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Performance of Dye-Sensitized Solar Cells with Natural Dye from Local Tropical Plants

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Abstract

Dye-sensitized solar cell (DSSC) is a class of third generation solar cells that are formed by placing a semiconductor between a photosensitized anode and an electrolyte, which allows the light to pass through the cell. Synthetic dyes, usually ruthenium-based and commonly used in DSSCs, are environmentally toxic and expensive than natural dyes. The aim of the study was to investigate native and cheap sources of natural dyes as photosensitizers for DSSCs using tropical plants. Dyes from four different local plant sources were successfully extracted, prepared, and characterized and were used as alternative, non-toxic, natural photosensitizers. The visible spectra of the extracts with peaks between 430-440 nm suggest that they are dominated by chlorophyll a (430-662 nm) and chlorophyll b (453-642 nm). When observed under ambient conditions, the fabricated DSSCs demonstrated high outputs for OCV_{max} *wherein 433, 397, 311, and 203 mV were obtained using dye-sensitizers from dried talisay leaves (Terminalla catappa), spent coffee grounds (Coffea spp.), fresh talisay leaves, and alugbati fruit (Basella alba), respectively. The observed open circuit potentials were comparable with other reported DSSCs. The output current, fill factor, and cell efficiency can be improved by co-sensitization and increasing the light-scattering capability, among other methods of constructing the DSSCs. Generally, with the limited impacts to the environment and cheap production cost, this research has opened opportunities for application of natural dye from local sources for renewable energy technologies.*

Keywords: dye-sensitized solar cells (DSSCs), natural dye, *Terminalla catappa*, *Coffea spp.*, *Basella alba*

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1. Introduction

Solar energy conversion (photovoltaic [PV]) systems are now prevalent in the market and have been identified in many different applications from the household level to industrial or commercial scales. Among the several components of a solar PV system is the solar cell, which converts the photons of different light sources into usable energy. Dye-sensitized solar cell (DSSC) is a class of third generation solar cells that are formed by placing a semiconductor between a photosensitized anode and an electrolyte allowing the light to pass through the cell (Bauer *et al.*, 2002). Clear glass substrates are used as electrode substrates because of their cheapness, availability, and high transparency in the visible spectrum. DSSCs are also credible alternative concept for inorganic solid-state photovoltaic devices (Ludin *et al.*, 2014).

The dye coated on the porous semiconductor titanium dioxide (TiO_2) film largely affects the conversion efficiency of the DSSC. In DSSCs, incident photons are absorbed into the dye molecules that are found on the surface of the mesoporous TiO_2 layer. The dye molecules become excited and oxidized, upon loosing and injecting electrons into the conduction band of the photo-anode network. The electrons travel through the TiO_2 layer towards the external load, reaching the counter-electrode. The electrons are then transferred to the electrolyte where the oxidized dye receives electron from I- ion to replace the lost electron. Simultaneously, the iodide molecules are oxidized to tri-iodide ions (I3-). Finally, regeneration of I- ion takes place at the cathode (counter-electrode), and migration of electron through the external load completes the circuit (Kim *et al.*, 2006; Ganesa *et al.*, 2008; Muthuraamana *et al.*, 2013). Even though these types of cells have lower conversion efficiency than the existing thin film and solid-state semiconductor-based technologies with the lower cost of materials and inexpensive production, they are expected to offer a price-performance ratio that can replace a significant amount of electricity generated by fossil fuels (Grätzel, 2003).

Recently, DSSCs have gained substantial considerations because they are easy to prepare and possess good architectural and environmental compatibility. They also have promising performance in diffuse light conditions. The first developed DSSCs revealed light absorption up to approximately 800 nm and energy conversion efficiency higher than 7%. Conversion efficiencies up to 11 and 13% have also been reported (Ono *et al.*, 2009; Taya *et al.*, 2013; Mathew *et al.*, 2014; Suhaimi *et al.*, 2015). Synthetic dyes provide better efficiency and high durability in DSSCs; however, they are more expensive, have tendency to undergo degradation, and consist of toxic materials. Among the successful dye-sensitizers in terms of performance and stability are ruthenium (Ru)-based compounds (Gokilamani *et al.*, 2013). These limitations provide opportunities to look for alternative, bio-compatible dye-sensitizers such as those derived from natural plant pigments like anthocyanin, carotenoid, flavonoid, and chlorophyll. These pigments are responsible for chemical reactions such as absorption of light. Their economic viability, non-toxicity, and complete biodegradation make them a popular research subjects, thus, enabling them to have wide utilization in DSSCs (Zhou *et al*., 2011).

With all these current information, this study primarily aimed to identify native and cheap sources of natural dyes that are rich in pigments such as anthocyanin, carotenoid, flavonoid and chlorophyll for application in DSSCs. Using tropical species of plants, natural dye were extracted and characterized and their effect on DSSCs as photosensitizers were investigated.

2. Methodology

2.1 Reagents and Equipment

Dye sensitizers were obtained from natural sources by aqueous and ethanolic extraction. The indium-titanium oxide (ITO) glasses (625 mm^2, 1.1 mm thickness, 10-15 Ω in^{-1} resistance), commercial TiO_2 (Degussa P-25), TritonX-100, and polyethylene glycol (PEG-400) were purchased from Sigma-Aldrich Germany. The redox electrolyte (Iodolyte AN-50) was purchased from Solaronix, Switzerland. All the reagents were analytical grade and required no further purification. The equipment used include a 722G single-beam visible spectrophotometer (wavelength range 325-1000 nm), Alexan digital multimeter, digital balance, digital lux meter, and Vulcan muffle furnace.

2.2 Extraction and Characterization of Natural Pigments

Natural pigments were extracted from various plant parts including achuete seeds (*Bixa Orellana*), alugbati stem and fruit (*Basella alba*), flame tree bark (*Delonix regia*), talisay leaves (*Terminalla catappa*), and spent coffee (*Coffea spp.*) grounds. The plant parts were washed five to six times with distilled water to remove dirt and other impurities, and then oven dried at 50 °C for 24 hours (h) to remove excess moisture. After oven drying, the products were pulverized and sieved to achieve uniform particle size. In extracting the pigments, 10 g of each powder of alugbati, achuete, flame tree bark, and spent coffee grounds were immersed separately in 50 mL ethanol (95%) for 48 h. Meanwhile, the pigments from talisay leaves were extracted by boiling small pieces of fresh leaves in distilled water for 1 h (ratio 2:1). After boiling the talisay leaves and alcohol extraction, all the mixtures were filtered using Whatmann filter paper number 40. The filtrates were transferred in 300-mL amber bottles and stored in a dark place at room temperature to preserve.

A dilution series containing 100, 50, 25, and 12.5% by volume of the extracts were prepared for each sources using ethanol as solvent in preparation for spectrophotometry. The absorption spectra and the absorption peaks of each component of the dilution series were observed in a single-beam visible spectrophotometer with ethanol as blank.

2.3 Preparation of the Working Electrodes

The ITO was used as electrode and counter-electrodes for the DSSCs. A thin film of TiO_2 paste was applied on the conductive side of the electrode. In preparing the TiO_2 paste, initially, 1.0 g of commercial TiO_2 powder was dissolved in 1.5 mL deionized water in a mortar and pestle, grinding the mixture for 10 min to form a smooth slurry. For another 20 min of continuous mixing, 0.5 g polyethylene glycol was slowly added along with 0.5 mL of acetic acid. The resulting thick paste was applied on the ITO glass by doctor blading and air-dried for 10 min. This was followed by sintering at 450 °C for 1 h in a muffle furnace.

Sintered electrodes with TiO_2 film were dipped in natural dye extracts for 48 h. The electrodes were rinsed and the excess dye were removed using ethanol.

The counter-electrode was fabricated by forming a thin film of carbon paste in another ITO glass. Carbon paste was prepared by mixing 130 mg of activated carbon powder in 0.4 mL of deionized water in a mortar and pestle. The mixture was ground for 10 min until it became smooth. The slurry was slowly added with two drops of Triton x-100 and two drops of acetic acid while being mixed for another 10 min. The resulting paste was applied in the conductive side of the ITO glass by doctor-blading followed by air-drying and sintering at 450 °C for 1 h.

2.4 Construction and Assembly of DSSCs

The conductive sides of the two ITO glasses containing TiO_2 film and carbon film were arranged face-to-face and fixed by binder clips. A few drops of redox electrolyte Iodolyte AN-50 was added between the ITO glasses. Based on the spectral properties of the extracts and their binding characteristics with the TiO_2 film, extracts from fresh and dried talisay leaves, spent coffee grounds, and alugbati fruit were selected as photosensitizers.

2.5 Data Gathering Procedure

Four pairs of DSSCs were constructed and tested during exposure to natural light. The intensity of the solar radiation was measured and recorded at a 10-min interval using a digital lux meter. To describe the performance of the DSSCs, the open circuit voltage, voltage drop and current output in close circuit condition were measured and recorded overtime using a digital multimeter. The maximum open circuit voltage (OCV) (V_{oc}), maximum voltage drop (V_{max}), short circuit current (I_{sc}), and maximum current (I_{max}) were determined and used to calculate fill factor and efficiency using the equations below.

$$\text{Fill factor (FF)} = \frac{V_{max} I_{max}}{V_{oc} I_{sc}} \qquad (1)$$

$$\text{Efficiency } (\eta) = \frac{V_{oc} I_{sc} FF}{P_{in}} \times 100\% \qquad (2)$$

where:

V_{oc} = open circuit voltage (mV)
I_{sc} = short circuit current density (mA/cm^2)
P_{in} = incident light power (mW/cm^2)
I_{max} = maximum current (mA)
V_{max} = maximum voltage (mV)
FF = fill factor

3. Results and Discussion

3.1 Spectral Analysis of the Plant Extracts

Flowers, leaves, and fruits exhibit various colors and contain several pigments that can be readily extracted by water, methanol, or ethanolic compounds for the use in DSSC fabrication (O'Regan and Grätzel, 1991; Kishiomoto *et al.*, 2005; Chang and Loy, 2010; Keka *et al*., 2012; Nishantha *et al*., 2012). Other than chlorophyll, the natural pigments that have been used in DSSCs include anthocyanin, flavonoid, carotenoids, betalains, and xanthophyll in which optimization of the structure of natural dyes to improve efficiency is promising (Zhou *et al*., 2011). Natural pigments were considered a promising alternative since they are readily available, low-cost, completely biodegradable, and environment-friendly. Also, they can be easily prepared.

The spectral properties of the plant extracts were characterized in terms of maximum absorption wavelength (λ_{max}) and peak absorbance (Table 1).

Table 1. Maximum wavelength and peak absorbance of the sample extracts obtained from various sources

Source	Plant Part	Wavelength λ_{max} (nm)	Absorbance (1st peak)	Wavelength λ_{max} (nm)	Absorbance (2nd peak)
Spent coffee grounds	ground coffee bean	430	0.925	560	0.690
Alugbati	stem	440	0.963	560	0.361
	fruit	430	0.978	560	0.255
Talisay	leaves (dried)	430	0.960	560	0.290
Talisay	leaves (fresh)	440	0.974	560	0.158
Achuete	seeds	430	0.982	560	0.490
Flame tree	bark (soft)	430	0.965	-	-
	bark (hard)	430	0.918	-	-

(-) indicates very low absorbance value that may be insignificant

The absorbance spectra of each extract were obtained (Figure 1). Among the samples scanned, extracts from achuete seeds have the highest peak absorbance at 0.982 while the extract from hard bark of flame tree has the lowest at 0.918. All of the samples registered peak absorbance between 430-460 nm. The differences in the absorption peaks is due to the presence of different pigments in which the extracts did not undergo any purification. The absorbance values of the samples on the first peak (blue region) show presence of chlorophyll *a* and chlorophyll *b* where the optical windows were 430 nm to 662 nm and 453 nm to 642 nm, respectively. Moreover, the presence of secondary peaks at 560 nm indicates the presence of secondary pigments, probably carotenoid and anthocyanin, which normally peaks between 460 and 570 nm.

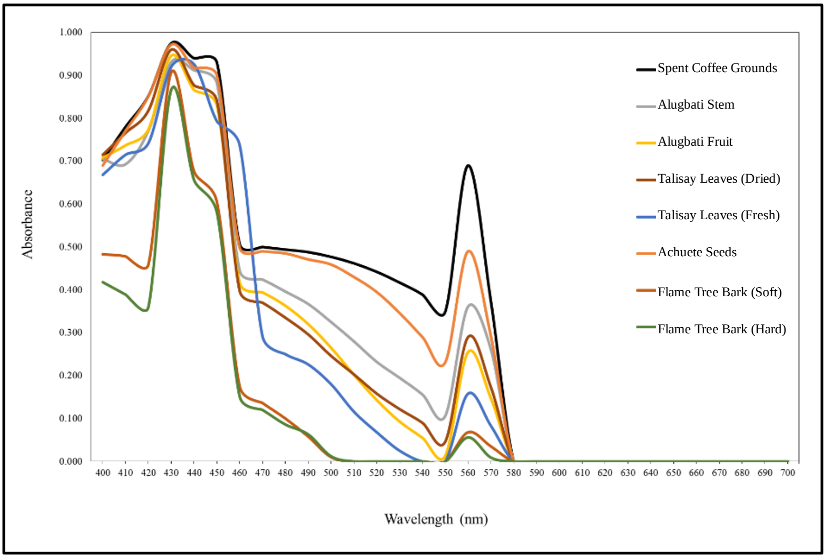

Figure 1. Absorption spectra of the plant extracts with peaks between 430-440 and 550-580 nm. The optical windows of chlorophyll *a* and chlorophyll *b* are 430 to 662 nm and 453 to 642 nm, respectively.

The appearance of the plant pigments and the color perceived by humans are caused by the structure of these pigments that interact with sunlight. These pigments are categorized into four different types that consist chlorophyll, flavonoids, anthocyanin, and carotenoids. Raw natural dyes are better than purified or commercial equivalents due to the presence of other compounds and enzymes that assist in dye adsorption and accumulation, and prevention of electrolyte recombination.

Chlorophylls are green pigments most commonly found in green plants, algae, and cyanobacteria whose primary function is to harvest light energy for photosynthesis (Scheer, 2003; Wang *et al*., 2005; Chang *et al*., 2010b). Among the six types, the most common and beneficial are chlorophyll *a* and chlorophyll *b* that absorb most light in the red and blue regions. This unique characteristic of the chlorophylls, attributed to their attractive compounds, is the main reason of their application in DSSCs (Davies, 2004). On the other hand, anthocyanins are responsible for the attractive color of flowers, fruits, and leaves of plants from scarlet to blue or from the purple-red-orange shades (Andersen and Jordheim, 2005; Chang *et al*., 2010a). Aside from fruits and seeds, the anthocyanins are also found in other plant organs as stems, tubers, and roots (Patrocinio *et al*., 2009). Next to chlorophyll, they are the most important group of pigments. They can modify the quantity and quality of light incident on the chloroplasts (Steyn *et al.*, 2002). When applied in DSSCs, the presence of the carbonyl and hydroxyl groups that bound to the surface of the TiO_2 particles help excite and transfer electrons to the conduction band of the film (Ludin *et al.*, 2014). Meanwhile, carotenoid pigments provide flowers and fruits with distinct yellow, red, and orange colors (Kishiomoto *et al.*, 2005; Davies, 2004; Ruiz-Anchondo *et al.*, 2010). They complement the chlorophylls by acting as accessory pigments in harvesting light (Vargas *et al.*, 2000) and by providing protection during photosynthesis through redox reactions (Wang *et al.*, 2005). Lastly, flavonoids occur in different colors and there are over 5000 naturally occurring flavonoids extracted from plants. They are divided into three classes: flavonoids, isoflavonoids, and neoflavonoids. Though prominent, not all flavonoids have the ability to capture visible light.

3.2 OCV Profiles of the DSSCs

Based on their visible adsorption characteristics and the binding properties with the mesoporous TiO_2 film, extracts from fresh and dried talisay leaves, spent coffee grounds, and alugbati fruit were finally selected as photo-sensitizers for the DSSCs.

Variations in the intensity of the solar light were monitored for four days during the testing of the performance of the DSSCs (Figure 2).

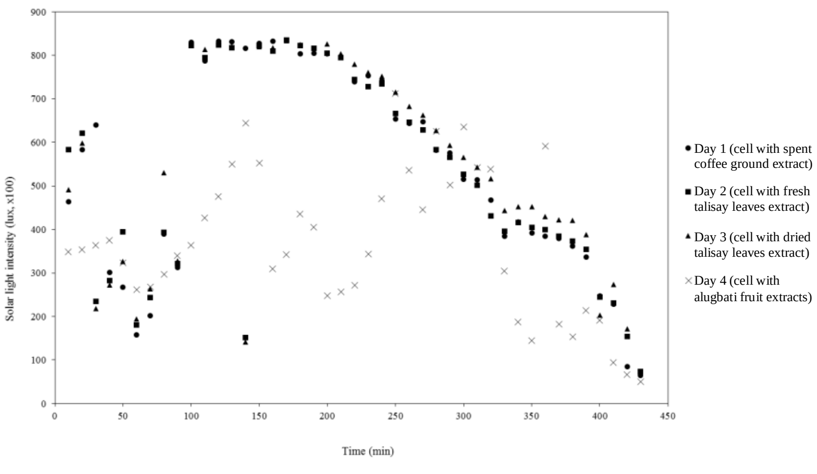

Figure 2. Solar light intensity (in lux) recorded during the observation of the performance of the dye-sensitized solar cells. The solar intensities recorded on day four were significantly different among others.

The daily observations revealed high variability on solar intensity. The maximum solar intensities recorded per day were 834 lux (x100) on days one and three; 835 lux (x100) on day two; and 712 lux (x100) on day four. The highest mean solar intensity was obtained on day three at 542.28±236.55 lux (x100) while the lowest was on day four at 712±165.70 lux (x100). Statistical analysis showed that the difference in the solar intensities were significant (F(3,168) = 6.381; p = 0.000) and highest on day four.

The observation of the DSSC performance (current-voltage or I-V characteristics) under normal light conditions offers an opportunity to assess their behavior in real conditions. However, I-V characteristics are commonly accomplished using solar simulators with fixed illumination of 100 mW cm^{-2} (Zhou *et al*., 2011; Ramanarayanan *et al*., 2017; Hosseinnezhad *et al*., 2018; Al-Alwani *et al*., 2020; Golshan *et al*., 2020).

The open circuit voltage (OCV) outputs of the DSSCs at the given solar intensities were obtained and compared (Figure 3).

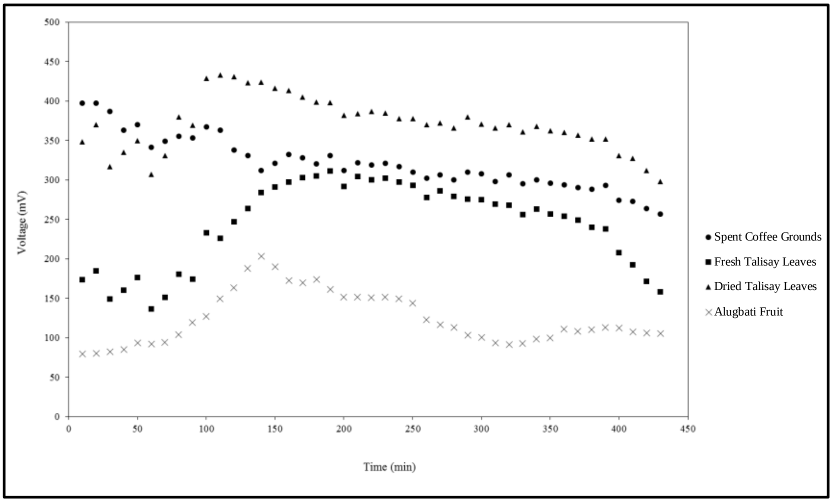

Figure 3. Open circuit voltage profiles of the dye-sensitized solar cells. The DSSCs sensitized with extracts from dried talisay leaves and alugbati fruit exhibit a morecurvilinear pattern wherein the OCV output gradually increasing and decreasing throughout the observation period.

In terms of the OCV$_{max}$, the DSSC with extracts of dried leaves of talisay produced the highest OCV at 433 mV while the DSSC with alugbati fruit extracts yield the lowest at 203 mV. The statistical analysis also showed that the difference among mean OCVs of the solar cells were highly significant.

The solar cell with the dried talisay leaves extract has the highest OCV output, followed by the DSSC with spent coffee grounds extracts (320.93±33.73 mV), fresh talisay leaves extracts (241.56±54. 13 mV), and alugbati fruit extracts (123.92±33.97 mV).

Furthermore, the cells sensitized with extracts from dried talisay leaves and alugbati fruit demonstrated patterns different from the others. The DSSCs with extracts from spent coffee grounds and fresh talisay leaves have initially higher OCV output which decreased overtime. Pearson r correlation of the solar intensity and the OCV output revealed medium to strong relationship between these variables (Table 2). These results suggest that an increasing solar light intensity increases the OCV output of the DSSCs at a highly significant level.

Table 2. Pearson *r* correlation coefficients of the solar light intensity and OCV outputs of the DSSCs

Dye Sensitizer	Pearson *r*	p-value
Spent coffee grounds	0.279	0.070
Talisay leaves (fresh)	0.753**	0.000
Talisay leaves (dried)	0.793**	0.000
Alugbati fruit	0.317*	0.038

** - significant at 1% level; * - significant at 5% level

3.3 Output Current of the DSSCs

The recorded intensities of the solar radiation during the observation of the output current (I) of the DSSCs were less variable except during day four (Figure 4). The maximum solar intensities recorded per day were: 828 lux (x100) on day one, 831 lux (x100) on day two, 823 lux (x100) on day three, and 837 lux (x100) on day four. The highest mean intensity was obtained on day two at 608.24±239.85 lux (x100) while the lowest was on day four at 406.10±337.16 lux (x100). Statistical analysis showed that the difference in the solar intensities were highly significant (F(3,164) = 4.773; p = 0.000).

The current outputs of the DSSCs were measured in closed-circuit condition and compared (Figure 5). The highest current output was obtained from the DSSC with extracts from spent coffee grounds at 41.60 μA while the lowest output was obtained with the alugbati fruit extracts at 10.30 μA. Statistical analysis revealed that the difference in the mean current obtained from each cell is highly significant (F(3,164) = 42.851; p = 0.000). The cell with spent coffee ground extracts has the highest mean current (22.24±12.61 μA), followed by the cells extracts from fresh talisay leaves (20.80±10.07 μA), dried talisay leaves (8.25±4.55 μA), and alugbati fruit (5.16±3.62 μA).

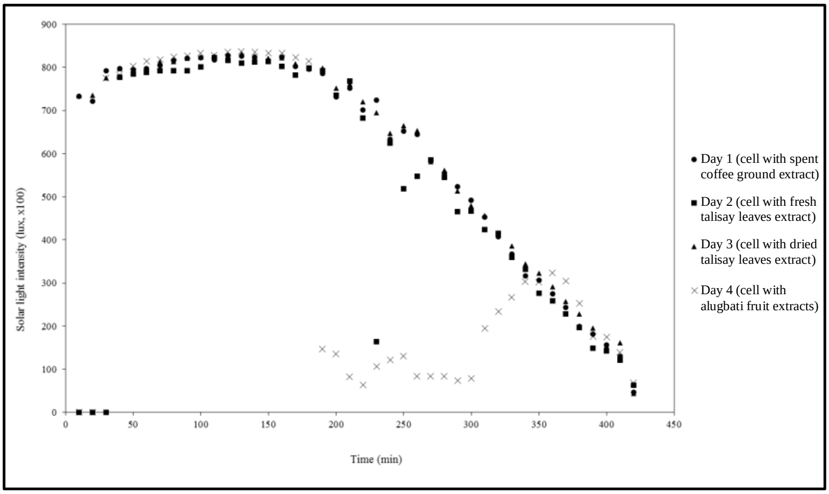

Figure 4. Intensities of solar light (in lux) recorded during the four-day observation of the output current of the DSSCs. Solar intensities were lowest on day four due to inclement weather conditions.

Based on the output current profile of each cell (Figure 5), the performance of the cells, which produced higher current output, also exhibits more stable behavior.

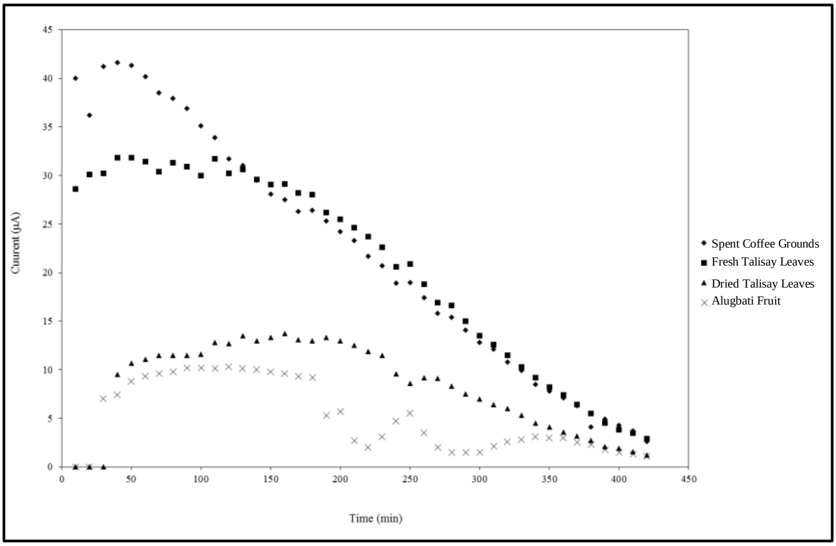

Figure 5. Current profile of the DSSCs obtained in closed-circuit condition. The solar cells with extracts from dried talisay leaves and spent coffee grounds exhibited higher current outputs among others.

Further analysis revealed that the intensity of the solar light and output current of the cells are strongly positively correlated (Table 3). These strongly suggest that the increasing solar intensity also increases the output current of the cells at a highly significant level.

Table 3. Pearson *r* correlation coefficients of the solar light intensity and current output of the DSSCs

Dye Sensitizer	Pearson *r*	p-value
Spent coffee grounds	0.900^{**}	0.000
Talisay leaves (fresh)	0.978^{**}	0.000
Talisay leaves (dried)	0.938^{**}	0.000
Alugbati fruit	0.937^{**}	0.000

** - significant at 1% level

3.4 Fill Factor and Efficiency of the Solar Cells

The photovoltaic properties of the DSSCs sensitized with four different natural plant extracts were examined by measuring the V_{oc}, I_{sc}, V_{max}, I_{max} and an average solar power input of 11.835 mW cm^{-2} (Table 4). The DSSCs have high open circuit voltages (V_{oc}), however, have low current output, fill factor and efficiencies.

Table 4. Photovoltaic properties of the DSSCs

Dye Sensitizer	V_{oc} (mV)	I_{sc} (mA cm^{-2})	V_{max} (mV)	I_{max} (mA cm^{-2})	Pin (mW cm^{-2})	Fill Factor	Efficiency (%)
Spent coffee grounds	397	0.00938	43.0	0.00832	11.669	0.0960	0.0031
Talisay leaves (fresh)	433	0.00794	86.0	0.00636	11.691	0.1592	0.0047
Talisay leaves (dried)	311	0.00324	47.8	0.00274	11.742	0.1300	0.0011
Alugbati fruit	203	0.00298	64.0	0.00206	12.240	0.2104	0.0010

Generally, DSSCs have better performance compared to other photovoltaic cells when operated at higher temperatures and diffuse light condition. The analyses of their life-cycles have demonstrated very limited impacts to the environment and the application of natural dyes provide positive environmental impacts (Parisi *et al.*, 2014). Intensive research and development on the DSSCs have reportedly increased their efficiencies up to 13% achieved using ruthenium-based compounds.

A review of the progress of DSSCs using natural sensitizers revealed a significant number of research works that showed varying efficiencies, ranging between 0.013-8.22. Among the requirements that natural sensitizers should meet include high absorption of visible light and strong binding with semiconductors to facilitate conduction of electrons (Iqbal *et al.*, 2019). To improve light harvesting, some studies suggest co-sensitization that will help absorb all incident light from the visible region to the infrared region. Through co-sensitization, the combination of two or more dyes with complementary spectra allow maximum absorption of light since the dyes also possess different absorption wavelengths. Another approach is to increase light scattering either by increasing the thickness of the thin film, increasing the light path length, including larger particles in the thin film, or coating of a scattering-layer on the top of the active layer (Gong *et al.*, 2017).

4. Conclusion and Recommendation

Different kinds of natural dye from alugbati, talisay, achuete, flame tree, and spent coffee grounds were extracted, prepared and characterized by visible spectroscopy to be used as photosensitizers for DSSCs. The absorption spectra of the plant extracts indicate the presence of chlorophyll *a* and chlorophyll *b*, and secondary pigments such as caretonoid and anthocyanin in smaller amounts. The DSSCs exhibited high open circuit potential comparable with other DSSCs reported, however, the output current, fill factor, and cell efficiency were low. Nevertheless, the obvious absorption and binding properties of these dye sensitizers with the mesoporous TiO_2 semiconductor offer new opportunities for research on natural dyes, coupled with the abundant supply and positive environment impacts. To improve their performance, it is highly recommended to optimize the extraction techniques and further characterize them in terms of quality and yield for future applications in DSSCs.

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