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Dye Sensitized Solar Cell Using Extract from Red and Yellow Four O'clock Flowers (*Mirabilis jalapa*)

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Abstract. Four o'clock flowers contain betalain compound namely betacyanin and betaxanthin. This compound is used as sensitizer on Dye Sensitized Solar Cell (DSSC). This study used water as a solvents with pH variations of 2, 4, and 6 for the extraction of betalain. Molecular characterization of dyes using UV-Vis spectrophotometer to determine the wavelength and FTIR to determine the functional groups. The HOMO and LUMO analysis using a Cyclic Voltammetry. This study showed absorbance of red and yellow four o'clock flowers extract is 532.50 nm which is betacyanin and 473.30 nm which is betaxanthin. FTIR analysis both of dyes produce wave number 3750-3000 cm^{-1} showed the presence of hydroxyl (O -H) and 1675-1500 cm^{-1} showed the presence of alkenes. The HOMO and LUMO analysis using cyclic voltammetry of betacyanin extract at pH 2 were -3.497 eV and -6.012 eV and betaxanthin were -3.623 eV and -5.803 eV. DSSC performance using betacyanin and betaxanthin dye showed an efficiency value of 0.208% and 0.0036%. Results showed that the extract betacyanin and betaxanthin of red and yellow four o'clock flowers have shown a good sensitizer agents in DSSC.

Keywords : Betacyanin, Betaxanthin, DSSC, Efficiency

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Introduction

The increasing use of fossil fuels has resulted in the depletion of energy sources from fossil. There have been many studies on alternative energy sources to substitute fossils, one of them is solar cells. Solar cells are a tool used to convert light energy into electrical energy. Currently, silicon-based solar cells are widely available in the market, but the price of silicon-based solar cells is relatively expensive.

O'Regan and Grätzel in 1991 introduced a dye sensitizer solar cell (DSSC), this solar cell is intended to replace solar cells based on inorganic materials such as silicon. DSSC is a solar cell that made from semiconductor material as an electron donor and a dye as a photon acceptor [1]. The advantage of DSSC over silicon-based solar cells is the fabrication process is relatively easy and low cost. The DSSC is composed of several parts: (a) The negative electode (anode) is a transparent inductive glass that has been coated with a semiconductor material (such as TiO_2), then immersed in a dye solution. (b) the electrolyte, serves as a place for the electron transfer cycle on the DSSC (c) the positive electrode (cathode) is a counter electrode, can be derived from platinum or graphite material [2].

The DSSC electron generation mechanism is photons are absorbed by the dye molecule and cause the dye electrons in the ground state (HOMO) to be excited to a higher state (LUMO). Electrons that have been excited will be forwarded to the semiconductor material and make the dye oxidized. The electrons will be forwarded to the negative electrode and towards the outer circuit (positive electrode), then the electrons reduce the oxidized dye back to its initial state, through electron transfer (redox) in the electrolyte solution and the cycle will be repeated [1].

Frequently, the fabrication of DSSCs used synthetic dyes that containing heavy metals such as ruthenium. The application of dyes from inorganic materials has the advantage such as being durable, has a high efficiency in converting light but the application can harm the environment because it contains heavy metals and the cost is relatively expensive [3]. The alternative that can be applied to replace synthetic dyes in DSSC is by replacing it with natural dyes. There have been many studies on various kinds of natural dyes such as anthocyanins, betalains, chlorophyll and curcumin which are obtained from flowers, leaves, stems, and rhizomes of a plant. The dyes are used in the DSSC have to meet following criteria: (a) the spectrum of the dye should be in the range of visible and near-infrared spectrum between 400-800 nm (b) has a binding group (chelate) such as carboxyl group (-COO) or hydroxyl (OH) [2]. This group has a negative charge which serves to bind the dye molecules in the semiconductor layer which has positive charge. Natural dyes have several advantages including a relatively inexpensive and easy to obtain, as well as being friendly to the environment and biodegradable. One of the natural dyes that can be used for DSSC is a betalain that comes from four o'clock flowers (Mirabilis jalapa). Four o'clock flowers included in the order of Caryophyllales. It is known that this order contains the betalain compound in its plants [4]. Betalain compound in four o'clock flowers come from betalamic acid which can give a red color which is betacyanin and a yellow color which is betaxanthin. The betalamic acid in the Caryophyllales plant comes from a tyrosine which is converted into L-DOPA with the help of enzymes. L-DOPA is a substrate compound that can form betalamic acid [5] and cyclo-DOPA [6]. Condensation between betalamic acid and cylo-DOPA produce betacyanin which gives a red color, while the condensation between betalamic acid and an amino produce the betaxanthin which gives a yellow color [4] (**Figure 1**).

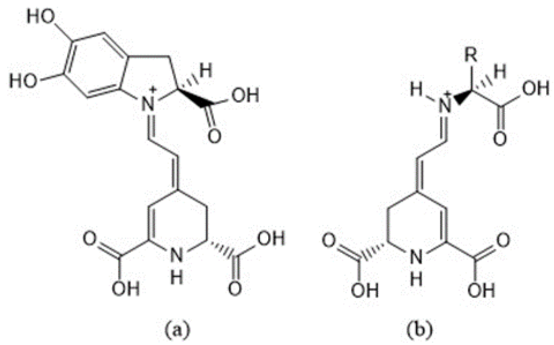


Figure 1. Chemical structure of (a) betacyanin and (b) betaxanthin [4]

Experimental

Materials

Red and yellow four o'clock flowers (Mirabilis jalapa), TiO_2 powder (Brataco), tween

80 (Brataco), poly ethylene glycol (PEG), kalium iodide (KI) (Merck), iodine (I2) (Merck), graphite pencil (Faber Castell), indium thin oxide glass (ITO) 2,5 x 2,5 cm with resistance 22-23 Ω, pH meter (ATC), FTIR (Brucker), UV-Vis (Shimadzu 1800), voltammetry type 797 VA computrace and digital multimeter (Masda).

Dye extract preparation

The dye is a fresh extract from the red and yellow four o'clock flowers. Classification of four o'clock flowers are showed on Table 1 [7] .

Table 1. The classification of four o'clock flowers

Kingdom	Plantae
Ordo	Caryophyllales
Famili	Nyctaginaceae
Genus	*Mirabilis*
Spesies	*Mirabilis jalapa*

The four o'clock flowers that have been obtained are washed with distilled water and cut into small pieces. Flowers are extracted by maceration. Flowers are immersed for 24 hours using a water solvent with pH variations of 2, 4, and 6 to determine the optimum pH. The ratio of flowers and the solvent is 1:10 (1 gram of flowers in 10 mL of solvent). The obtained exctract was filtered with filter paper and stored in the light-tight container.

Fabrication of DSSC

The TiO_2 paste was made using sol-gel method [8]. This method is used to make the particle size into colloidal [9]. The preparation of TiO_2 paste was carried out by weighing 0.2 g of TiO_2 powder, then added 0.4 mL of 0.1 M HNO_3 and 0.08 g PEG, then stirred in a mortal. Then added 0.05 ml tween 80 using a pipette and stirred until a homogeneous mixture. TiO paste is coated on the inductive glass by doctor blade method with an area of 1 cm^2 and heated on a hot plate at the temperature of 450° C for 1 hour [10]. The working electrodes that have been coated with TiO_2 are immersed for 24 hours in a solution of four o'clock flower extract, then rinsed with ethanol to remove the extract that not bind to the electrodes. The counter electrode is made from pencil graphite by shading the surface on inductive glass. The electrolyte solution was prepared by mixing a solution of 1.6 g KI 0.5 M with 0.254 g of iodine, then added 20 mL of PEG. The mixture was stirred using a magnetic stirrer until it was homogeneous [11]. DSSC is made by assembling the electrode like a sandwich with the arrangement working electrode/electrolyte/counter electrode (**Figure 2**).

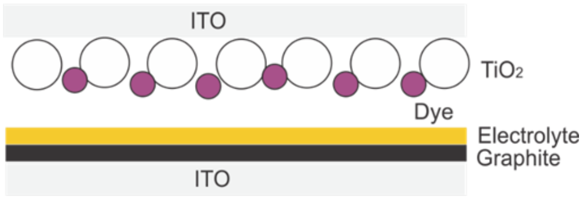


Figure 2. DSSC circuit

Dye characterization

Four o'clock flowers extracts were characterized using a UV-Vis spectrophotometer to determine the wavelength. The range that applied was 400-800 nm. The band gap energy of the dye solution was calculated using the Tauc plot method (the method was used to determine the optical bandgap by looking at the graph relationship E on the x-axis and (αhυ) 1/m on the y-axis) [12]. The functional groups of the dye molecules were characterized using FTIR. The HOMO and LUMO were characterized using cyclic voltammetry with ferrocene as a reference which has a known energy level of -4.4 eV. The calculations are carried out using empirical equations (1) and (2) [13].

$$E\ HOMO = -e\ [E_{ox}^{onset} + 4.4]\ eV \qquad (1)$$

$$E\ LUMO = -e\ [E_{red}^{onset} + 4.4]\ eV \qquad (2)$$

The performance of the DSSC was measured outdoors with a direct sunlight source. Digital multimeter is used to determine the maximum current (I_{max}) and voltage (V_{max}). The maximum power (P_{max}) of the DSSC can be found by the following equation (3) [14] and The efficiency of DSSC performance is known by the following equation (4).

$$P_{max} = V_{max} \times I_{max} / A \qquad (3)$$

$$\eta = (P_{max} / i) \times 100\% \qquad (4)$$

where A is area and i is intensity of light.

Results and Discussion

Effects of pH variation on dye extraction

The extract obtained was measured by UV-Vis spectrophotometer to determine the absorbance. **Figure 3** shows that pH 6 is the optimum pH of the red and yellow four o'clock flower extracts. This is possible due to the natural pH of the betalain compound is pH 6 in a water solvent [8].

Dye characterization

Absorption spectra of the dye extract was determined by UV-Vis spectrophotometer. **Figure 4** describes the absorption of the red four o'clock flower extract, the absorption showed in the range 500-600 nm. Maximum wavelength (λ_{max}) of the extract is 532.50 nm. This absorption is similar to the spectrum of betacyanin compounds (λ_{max} = 535 nm) which is commonly found in Caryophyllales plants [8]. **Figure 5** describes the absorption of the yellow four o'clock flower extract in the range of 400-500 nm. Maximum wavelength (λ_{max}) of the extract is 473.30 nm. This absorption is similar to the spectrum of the betaxanthin compound. The band gap energy in both dyes is known 2.18 eV for betacyanin and 2.46 eV for betaxanthin. The band gap value of the betacyanin is lower than betaxanthin, this is possible due to the wavelength of the betacyanin is greater than betaxanthin, so that it requires lower energy to excite its electrons [15].

FTIR Analysis of The Dye Extraction

The functional group of the red and yellow four o'clock flower extracts was analyzed using a FTIR spectrophotometer. **Figure 6** describes the spectrum of betacyanin and betaxanthin compounds from red and yellow four o'clock flowers. The results showed that both compound have a

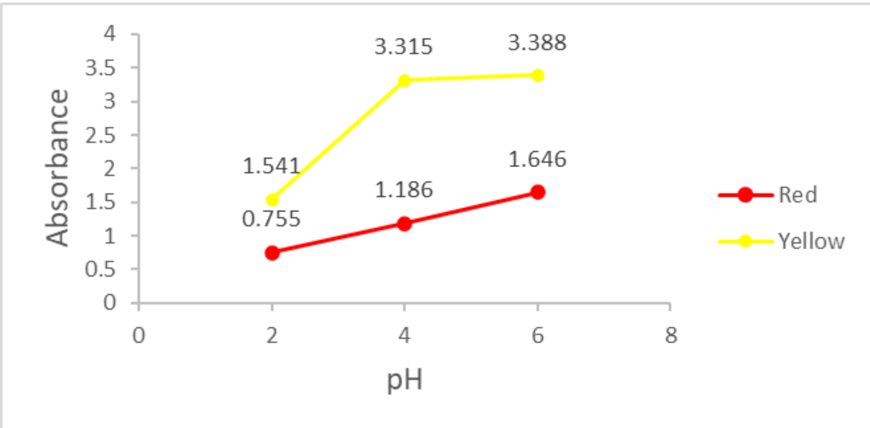


Figure 3. The effect of pH variations on the red and yellow four o'clock flower extracts

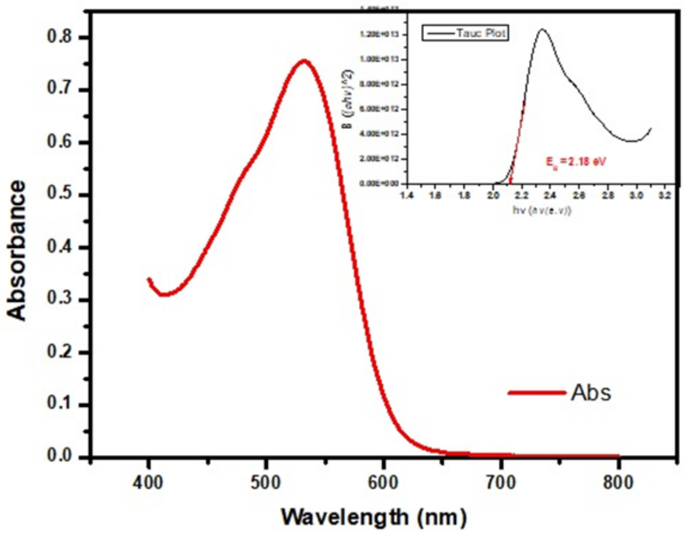


Figure 4. The absorption spectrum of red four o'clock flowers

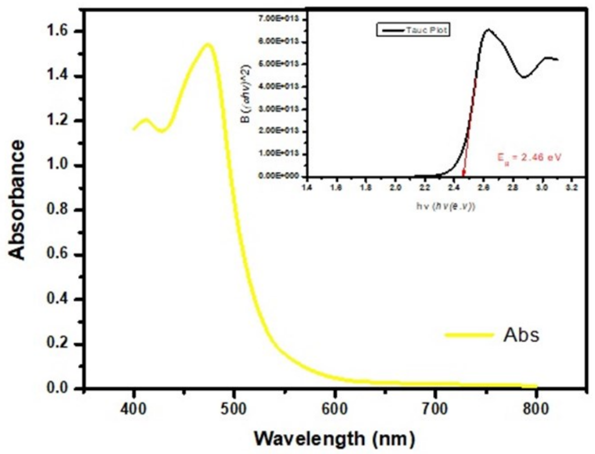
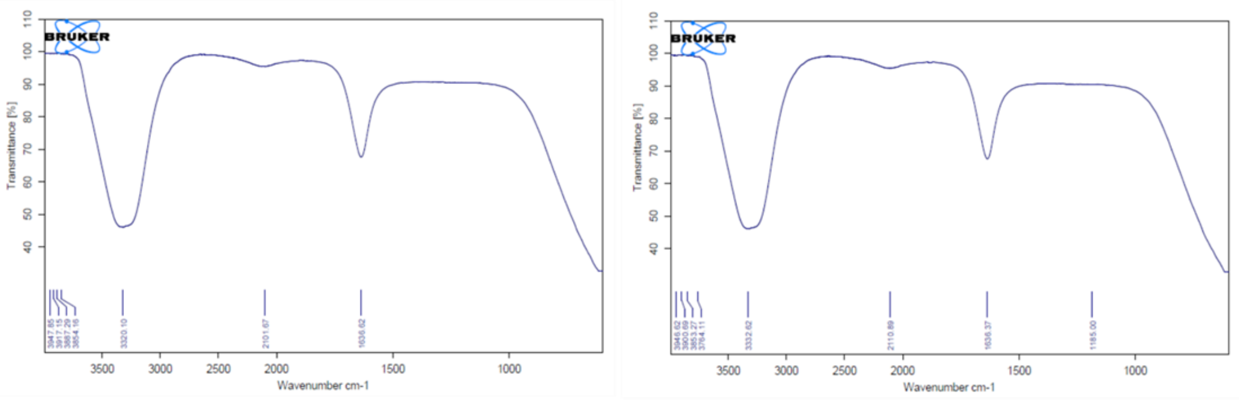


Figure 5. The absorption spectrum of yellow four o'clock flowers

similar spectrum. The spectrum of the wave number 3750-3000 cm^{-1} showed the presence of a hydroxyl group (O-H). The spectrum of the wave number 1675-1500 cm^{-1} is the stretching from C=C of alkene and aromatic groups.

reduction peak both of dye extract. It has shown that on pH 2 has a clear oxidation and reduction peak. This is due to dye's molecule has a good stability and the molecule has accumulated on the surface of electrode.

In **Table 2** shows the energy values of HOMO and LUMO from betacyanin and betaxanthin extracts from red and yellow four o'clock flowers at pH 2, 4, and 6. The HOMO and LUMO values of the red and yellow four o'clock flowers have shown that LUMO energy is greater than the energy of TiO_2 (-4.2 eV) and the HOMO energy is lower than the electrolyte energy (-4.94 eV), so that the dye extract can act as a sensitizer that can be used in DSSC. The LUMO energy of the dye is very important, this is due to the closer the LUMO energy of the dye is to the TiO_2 energy, the more effective the electrons will be injected into the semiconductor layer.



(a) (b)

Figure 6. The FTIR spectrum of (a) red and (b) yellow four o'clock flower extracts

Homo and Lumo analysis

HOMO and LUMO of betacyanin and betaxanthin was characterized by cyclic voltammetry. The measurements were applied with a potential (-1.6) -1.6 V, a scan rate of 300 mV, a deposition time of 10 s and variation pH 2, 4, and 6 [16]. The dyes are used as a sensitizer on the DSSC should less than HOMO value of electrolyte energy, which is -4.94 eV and LUMO is higher than TiO_2 semiconductors energy, which is -4.2 eV [17]. This is in order to the electron transport cycle can continue (**Figure 7**).

In **Figure 8** describes the oxidation and

DSSC performance

DSSC measurements were carried out directly using sunlight with an average measured light intensity of 54.8 mW/cm2. The dye extracts are used as sensitizers on the DSSC at pH 2, this is due to the dye molecule shows the good stability based on the oxidation and reduction at the voltammetry measurements.

In Table 3 shows the DSSC measurement results from red and yellow four o'clock flowers. Based on the results in the table, it can be seen that the efficiency of the DSSC using red four o'clock flowers is 0.208% and has a higher efficiency value than the yellow four o'clock flowers that is 0.0036%. It is possible that the energy gap value of betacyanin (2.18 eV) is lower than that of betacyanin (2.46 eV), so that the energy required by the betacyanin is lower to excite its electrons. The binder (chelating) group also affects the performance of the DSSC where the binding group on the betacyanin has 5 binding groups and more than the betaxanthin that has 3 binding groups (see Figure 1), thus affecting the electron transfer process from the dye to the semiconductor layer. This result is higher then previous studies [19] that using four o'clock flowers with alcohol solvent as a sensitizer and given an efficiency of 0.006 %.

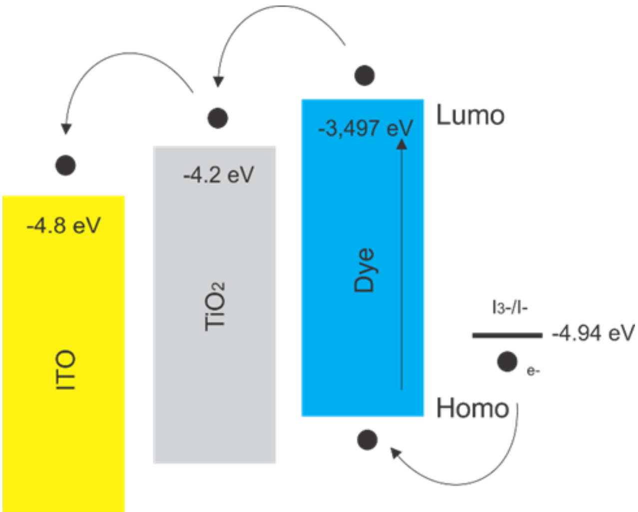


Figure 7. The electron flow diagram of DSSC [18]

Table 2. HOMO and LUMO values of betacyianin and betaxanthin extracts from red and yellow four o'clock flowers

Four O'Clock Flowers	pH	LUMO (*eV*)	HOMO (*eV*)
Yellow	2	-3.623	-5.803
	4	-4.05	-6.23
	6	-4.044	-6.224
Red	2	-3.497	-6.012
	4	-3.979	-6.439
	6	-3.791	-6.251

Table 3. The DSSC efficiency of red and yellow four o'clock flowers

Four O'Clock Flowers	Voltage (*mV*)	Current (*mA*)	Power (*mW*)	Efficiency (*%*)
Yellow	2.0	0.001	0.002	0.0036
Red	7.6	0.015	0.114	0.2080

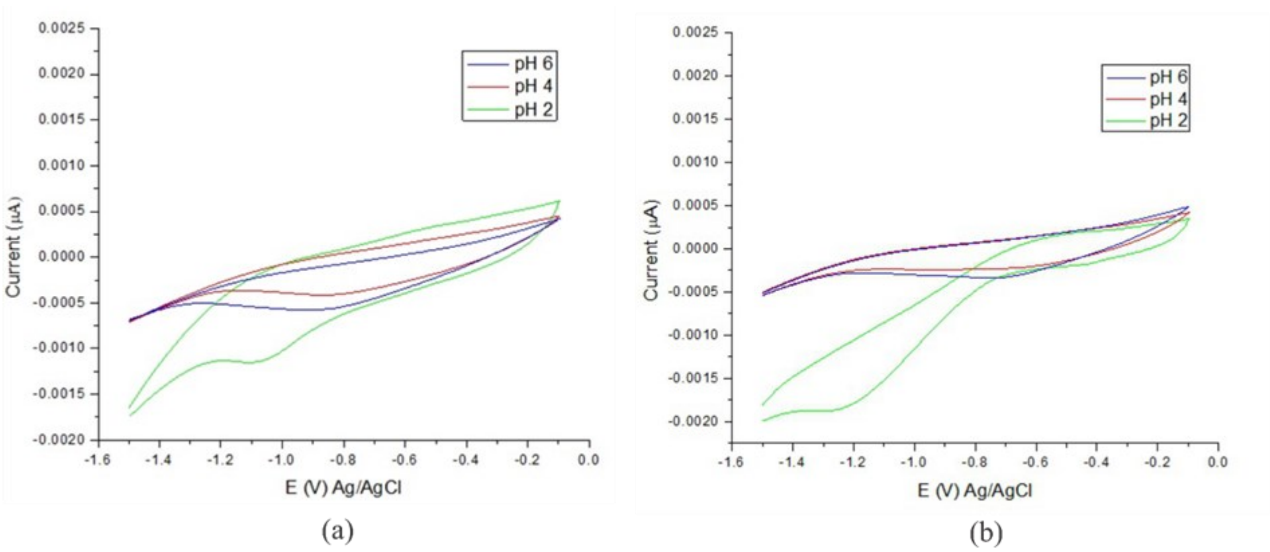


Figure 8. The voltammogram of (a) red and (b) yellow four o'clock flower in various pH variations

Conclusion

The results of this study indicate that the extract of betacyanin and betaxanthin from four o'clock flowers can be used as a sensitizing agent in DSSC. The wavelength of betacyanin is 532.50 nm and betaxanthin is 473.30 nm and showed ranges in the visible zone. FTIR analysis of red and yellow four o'clock flower extracts showed the presence of a hydroxyl group (OH) as a binder in the semiconductor layer. The results of HOMO and LUMO analysis using cyclic voltammetry on betacyanin and betaxanthin extracts from four o'clock flower have met the criteria for a sensitizer agent on the DSSC. The DSSC efficiency of the betacyanin extract was 0.208% and showed better results than the betaxanthin extract of 0.0036%. This is possible because the energy gap of the betacyanin (2.18 eV) is lower than that of betaxanthin (2.46 eV) which causes the energy needed by electrons to be excited is lower in betacyanin and the number of binding groups of betacyanin is more than betaxanthin, which affects the electron transfer process into the semiconductor layer.

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