in providing financial support under the project FRGS/1/2015/SG06/UITM/02/5 grant and Universiti Teknologi MARA (UiTM) for the facilities provided

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