Potential of Purple Cabbage (*Brassica oleracea var. capitata f.*) and Duwet Fruit (*Eugenia cumini*) as sensitizers in Dye Sensitized Solar Cell (DSSC)

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Abstract. Dye-Sensitized Solar Cell (DSSC) prototype has been investigated using purple cabbage (*Brassica oleracea var. capitata f.*) and duwet fruit (*Eugenia cumini*) as natural dyes. Dark purple natural dyes have been extracted from purple cabbage and duwet fruit. The extracts were used as sensitizing ingredients to make sensitizers in DSSC. Natural dyes were extracted with ultrasonic extraction methods using ethanol and distilled water at 30 °C with frequency 40 Hz for 30 minutes. The properties of purple cabbage and duwet fruit dye have been investigated by UV-Visible Spectrophotometer. The results showed that extracts of purple cabbage and duwet fruit had a dark red color, broad spectrum in 500-550 nm and photon energy of 2.28-2.37 eV. Both of the extracts have the same color and have the potential as sensitizers in DSSC development.

1. Introduction

Dye-sensitized solar cells (DSSC) are photoelectrochemical devices for the conversion of visible-range light into electricity [1]. The conversion of light into electricity are based on sensitization of wide band gap semiconductor. There are parts that construct the DSSC and all of these parts are aim to improve the efficiency of the DSSC itself. One of these parts are the dye, the absorption spectrum of the dye and its anchoring group promotes efficient electron injection into the conduction band thus increase the conversion efficiency of DSSC [2].

DSSC can achieve conversion efficiency as high as 12.8% using synthetic organic dyes such as organic silyl-anchor dyes [3]. However, synthetic dyes are expensive and have tedious synthesizing method, therefore nature based dyes from plants are still considered as a viable option to dye-sensitized because of its biodegradability, abundant resources, low-cost and safe handling. Dyes contain pigment that creates color and an important compound which are essential to DSSC efficiency calculation. Natural pigments from natural sources have many kinds, but anthocyanins, betalains, and chlorophyll are the major contributors to natural pigment coloring [4].

In Indonesia, duwet fruit comes from duwet trees that grow wild in tropical forest or become an ornamental plant in gardens. This fruit is indigeneous to Indonesia and South - Southeast Asia. It has deep red color due to anthocyanin pigment that creates the color [5]. While red cabbages are commonly cultivated for food on high areas in Indonesia. Red cabbage is not indigeneous to Indonesia and comes from Europe. Red cabbage too has deep red color due to anthocyanin pigment[6].
Anthocyanins are glycosides of polyhydroxy and polymethoxy derivatives of 2-phenylbenzopyrylium or flavylium salts [7]. It is found frequently in plants, mainly in flowers and/or fruits. Anthocyanin is a watery plasoluble substance, thus soluble in polar solvents. This pigment is one of the most important pigments due to their range of absorption and ability to transfer electrons efficiently in DSSC applications. These pigments absorb light at visible range and also quick to make bonds with TiO$_2$ due to absorption of cyanine which leads to development of effective and strong complex via OH- displacement and formation of water molecules. This can be happening due to the presence of carbonyl (C=O) and a hydroxyl group (OH) contained in anthocyanin [4]. It helps the pigment to attach with TiO$_2$ surface and then stabilize the excited states, resulted in maximum absorption by having lower energy. Furthermore, in visible light spectrum, anthocyanin exhibit broad region of absorption and attributed to charge transfer transitions [2].

Researches found that different solvents are important in extracting pigments from plants. This phenomena is present due to the effect brought by the bonding between the dyes and TiO$_2$ surface that results in change of absorption spectrum of the dyes. Anthocyanin’s solubility depends on the polarity of the solvents, ethanol is more protic than water, this is due to water properties that brings high dielectric constant because of its amphiprotic properties that depends on its chain length. Ethanol solution create less aggregation of the dye molecules, and as extract solvent in extracting nature based dyes shows higher efficiency than using water as much as 0.71% and 0.52% [8]. Therefore, the influence of extraction solvents has been investigated in this paper.

In this paper, natural dye of the same color and kinds were extracted from a different sources, that is duwet fruit and purple cabbage. Additionally, two solvents of the same type that is ethanol and distilled water were also investigated. These extracted dyes from different extract solvent were characterized by UV-Vis Spectrophotometer to see the absorption spectra. The photon energy of each dyes and absorption coefficient were also studied.

2. Experimental Details

2.1. Extraction of Pigment

10 g of duwet fruits is soaked in 15 mL of ethanol or 15 mL of distilled water (DI) at room temperature as the extract solvent. Remove the seed from the fruit and crushed using a mortar into small size. Then, extract the pigment by placing the sample into the ultrasonic cleaner for 15 minutes with the frequency of 40 Hz at temperature of 30 $^\circ$C. The extraction temperature should be keep below 50 $^\circ$C to prevent the destruction of anthocyanin molecules due to the losses of α-diketone formation and glycosyl moieties. Then, pour the solvents into a centrifuge machine for 25 minutes and stirred with 2500 rpm followed with evaporation to obtain the sample as shown in Figure 2. Do the same for the purple cabbage. Duwet fruit create deep red colour in both of the solvent, while purple cabbage have deep purple extract in water and deep red colour in ethanol [2].

Figure 1. Process of Extraction to Obtain the Dye
Figure 2. Colour of the samples after extraction

2.2. Characterization and Measurement
The samples are characterized using Shimadzu UV-Visible Spectrophotometer. This characterization will show the absorbance rate of the dyes in visible light spectrum. There are two things that been calculated, first is the band gap of dye absorbed by TiO$_2$ surface and second is absorption coefficient [2].

The bandgap of dye absorbed by TiO$_2$ surface is calculated using formula in (1). Where $h$ is the Planck’s constant, $\nu$ is the frequency, $\lambda$ is the wavelength and $c$ is the speed. The numerical values of the symbols are $h = 6.63 \times 10^{-34}$ Js, $c = 3.0 \times 10^8$ m/s, $1\text{eV} = 1.60 \times 10^{-19}$ J and $E$ stands for photon energy.

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

While the absorption coefficient of each wavelength is calculated using K boltzmann constant and the formula in (2). The absorption coefficient is used to investigate how far the light of a particular wavelength can penetrate into a material before it is absorbed.

$$\text{absorption coefficient} = 4\pi k/\lambda \quad (2)$$

3. Result and Discussion
3.1 Solvent Effect on Extraction
Effect of solvent on extraction were shown on Figure 3, broad range from 450-600 nm were shown from duwet fruit dye absorbance, maximum wavelength of 531.40 nm for ethanol and 524.40 nm for distilled water. It was shown that the absorbance of the dye extracted by ethanol has less gap and seems broader than the one extracted by distilled water. While from the data, the peak absorbance seems didn’t have much different with 1.823 in ethanol and 1.845 in distilled water.
Figure 3. Absorbance Spectrum of two solvent
As for purple cabbage, the same phenomena had been identified, broad range from 450-600 nm from both of the solvents. But, there are differences in absorbance shape, purple cabbage extracted with distilled water were sharper and had high absorbances. It’s wavelength was 535.80 nm and had absorbance of 2.075.

The effect of solvent in the colour of the dye was identified only in purple cabbage (Fig.2). The color of the dye from purple cabbage extracted by distilled water was deep purple, while ethanol was deep red. This situation were due to the sensitivity of purple cabbage to the change in pH. While the solvent itself was absolute, the water content from the sample is causing the solvent to react, creating the change in pH. The solubility of anthocyanin pigment in the acidic vacuoles that cause the brilliant colors and also absorbs the light at its longest wavelength.

The sample extracted by ethanol had broader absorption spectra due to anthocyanin pigments can be present in the condensation of alcoholic-bound protons with a hydroxyl group on TiO2 surfaces by chemical adsorption[9], thus enhance the conversion efficiency of DSSC by bounding stabilization of TiO2 surface and then shifting towards the lower energy of maximum absorption.

3.2 Absorption Coefficient and Estimation Bandgap of the Dyes

Table 1 shown that the absorption coefficient of the duwet fruit dyes was higher than purple cabbage, moreover in both sample ethanol have smaller coefficient. Meaning that light can penetrate better on purple cabbage extracted with ethanol.

| Dyes         | Extracting Solvent | Peak Abs. (nm) | Absorption Range (nm) | Photon energy (eV) | Absorption Coefficient (k m⁻¹) |
|--------------|--------------------|----------------|-----------------------|--------------------|-------------------------------|
| Duwet Fruit  | Distilled Water    | 535.8          | 450-600               | 2.32               | 2.02                          |
|              | Ethanol            | 543.6          | 450-600               | 2.28               | 1.99                          |
| Purple Cabbage| Distilled Water    | 524.4          | 450-600               | 2.37               | 2.06                          |
|              | Ethanol            | 531.4          | 450-600               | 2.34               | 2.04                          |

Energy bandgap was a difference in energy between the conduction and valence band. If the dye has a lower band gap, then the electron need lower energy in order to recombinant the electron resulting faster movement of electrons from the valence band to the conduction band. From the calculation, duwet fruit have photon energy of 2.37 eV in distilled water and 2.34 eV in ethanol. Purple cabbage have photon energy of 2.32 eV in distilled water and 2.28 eV in ethanol. It shows that purple cabbage has lower band gap than duwet fruit; it is also showed that extraction with ethanol can create lower band gap than extraction with distilled water.

However, that did not mean that duwet fruit does not have potential for DSSC sensitizer, compared to other natural based resources such as turmeric or coffee [2], duwet fruit was still potential due to its lower bandgap and lower absorption coefficient. Moreover, Figure 3 indicates that duwet fruit absorption spectrums are more stable on extraction with different solvents. This could be happening because duwet fruit pigment was not changing color when react with different solvent.

In general, the absorbance graph can conclude that both samples can absorb light photons causing excited electrons productions which allows the TiO2 conduction band on acceptable performance thus increase the conversion efficiency of DSSC [10]. Moreover, dyes which contained anthocyanin pigment have enough hydroxyl groups to bind with TiO2 tightly causing ability to inject electrons into the TiO2 conduction band when excited with visible light [11].
4. Conclusion

The adsorption characteristic of sunlight harvesting and solvent effects on extraction of two natural dyes duwet fruit and purple cabbage were investigated. The results show that both dyes have lower band gap and absorption coefficient with ethanol, creating deep red color. Both of the dyes have broad region spectrum in the range of 450nm-600nm resulting in more light can be absorbed by DSSC.

Both of the dyes were potential as sensitizers in DSSC due to low band gap respectively 2.34eV and 2.28eV for duwet fruit and purple cabbage with ethanol. Moreover, both of the dyes too have low absorption coefficient at 2.04 k m⁻¹ for duwet fruit and 1.99 k m⁻¹ for purple cabbage.

Low band gap means more light because of faster movement of electrons, and lower absorption coefficient. That were means less energy to penetrate the materials. Both of this characteristic can improve the DSSC by raising the efficiency.

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