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PHOTODEGRADATION EFFECT ON OPTICAL PROPERTIES OF MANGOSTEEN PERICARP, BLACK GRAPE PEEL AND VIOLET *BOUGAINVILLEA* FLOWERS AS PHOTOSENSITIZER FOR SOLAR CELL APPLICATION

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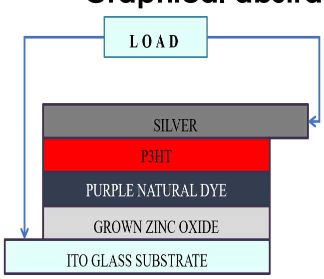
Graphical abstract



Abstract

Alternative energy sources such as wind, solar, biomass, hydro, and geothermal have become imperative for green energy solutions. A growing demand of hybrid solar cells is yet another promising option toward green energy providing the opportunity to explore natural dye extracts from the plant. The natural dyes were extracted from mangosteen pericarp (MP), black grape peel (BGP), and violet *bougainvillea* flowers (VBF), respectively. The natural dyes were then undergoing degradation under exposure to the light for six weeks. UV-vis spectroscopy was used to characterize the optical absorption of the natural dyes. UV-vis result showed that MP absorbs three ranges of light, 400-600 nm (chlorophyll a), 530- 550 nm (anthocyanin), and 650-670 nm (chlorophyll a). After 6 weeks, MP gives the best in sustaining itself by having the lowest percentage of photodegradation (50.73 %) compare to BGP (83.88%) and VBF (65.66%). The natural dyes gave the FTIR vibration peaks of OH, C-H, C=O, and C-O-C functional groups. Therefore, this study provides significant contributes towards explaining the potential of MP as the promising photosensitizer in the development of the hybrid solar cell.

Keywords: Photodegradation, anthocyanin, chlorophyll, percentage of photodegradation

Abstrak

Sumber tenaga alternatif seperti angin, suria, biojisim, hidro dan geotermal amat penting bagi penyelesaian tenaga hijau. Permintaan terhadap sel solar hibrida yang semakin meningkat telah memberi peluang untuk meneroka ekstrak pewarna semulajadi daripada sumber tumbuhan. Pewarna semulajadi diestrak daripada kulit manggis (MP), kulit anggur hitam dan bunga *bougainvillea* ungu. Kemudian, pewarna semulajadi mengalami proses degradasi dibawah pancaran cahaya selama enam minggu. Bagi pencirian penyerapan optik pewarna semula jadi, spektroskopi UV-Vis telah digunakan. Hasil kajian menunjukkan bahawa MP menyerap tiga julat cahaya, iaitu 400-600 nm (klorofil a), 530-550 nm (antosianin) dan 650-670 nm (klorofil a). Selepas enam minggu, MP menunjukkan ketahanan kepada cahaya yang sangat baik dengan mempunyai peratusan fotodegradasi terendah (50.73%) berbanding BGP (83.88%) dan VBF (65.66%). Spectra FTIR MP, BGP dan VBF menunjukkan kehadiran kumpulan berfungsi tegangan OH, C-H, C=O, C-O-C. Oleh itu, kajian ini menjelaskan bahawa MP berpotensi sebagai fotosensitizer yang memberangsangkan dalam pembinaan sel suria hibrida.

Kata kunci: Fotodegradasi, antosianin, klorofil, peratusan fotodegradasi

1.0 INTRODUCTION

The increasing demand for energy requires our quick action to utilize renewable energy sources effectively. The conversion of solar energy into electric energy by solar cells is a highly promising and environmentally friendly method for electric generation [1]. Among the various solar cells, hybrid dye sensitized solar cell (H-DSSC) is an attempt to produce clean energy. In H-DSSC, the photons are converted into electric current by charge injection from excited dye molecules into the conduction band of a wide band gap semiconductor [2]. Dye act as a sensitizer to absorb the light available on the surface of the metal oxide semiconductor because sensitizers have broad absorption band to harvest a large fraction of sunlight [3].

The performance of H-DSSC depends on the dye utilized as a sensitizer. The light-harvesting range of the dye should extend from visible to near-infrared regions [1]. Rutherium (II), Ru based complexes had received particular interest as photo sensitizer due to their favorable photo electrochemical properties and high stability in the oxidized state. However, the shortage of noble metal and thehigh cost of Ru dyes limits their large scale commercialization [4]. Hence, natural dyes were introduced as a viable alternative to the synthetic dyes because it is environmentally friendly, biodegradable and cost effective.

Anthocyanin based sensitizers are one of the most economical ones as it is 50 times more cost-effective compared to Ru based DSSC as suggested by Furukawa *et al*. [5]. Earlier Amogne *et al*. reported the researchers manufactured DSSCs using anthocyanin extracted from raspberries, sham berries, grape and hibiscus green leaves, resulting a conversion efficiency from 0.04 to 1.50% [6]. These results are quite encouraging and remain one of the motivated factors to pursue natural dyes. Anthocyanin is one of the derived structures taken from flavanol. Examples of anthocyanin are delphinidin (blue to red), pelargonidin (orange), and cyanidin (orange to red). Red, blue and purple are the color usually appear in anthocyanins [7]. Besides, anthocyanins are most distinguished by their spectrum of colors, which is defined by the wavelength.

Chlorophyll is a common and dominant natural color pigment with absorption within visible light range, converting sunlight to chemical energy [8]. This color pigment absorbs light from red(577-492 nm), blue (492-455 nm), and violet (455-390 nm) wavelength and reflected as green (577-492 nm) wavelength [9]. Maximum absorption of chlorophyll a at 433 nm and 665 nm while chlorophyll b at 465 nm and 652 nm [10].

In this research, mangosteen pericarp (*Garcinia mangostana L.*), black grape peel (*Vitis vinifera*), and violet *Bougainvillea* flowers (*Bougainvillea spectabilis*) were chosen as photo-sensitizing sources for the re-use of waste. Generally, mangosteen pericarp (MP) is a kind of fruit waste and not be consumed by humans and animals, yet it contains a concentrated purple pigment that can be used as the photosensitizer. Black grape peel (BGP) is chosen because it identifies the different dye in the fruit of the peel that can and cannot be eaten. While the violet *Bougainvillea* flowers (VBF) is chosen because they are readily available. A detailed comparison will be discussed in this paper on the degradation of dye in different sources. Finally, the dye which is strong and less degradation and is chosen as photosensitizer in H-DSSC.

2.0 METHODOLOGY

Mangosteen and black grape fruits were purchased from a local market at Terengganu, Malaysia. Meanwhile, violet Bougainvillea flowers were collected from a garden at a village in Terengganu, Malaysia. All aqueous solutions were prepared using ethanol.

Figures 1 (a), (b), and (c) show the natural part of plants used. The mangosteen pericarps, black grape peels, and violet *Bougainvillea* flowers were washed thoroughly with deionized water to remove dust and organics impurities before extraction and oven-dried at 60 oC for 12 hours. The dried plants were crushed into a fine powder using a grinder (Retsch RM 200).

Figures 1 (d), (e), and (f) were showing the colour of mangosteen pericarps, black grape peels, and violet *Bougainvillea* flowers powders were dark red, black, and violet, respectively. 5g of samples were put in 100 ml bottles containing 50 ml of ethanol, and then the solutions were kept for three days in the refrigerator. Subsequently, the extracts were filtered with filter paper (Whatman no.1), and purple extract was collected in a 50 ml beaker [11]. Figure 1 (g), (h), and (i) indicate the colour of the solution of the dye after extraction. The colour of vivid pigments in mangosteen pericarps, black grape peels and violet *Bougainvillea* flowers were dark yellow, dark purple and dark green, respectively. Meanwhile, the experiment for the photodegradation of natural dyes was setup as shown in Figure 2.

Figure 1 (a) Mangosteen pericarp, (b) Black grape peels, (c) violet *Bougainvillea* flowers, (d) Powder of mangosteen pericarp, (e) Powder of black grape peel, (f) Powder of violet *Bougainvillea* flowers, (g) Extraction of mangosteen pericarp, (h) Extraction of black grape peels and (i) Extraction of violet *Bougainvillea* flowers

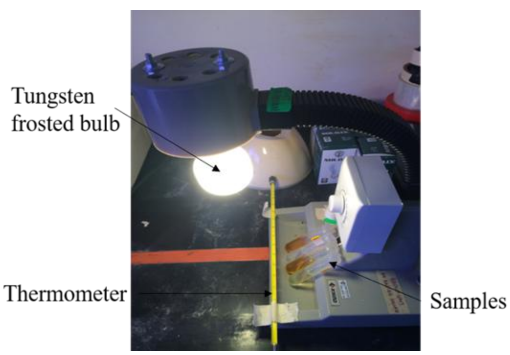


Figure 2 Experiment setup for photodegradation of natural dyes

UV-vis spectroscopy was used to characterize the optical absorption properties of natural dyes before and after light exposure. Light absorption measurements of natural dye solutions were performed at the wavelength range of 200-900 nm by Perkin Elmer Lambda 35 UV-visible spectrophotometer. The FTIR spectra of natural dyes were recorded using a FTIR spectrophotometer (IR Tracer-100) [12].

The data of the degradation of color pigment of mangosteen pericarp, black grape peel, and violet *Bougainvillea* flowers were presented in terms of percentage by using formula at equation 1.

$$\text{Percentage of photodegredation} = \frac{A_0 - A_1}{A_0} \times 100\% \quad (1)$$

A_0 was defined as absorbance before exposure, and A_1 was defined as absorbance after exposure to light. While the energy gap of the three dyes was determined using equation 2.

$$E_g = hc / \lambda \quad (2)$$

Where E_g is energy gap, *h* is Planck constant (6.23 x 10^{-34} m^2kg/s), c is the speed of light (3.00 x10^8 m/s), and λ is the wavelength of the absorption spectra.

3.0 RESULTS AND DISCUSSION

3.1 UV-Visible Absorption of Natural Dyes

Figure 3 shows the UV-Visible absorption spectra of the natural dyes used in this study. The figure shows that mangosteen pericarp absorbs two ranges of light wavelengths, namely at 400-600 nm and 650-670 nm, with maximum peaks at 401 nm and 665 nm, respectively. Meaning that mangosteen pericarp can absorb a very wide range of light spectrum [13, 14]. Extraction of black grape peel shows the presence of anthocyanin with a maximum absorption peak at wavelength 470-550 nm [15, 16]. Meanwhile, there was the presence of chlorophyll a at 402 nm and 664 nm. Figure 3 (c) shows absorption spectrum of violet *Bougainvillea* flowers extract. It was found two absorption peaks, at 409 nm and 665 nm which can be associated with the chlorophyll *a*. The chlorophyll *b* is estimated from the absorbance at 441 nm and 608 nm. Furthermore, beta carotene characteristic presence at 475 nm [17].

The color and stability of anthocyanin are influenced by pH, light, temperature, and structure. The pH of 100% ethanol is 7.33, whereas the pH of pure water is 7.00. The pH of the solution affects the pigment of anthocyanin. Anthocyanin is one of the subclasses of phenolic phytochemicals. Anthocyanin is in the form of glycoside (anthocyanidin glycosides and acylated anthocyanin). Then again, anthocyanin is the glycosylated form of anthocyanidins. The conjugated bonds of anthocyanin bring about red, blue and purple-colored plants [18]. The difference in UV-vis absorption is due to the different sources of natural dye, whereas MP and BGP are fruit while VBF is a flower. Hence the types of anthocyanin may differ.

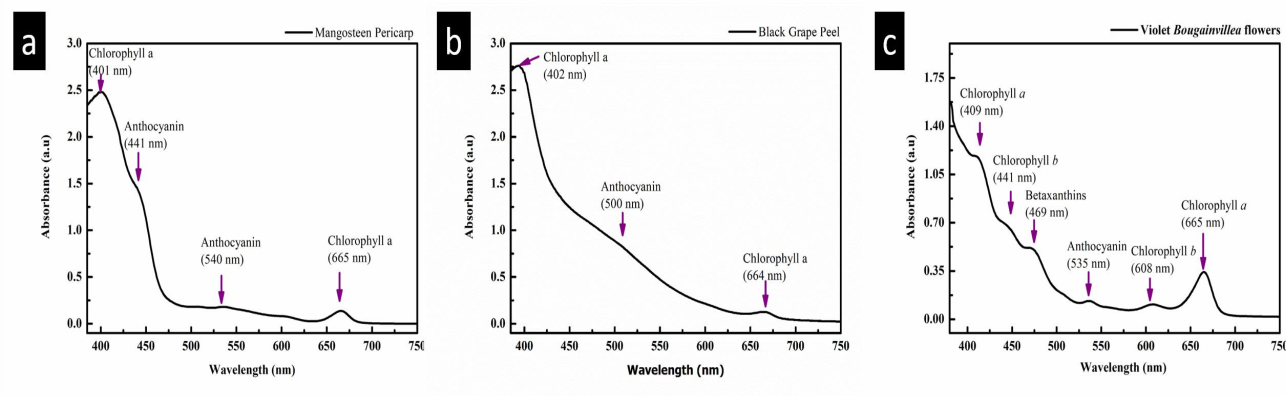


Figure 3 UV-Vis absorption of PNDs extracted from mangosteen pericarp, black grape peel and violet *Bougainvillea* flowers

3.2 Functional group of Natural Dyes

The FTIR characterization was used to prove the presence of a functional group of anthocyanin content in the ingredients of the dye solution, as shown in Figure 4. The values referring to the emerging bands and the functional groups present are summarized in Table 1. The broad uptake at region a indicate the presence of OH group and hydrogen bonding that occur as intermolecular interaction of anthocyanin. Meanwhile, to the peak appearing at b region for C-H stretching. The presence of C-H stretching vibration confirms the chlorophyll derivatives in natural dyes and is well matched with UV-Vis absorption spectra in Figure 3 [19]. In addition, two adjacent peaks at region c indicate the carbonyl group (C=O). The band in region d corresponds to C-O-C ester stretching. The FTIR spectra of these compounds show benzene group's vibration peaks at region e.

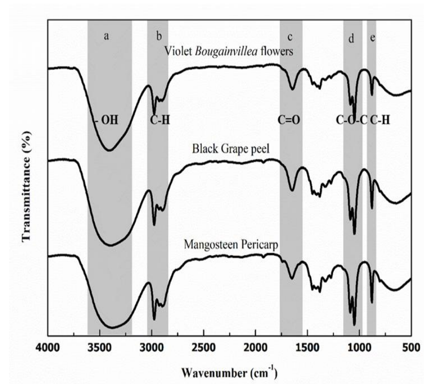


Figure 4 FTIR spectra of mangosteen pericarp, black grape peel and violet Bougainvillea flowers

Table 1 FTIR characterization of bonding present in mangosteen pericarp, black grape peel and violet Bougainvillea flowers

Sample	Intensity (cm^{-1}) a (-OH)	b (C-H)	c (C=O)	d (C-O-C)	e (C-H)	Ref.
Mangosteen pericarp	3403.61	2970.77	1651.52	1045.32	870.87	[13, 20-22]
Black grape peel	3402.52	2978.39	1651.51	1045.31	879.60	[23-25]
Violet *Bougainvillea* flowers	3410.15	2970.77	1642.80	1045.32	879.59	[19]

3.3 Photodegradation of Natural Dyes

3.3.1 Appearance Color of Solution Dye

After six weeks of exposure to the light, the extraction of mangosteen pericarp, black grape peels, and violet *Bougainvillea* flowers showed its discoloration due to degradation, as shown in Figure 5.

The yellowish of mangosteen pericarp dye turns to light yellow, while the black grape peels dye also turns to light yellow. At the beginning of the extraction, the extraction of black grape is dark purple. Lastly, the extraction of violet Bougainvillea flowers turns colourless after exposure to light for six weeks.

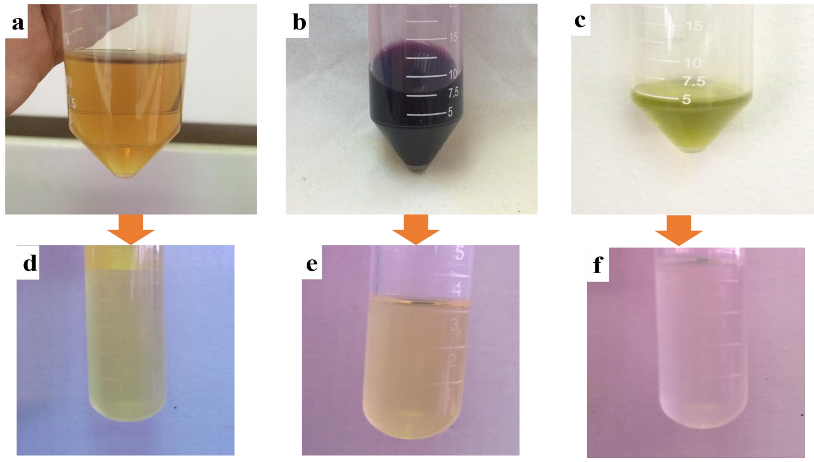


Figure 5 Discoloration of (a) Mangosteen pericarp (b) Black grape peel and (c) Violet Bougainvillea flowers after undergoing photodegradation (d, e and f)

3.3.2 UV-Visible Absorption of Photodegraded Solution Dye

Figure 6 shows the absorption spectrum of mangosteen pericarp, black grape peel, and violet Bougainvillea flowers after the photodegradation process for six weeks. The values referring to dotted lines in the Figure 6 are summarized in Table 2-4. The reference for the absorption was denoted by week 0. There was a progressive decline of the primary band Intensity (666 nm) for mangosteen pericarp (665 nm) for black grape peel, and violet Bougainvillea flowers. In this study, we focused on the chlorophyll peak at wavelength 650 - 700 nm and anthocyanins peak at 470 – 550 nm. The extraction of mangosteen pericarp shows the most decline at chlorophyll a peak, which is 88.98%, compared to black grape peel (56.66%) and violet Bougainvillea flowers (73.76%). Hence, the absorption of dye into the light become declines over the time. Photodegradation of anthocyanins in BGP was 83.88% highest compared with VBF was 65.66%, and MP was 50.73%.

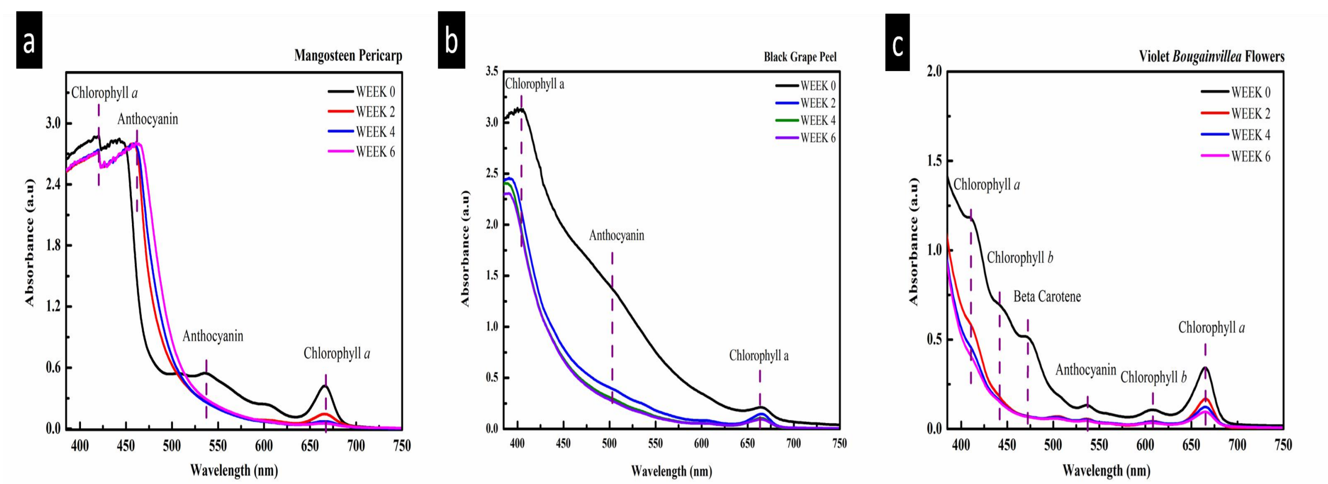


Figure 6 UV-VIS absorption of (a) Mangosteen pericarp, (b) Black grape peels and (c) Violet Bougainvillea flowers, after undergoing photodegradation for 0, 2, 4, and 6 weeks

Table 2 Photodegradation of Anthocyanin and Chlorophyll a in mangosteen pericarp after exposure to the light for 6 weeks

Mangosteen pericarp	Anthocyanin	Chlorophyll *a*		Ref.
Range absorption (nm)	530-550	440-460	650-670	[14, 21, 26]
Maximum peaks (nm)	540	444	665	
A_{wo}	0.545	2.816	0.420	
A_{w4}	0.286	2.690	0.0736	
A_{w6}	0.268	2.590	0.0457	
% Degradation	50.73	8.952	88.98	

Table 3 Photodegradation of Anthocyanin and Chlorophyll a in black grape peel after exposure to the light for 6 weeks

Black grape peels	Anthocyanin	Chlorophyll *a*		Ref.
Range absorption (nm)	470-550	390-420	650-680	[15]
Maximum peak (nm)	500	404	664	
A_{wo}	1.405	2.550	0.216	
A_{w4}	0.309	1.158	0.106	
A_{w6}	0.296	1.141	0.094	
% Degradation	83.38	55.23	56.66	

Table 4 Photodegradation of Anthocyanin and Chlorophyll a in violet Bougainvillea flowers after exposure to the light for 6 weeks

Violet *Bougainvillea* flowers	Beta Carotene	Anthocyanin	Chlorophyll				Ref.
			a		*b*		
FRange absorption (nm)	460 – 500	500-550	400-425	650-670	425-450	600-625	[27, 28]
Maximum peaks (nm)	469	535	409	665	441	608	
A_{w0}	0.52	0.13	1.18	0.34	0.49	0.11	
A_{w4}	0.07	0.05	0.46	0.12	0.17	0.04	
A_{w6}	0.07	0.05	0.39	0.09	0.16	0.04	
% Degradation	86.48	65.66	66.97	73.76	68.41	63.55	

3.3.3 FTIR Analysis of Photodegraded Solution Dye

The functional groups active in anthocyanin, betaxanthins, chlorophyll a, and chlorophyll b can be seen in their structure, as shown in Figure 7. Using the FTIR spectroscopy, it shows that the functional group of anthocyanin and chlorophyll changed their peaks due to the photodegradation effect, as shown in Figure 8. The details of the wavenumber changes were recorded in Table 5. Referring to the peak a (-OH stretching of hydroxyl group), extraction of mangosteen pericarps, black grape peels, and violet Bougainvillea flowers showed the peaks becomes greater and flatten as the times of exposure is increased. Meanwhile, the C-H stretching of the methyl group (peaks b and e) showed no changes in their peaks. Referring to peak c (C=O stretching of carbonyl group), the peak was shifted to the left (1-4 cm^{-1}) as exhibit in the graph as there were changes in the wavenumber. Besides, this situation also happened to the peak d (C-O-C stretching of methoxy group), where the peaks shifted to the left (1-4 cm^{-1}) after six weeks of exposure to the light.

It can be observed that three functional groups (-OH, C=O and C-O-C) show peak shift after exposure to the light due to the light penetration, which could cause the structure transform of anthocyanins, betaxanthins, and chlorophyll. The hydroxyl group in these natural dyes was identified as the most reactive functional group that was rather easily replaced by other substituents.

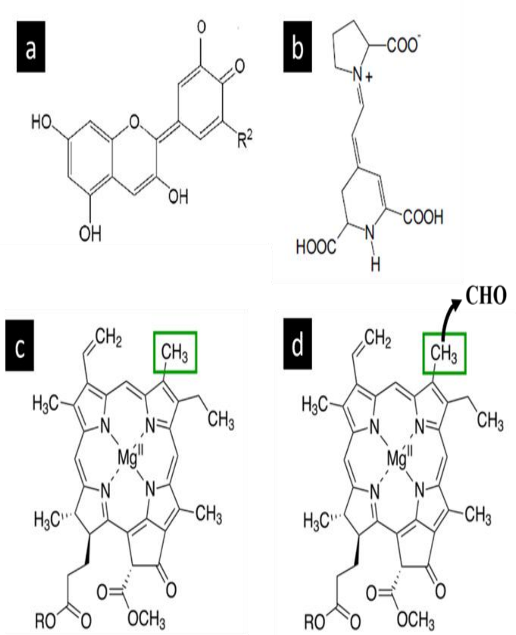


Figure 7 Molecular structure of (a) anthocyanin, (b) betaxanthins, (c) chlorophyll a, (d) chlorophyll b [8, 29, 30]

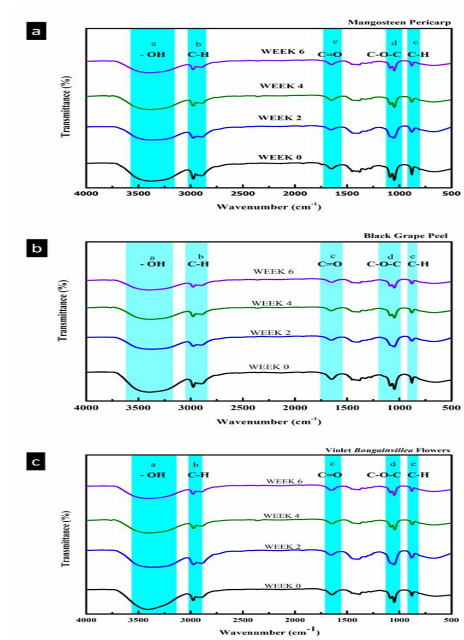


Figure 8 FTIR spectra of the extraction of (a) Mangosteen pericarp, (b) Black grape peel, and (c) Violet *bougainvillea* flowers, after undergoing photodegradation

Table 5 The frequency changes in FTIR spectra of the extraction of the mangosteen pericarp, black grape peels and violet *Bougainvillea* flowers

Peak	***a*** **(cm^{-1})**		***b*** **(cm^{-1})**		***c*** **(cm^{-1})**		***d*** **(cm^{-1})**		***e*** **(cm^{-1})**	
Period (Week)	0	6	0	6	0	6	0	6	0	6
Mangosteen pericarp	3383	3390	2974	2974	1651	1652	1048	1049	879	879
	-OH		C-H		C=O		C-O-C		C-H	
Black grape peels	3348	3383	2974	2974	1643	1647	1045	1049	879	879
	-OH		C-H		C=O		C-O-C		C-H	
Violet *Bougainvillea* flowers	3321	3414	2974	2974	1639	1643	1045	1049	879	879
	-OH		C-H		C=O		C-O-C		C-H	

3.3.4 The Energy Gap of Natural Dyes Before and After Degradation

The mangosteen pericarp, black grape peel, and violet Bougainvillea flowers tend to degrade are evident, as shown in Table 6. The optical energy gap of mangosteen pericarp became narrow, from 1.824 to 1.804 eV, after six weeks of exposure to the light. The calculated optical energy gap for black grape peel is 1.826 eV, compared to its value after exposure, which is 1.814 eV. Meanwhile, the optical energy gap for violet Bougainvillea flowers extracts before and after exposure are 1.832 and 1.829 eV, respectively. The results show that the optical energy becomes narrower as the light exposure is getting longer. Decreasing the energy gap can be attributed to form a trap level between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy states, making the energy transitions workable and results in the reduction of the optical band gap [31]. Thus, mangosteen pericarp has a greater possibility to exhibit higher photo-catalytic activity in the visible region.

Table 6 Energy gap of natural dyes (a) Mangosteen pericarp, (b) Black grape peel, and (c) Violet *Bougainvillea* flowers

Natural Dye	Optical Energy Gap (eV)	
	Before expose to light	After 6 weeks expose to the light
Mangosteen pericarp	1.824	1.804
Black grape peel	1.826	1.814
Violet *Bougainvillea* flower	1.832	1.829

4.0 CONCLUSION

In this research, natural dyes from mangosteen pericarp, black grape peel, and violet Bougainvillea flowers have their strength in sustaining their colour pigment. Natural dyes can be quickly and safely extracted by a simple technique, using ethanol. The UV-visible absorption of the extracted dyes where studied. The absorption spectrum is measured in the range of wavelengths of 350-750 nm. Photodegradation affect the optical properties of the dyes can be seen through the changes in absorbance spectrum (UV-vis analysis) and shifting peaks of the functional group (FTIR analysis). Among the dyes extracted, mangosteen pericarp gave the longest life-time by proven its percentage of degradation (50.73%) after 6 weeks. Further research remains to be required to improve the performance of natural dyes for solar cell application. This simple, cost-effective, and environmental-friendly extraction with good sustaining towards light shows that mangosteen pericarp has the potential for hybrid solar cell.

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