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Utilization of Natural Dyes from *Zingiber officinale* Leaves and *Clitoria ternatea* Flowers to Prepare New Photosensitisers for Dye-Sensitised Solar Cells

Norasikin A. Ludin[1], *Mahmoud A.M. Al-Alwani*[2,3], *Abu Bakar Mohamad*[3], *Abd. Amir H.Kadhum*[3], *Norul Hisham Hamid*[4], *Mohd Adib Ibrahim*[1], *Mohd Asri Mat Teridi*[1], *Tarik M. Ali Al-Hakeem*[5], *Abduljabbar Mukhlus*[6], *Kamaruzzaman Sopian*[1]

[1] Solar Energy Research Institute, Universiti Kebangsaan Malaysia, Bangi 43600, Selangor, Malaysia
[2] Department of Biology, College of Education for Pure Sciences/Ibn Al-Haitham, University of Baghdad, Baghdad, Iraq
[3] Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, Bangi 43600, Selangor, Malaysia
[4] Institute of Tropical Forestry and Forest Products, Universiti Putra Malaysia, Serdang 43400, Selangor, Malaysia
[5] Isra'a University Collage, Pharmacy Department, Baghdad, Iraq
[6] Department of Biology, Madenat al Elam University College, Al Tajy, Baghdad, Iraq
*E-mail: mamash73@yahoo.com

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Chlorophyll and ternatin were extracted from *Zingiber officinale* leaves and *Clitoria ternatea* flowers, respectively. These natural dyes were applied as sensitisers in TiO_2-based dye-sensitised solar cells (DSSCs). Among 10 different solvents, the ethanol extracts revealed the highest absorption spectra of natural dyes extracted from *Z. officinale* and *C. ternatea*. A major effect of temperature increase was the increased extraction yield. High chlorophyll and ternatin yields were obtained under extraction temperatures of 80 °C and 70 °C, respectively. A notable decrease in *C. ternatea* dye concentration at temperatures >70 °C was also observed. High dye concentrations were obtained using acidic extraction solutions, particularly those with a pH value of 4. Experimental results showed that the DSSC fabricated with chlorophyll extracted from *Z. officinale* leaves exhibited a conversion efficiency of 0.30%, open-circuit voltage (V_{oc}) of 0.56 V, short-circuit current (I_{sc}) of 0.8 mA/cm^{-2} and fill factor (*FF*) of 57.93%. The DSSC sensitized with ternatin from *C. ternatea* flowers displayed a conversion efficiency of 0.13%, V_{oc} of 0.54 V, I_{sc} of 0.3 mA/cm^{-2} and *FF* of 81.82%.

Keywords: DSSC, *Zingiber officinale*, *Clitoria ternatea*, natural dyes, chlorophyll, ternatin

1. INTRODUCTION

The development of photovoltaic cells (PVC) has been the subject of intensive energy research over the last thirty years. Third-generation PVC technologies differ from those of first- and second-generation with their optimised efficiency and considerably decreased production costs (Green 2006). Most solar cells of third-generation are still in the research stage; these cells contain dye-sensitised solar cells (DSSCs) [1, 2]. DSSC is device that directly converts sunlight into electricity based on the sensitisation of semiconductors, such as ZnO and TiO_2 [3]. The basic structure of a DSSC is similar to that of original Grätzel design. The DSSC structure possesses three primary parts: (1) semiconductor film electrode (anode) which is a conducting glass electrode with a porous layer of TiO_2 coated with a dye as light sensitiser (2) electrolyte layer, which surrounds the dye and acts as a source to compensate for lost electrons; and (3) counter electrodes (cathode), which are typically conducting glass coated with graphite or platinum [4]. The principal steps for DSSC to work are (1) visible light absorption (2) charge separation (3) charge collection [5]. The efficiency of a fabricated solar is dependent on the performance of each of these steps. The performance of DSSC was maximised by the material and cell design. The sensitiser, as the light harvester in a DSSC, should possess an absorption spectrum that covers a broad region from the visible light spectrum and anchoring groups, such as hydroxyl or carboxyl groups, for binding with the TiO_2 film [6].

The electricity is generated on an anode, which is consisting of a sintered semiconductor TiO_2 film on TCO (transparent conductive oxide); this TCO, which is typically F-doped SnO_2 or indium SnO_2 is used to cover a glass sheet and allow sunlight to pass through the DSSC that is sensitised with a dye and penetrated with a redox couple electrolyte [7]. Nanocrystalline TiO_2 provides an indispensable large surface area for natural dye absorption. Dye molecules, as photosensitisers of photoelectrode in fabricated DSSC, collect light photons and produce excited electrons from the highest occupied molecular orbital (HOMO) in the ground state to the lowest unoccupied molecular orbital (LUMO) in excited state [2]. DSSCs differ from other types of PVCs, such as classic silicon cells, in both their physical processes and the chemical construction that control the cells operation [8]. The main parameters determining the power conversion efficiency of the DSSCs include the absorption of dyes, which are used as sensitisers, and the anchorage of the dyes on the surfaces of semiconductors [9]. In nature, some leaves, flowers, seeds and fruits consist of several natural pigments that can be readily extracted to prepare the natural sensitisers for DSSCs [10]. The use of natural dyes in solar cell is promising in the development of DSSC technology. Furthermore, such utilisation decreases the high costs of chemical synthesis and noble metals. Therefore, DSSC has received considerable attention from the academic and industrial communities [11-13]. Generally, plant cells absorb sunlight wavelength at the range of visible light spectrum and reflect sunlight in other regions of the visible light. Consequently, the plant appears coloured. The chemical structures of plant dyes determine its absorption of different light wavelengths and the colour and the energy conversion efficiency of the dyes [14]. The extraction yield of natural pigments from plant tissues depends on various extraction conditions, especially light, solvent type, temperature and pH of extracts [15]. Different extraction techniques are used to increase the extraction yield and enhance the quality of natural dyes from various plant species [16]. The three most commonly used extraction methods are cold organic solvent, Soxhlet hot organic solvent and heating in water. Each extraction method affects the performance of the sensitiser in DSSC [17].

In the present study, natural dyes were extracted from *Zingiber officinale* leaves and *Clitoria ternatea* flowers to prepare natural sensitisers to fabricate DSSC. The effects of three main parameters namely, temperature, solvent and pH on natural extract yield were investigated. The absorption spectra peaks and functional groups of the extracted dyes from *Z. officinale* leaves and *C. ternatea* flowers were assigned using UV–Vis spectroscopy and Fourier transform infrared spectroscopy (FTIR) analysis. Also the scanning electron microscope (SEM) and X-ray diffraction were used to study the optical properties of deposited TiO_2. Energy dispersive X-ray (EDX) analysis was utilised to investigate the inhibition of TiO_2 crystallinity. To evaluate the performance of extracted dyes as photosensitisers, DSSCs were fabricated. In addition, the main parameters of solar cell namely, open-circuit voltage (V_{OC}), short-circuit current (I_{SC}), fill factor (*FF*), efficiency (η) and maximum power point (P_{max}), were also determined.

2. MATERIALS AND EXPERIMENTS

2.1 Materials

Scientific classification of plants

Kingdom: Plantae	Kingdom: Plantae
Order: Zingiberales	Order: Fabales
Family: Zingiberaceae	Family: Fabaceae
Genus: *Zingiber*	Genus: *Clitoria*
Species: *officinale*	Species: *ternatea* L.
Common name: Ginger	Common name: Blue pea
Part used: Leaves	Part used: Flowers

Ginger is the common name of *Z. officinale*. Ginger is indigenous to southern China and grown in other countries of Asia, such as Malaysia. Ginger rhizomes are a mixture of zingerone, gingerols and shogaols, which cause the characteristic odour and flavour of ginger; the green leaves are a source of chlorophyll pigments [18]. *C. ternatea* flowers display attractive deep blue colour, which can also be pure white and considerably short pedicel late. This plant is native to tropical equatorial Asia, but it has been introduced to Australia and Africa. A wide range of secondary metabolites, including flavonol glycosides, triterpenoids, steroids and anthocyanins, has been isolated from *C. ternatea* [19].

2.2 Experimental

2.2.1 Preparation of natural dye sensitisers

Fresh *Z. officinale* leaves and *C. ternatea* flower petals were washed with water and oven dried at 45 °C for 24 h and 40 °C for 8 h, respectively. Using a grinder (Mulry function disintegrator SY-04) the dried materials were crushed into fine powder. Plant materials were stored in a dry dark place at room temperature for later use.

2.2.2 Preparation of DSSCs

TiO_2 paste was prepared according to the methodology described in our previous study [20-22]. FTO was used as a basis for the photoelectrode. To prepare the FTO substrate, conductive glass (3 cm × 2.5 cm) was cleaned using acetone. The FTO sheet was wiped with ethanol to remove any oil, fingerprint and impurity. Multimeter (SANWA, YX360TRF) probes were used to measure resistance across two points on the glass surface. Using transparent tape (Scotch, Magic^{TM} Tape), FTO glass was taped down with its conductive side facing up. Using doctor blade technique, TiO_2 paste was spread evenly onto an area of 1 cm^2 on the conductive face of the FTO substrate.

The dry TiO_2 electrode was placed facing up and the conductive side of the catalyst-coated counter electrode was positioned to face the TiO_2 layer and sealed by gum**.** The device was injected with liquid electrolyte that contained lithium iodide/iodine (LiI/I_2) into the space between TiO_2 photo anode and cathode through a hole in the counter electrode to prevent the electrolyte from leaking.

2.2.3 Characterisation and measurements

The UV–Vis absorption spectra extracted dyes from *Z. officinale* leaves and *C. ternatea* flower petals were recorded using a UV–Vis spectrophotometer (Perkin Elmer, Lambda 35). The FTIR spectra of the extracted dyes were recorded using a FTIR apparatus (Thermo Scientific, NICOLET 6700). The conversion efficiencies of the fabricated DSSCs were measured under simulated solar light (AM 1.5 100 mW/cm^2). *FF* can be estimated on the basis of the photo current–voltage (*I*–*V*) curve by using the following formula:

$$\mathrm{FF} = (I_{\max} \times V_{\max}) / (I_{sc} \times V_{oc})$$

where $I_{\max}$ and $V_{\max}$ are the photocurrent and photovoltage of maximum power output (P_{max}) respectively; I_{sc} is the short-circuit photocurrent and V_{oc} is the open-circuit photovoltage. The overall solar conversion efficiency (η) of a DSSC is defined as follows:

$$\eta = (I_{sc} \times V_{oc} \times \mathrm{FF}) / P_{in}$$

where P_{in} is the input power.

The calibration standard curve was prepared to measure the concentration of the dyes solutions via determine maximum absorption spectra of each dye solution using UV-Vis spectrometer. The calibration curves for the extracts from *Z. officinale* leaves and *C. ternatea* flowers were prepared by dissolving 10 mg of pure dye in 20 ml of optimized solvent (ethanol). Then, 1 ml to 5 ml aliquots of these stock solutions were diluted in 100 ml of ethanol. Five different calibration standard solutions of each plant dye were prepared with concentrations of 0.01g/l to 0.05g/l. The absorbance at the maximum absorption wavelength $\lambda_{\max}$ of each dye was then measured.

3. RESULTS AND DISCUSSION

3.1 Chemical structure of the extracted natural dyes

3.1.1 Absorption spectra of the extracted dyes

The absorption spectra of the dye extracted from *Z. officinale* leaves and *C. ternatea* flower petals showed absorption peaks at the blue and red regions and green-yellow region, respectively. As shown in Figure 1, the absorbance peaks at 663 and 409 nm indexed to chlorophyll were present in the spectrum of the dye from *Z. officinale* leaves. The peaks at 570 and 618 nm indexed to anthocyanin were present in the spectrum of the dye from *C. ternatea* (Figure 2). The anthocyanin obtained from *C. ternatea* flower is ternatin [23, 24]. The absorption spectrum obtained from *Z. officinale* leaves in the current study agrees with the absorption peak of chlorophyll [25].

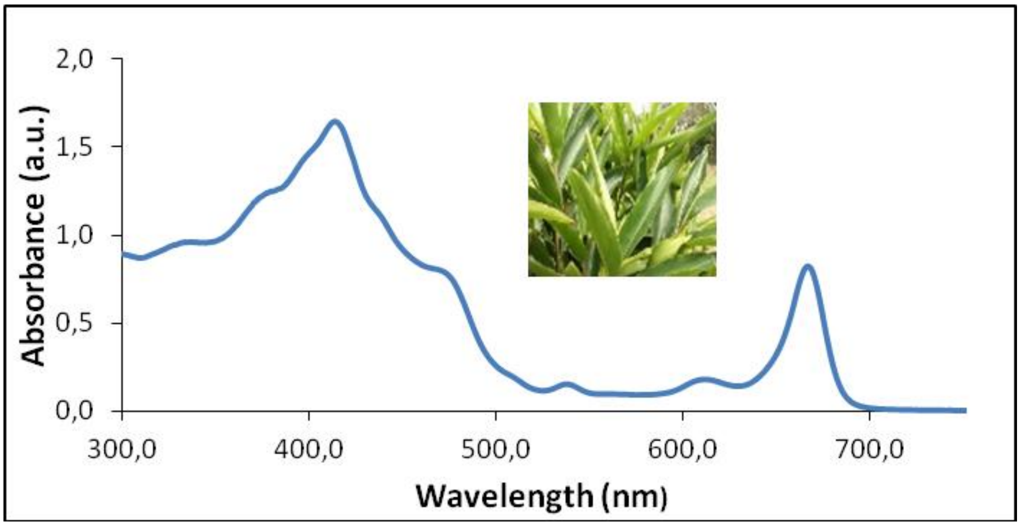


Figure 1. Absorption spectrum of chlorophyll extracted from *Zingiber officinale* leaves

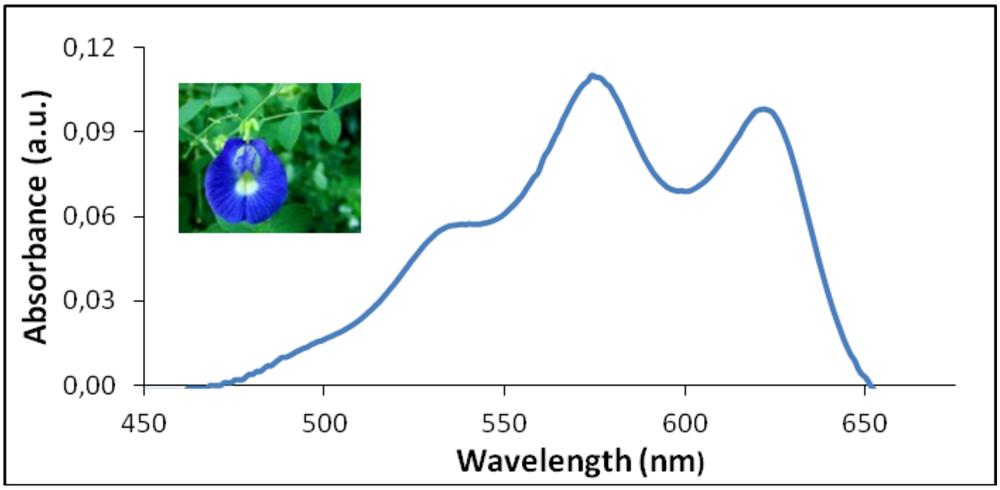


Figure 2. Absorption spectrum of ternatin extracted from *Clitoria ternatea* flowers

3.1.2 FTIR analysis of the extracted dyes

The FTIR spectra of the dyes extracted from *Z. officinale* leaves and *C. ternatea* flower petals are shown in Figures 3 and 4, respectively. The FTIR spectra of the dyes from *Z. officinale leaves* and *C. ternatea* flowers showed almost similar functional group positions. A peak between 3000 cm^{-1} and 3700 cm^{-1} was indexed to the OH group. Peaks at 1074 and 1105 cm^{-1} were attributed to C–O group. Peaks at 1634 and 1645 cm^{-1} with slightly different transmittance intensities were attributed to the C=O and H–C–H groups respectively. The spectral region within 1500–2000 cm^{-1} indicated the infrared absorption of C=C [26-28].

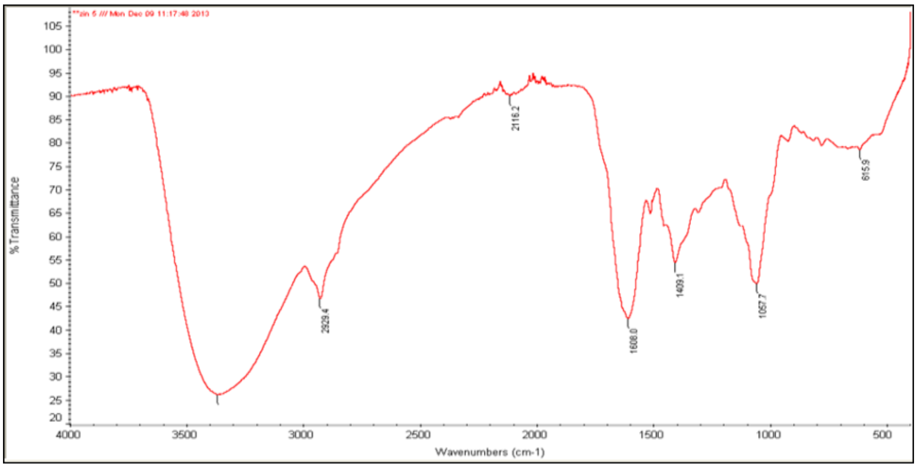


Figure 3. FTIR spectrum of dye extracted from *Z. officinale* leaves

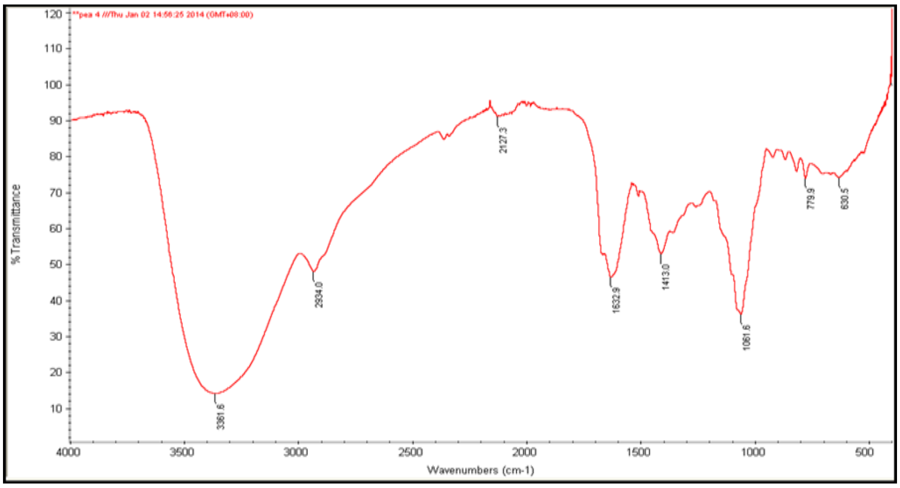


Figure 4. FTIR spectrum of dye extracted from *C. ternatea* flowers

3.1.3 Effects of extraction solvent pigment extraction

Figures 5 and 6 show the effects of 10 different extraction solvents on the absorbance of dyes extracted from *Z. officinale* leaves and *C. ternatea* flower petals. Ethanol, water, methanol, acetonitrile, chloroform, acetone, ethyl ether, *n*-butyl, *n*-hexane and ethyl acetate were used as extraction solvents. Ethanol extracts obtained from *Z. officinale* leaves and *C. ternatea* flowers exhibited the optimum absorbance values of 0.521 and 1.702a.u. respectively. The extraction capabilities of polar organic solvents such as ethanol lead to these results [29]. Ethanol as an organic solvent has been extensively used to extract natural organic dyes from various plant species [30]. Current study results are in agreement with those of Chatha (2006) who reported that they were used polar solvents to obtain high yields from rice species [31].

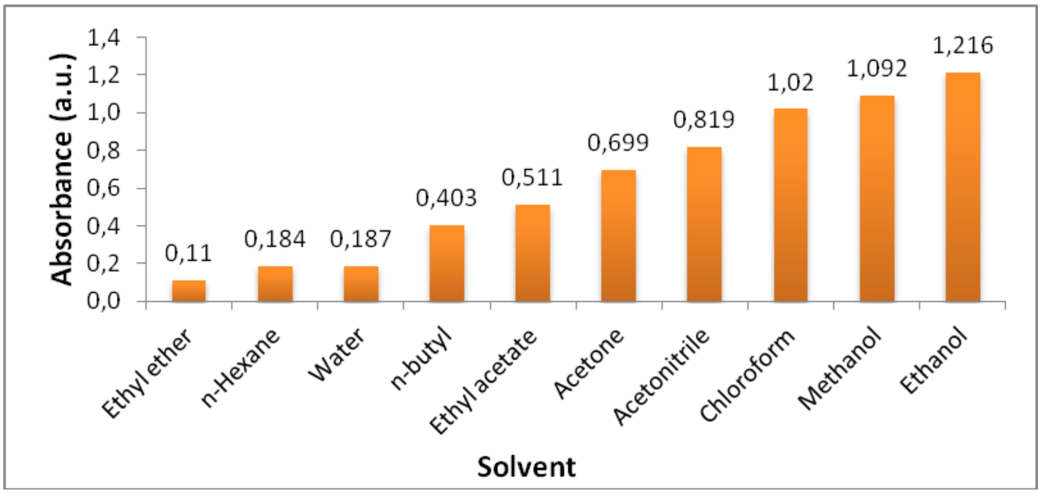


Figure 5. Effects of different solvents on the extract absorbance of *Z. officinale*

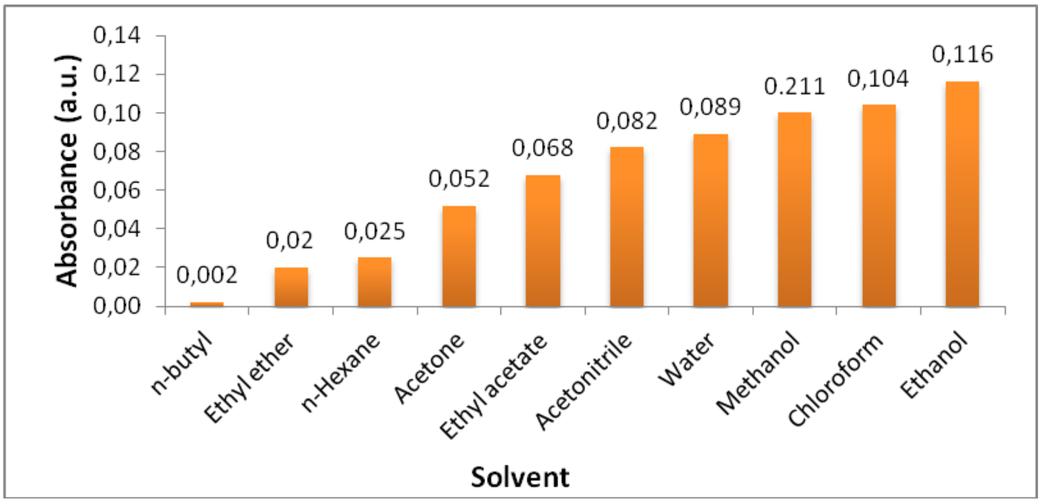


Figure 6. Effects of different solvents on the extract absorbance of *C. ternatea*

3.1.4. Effects of temperature on dye extraction

The effects of five different temperatures (40 °C, 50 °C, 60 °C, 70 °C and 80 °C) on the extraction of pigments from *Z. officinale* leaves and *C. ternatea* flower petals were investigated. Figure

7 illustrates the effects of temperature on the extraction of natural dyes from *Z. officinale* leaves. Aqueous solution of the optimal solvent (ethanol: water, 70:30 v/v) and the temperature of 80 °C provided the highest pigment yield. The boiling point of the ethanol/water mixture was 85 °C. As shown in Figure 7, the concentration of extracted dye from *Z. officinale* leaves increased gradually from 0.35 to 1.122 with the increase of temperature from 40 °C to 80 °C. This result suggested that natural organic dyes are stable at temperature less than 80 °C. The physicochemical properties of ethanol are influenced with high temperature, which decreases the ethanol dielectric constant and the polarity of solvent, thereby enhancing the solubility of polar organic compounds [32]. Jinasena extracted the chlorophyll dye from *Alternanthera sessilis* with various extraction temperatures; they reported that the absorbance of extracted dye improves with increased temperature [33].

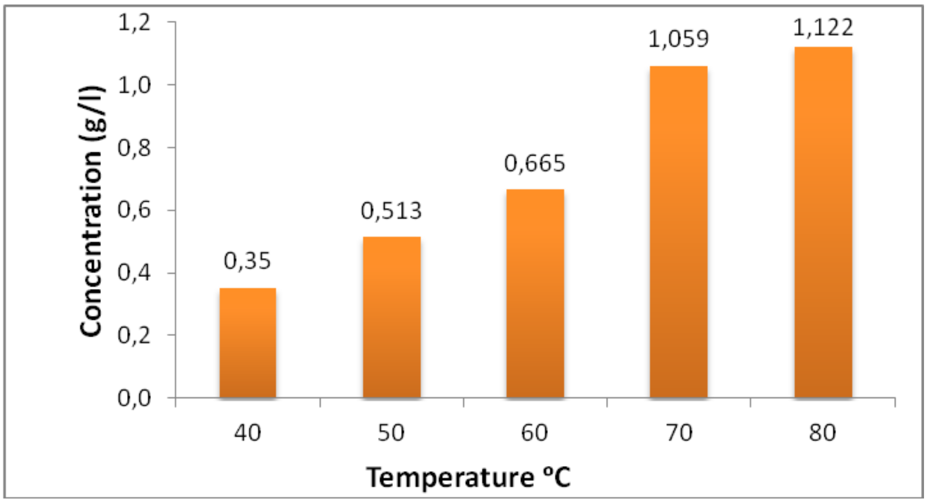


Figure 7. Effects of different temperatures on the dye concentration of *Z. officinale*

The concentration of petal extracts of *C. ternatea* increased from 2.417 at 40 °C to 21.481 at 70 °C (Figure 8). This increased of dye concentration due to the effect of temperature. Increase of temperature may be caused by an increase in pigment molecule diffusivity and pigment solubility; these properties are related to the increase in the internal energy of molecules, which increases the extract concentration [34]. Thus, a major effect of the increased temperature was the increased extraction yield. The present results showed that the optimal temperature was approximately 70 °C. A remarkable decrease in dye concentration at temperatures more than 80 °C was also observed. For instance, dye concentration decreased from 21.481 at 70 °C to 13.087 at 80 °C. Given the high susceptibility of dyes to high temperature, the increase in temperature resulted in a decreased dye yield. Temperatures at >70 °C probably caused a decrease in the extract concentration due to chemical structure degradation of pigments. Durling reported that an increase in extraction temperature increases the extraction yield; additionally, the dye solution concentration decreases because of the extraction of additional inactive compounds at increased temperature (80 °C) [35].

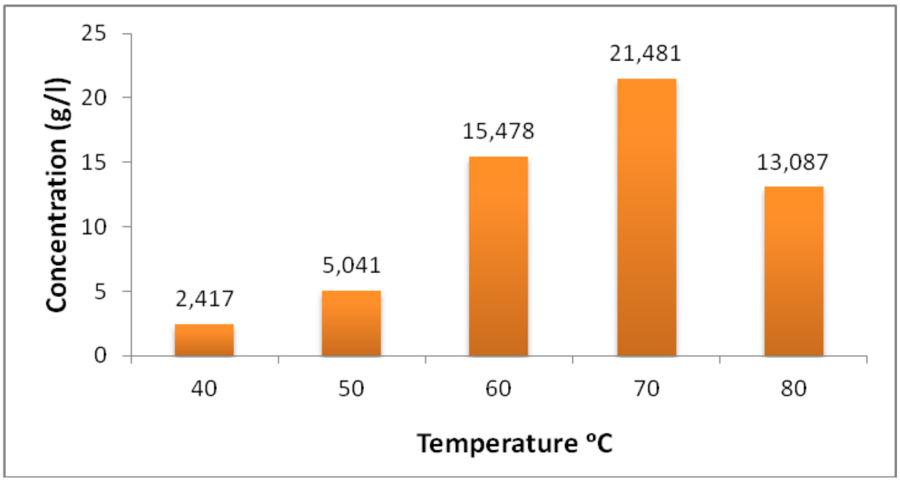


Figure 8. Effects of different temperatures on the dye concentration of *C. ternatea*

3.1.5 Effects of pH on dye extraction

To obtain high dye yields, the pH of the extraction solvent was optimised. Dyes from the *Z. officinale* leaves and *C. ternatea* flower petals were extracted using an aqueous ethanol solution (ethanol:water 70:30 v/v) with pH 4–9 at 80 °C for 45 min. As shown in Figures 9 and 10, acidic extraction solutions with pH 4 contained highest dye concentrations. When the extraction solution pH increased from 4 to 9, gradually the extracted dye concentrations decreased from 10.237 and 17.755 g/l to 4.777 and 2.332 g/l, respectively. Dye concentrations increased with decreased pH and reached the maximum yield in the extraction solution with pH 4. These results indicated that extraction solvents with pH values of 4–6 can be used to obtain high dye yields. Elemental analyses of natural extracts of *Z. officinale* leaves and *C. ternatea* flowers (C, H, N elemental analysis) showed the presence of N contents (2.229 and 1.345 % respectively), the alkalinity and the solubility of these nitrogenous compounds will increase in acidic media (low pH), and this will increase the concentration of natural extracts. Devi indicated that pH considerably affects the stability of extracted dyes [36]. The present result is in agreement with those of previous works [37, 38].

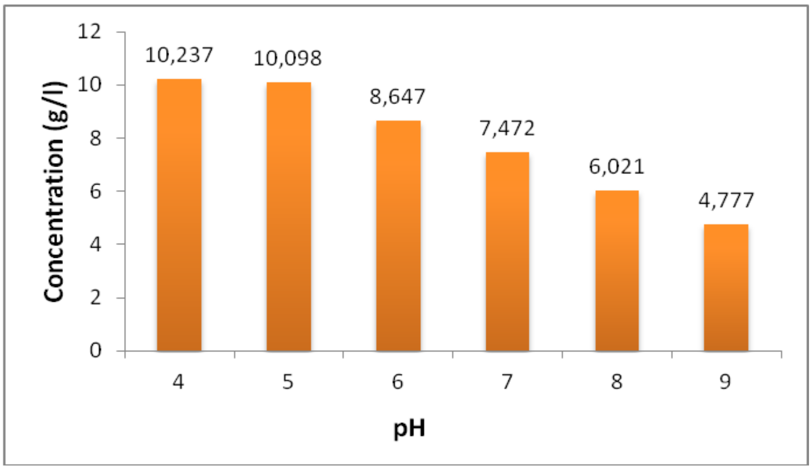


Figure 9. Effects of different pH values on the dye concentration of *Z. officinale*

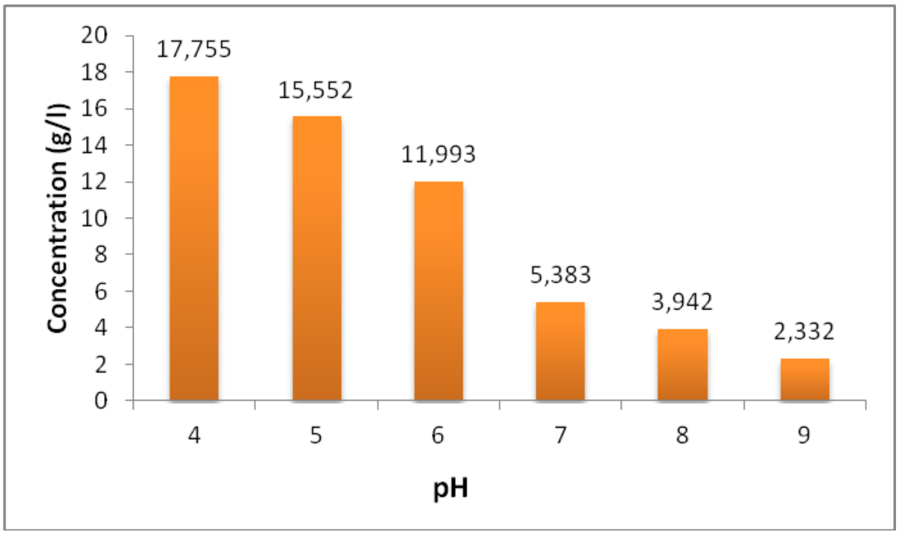


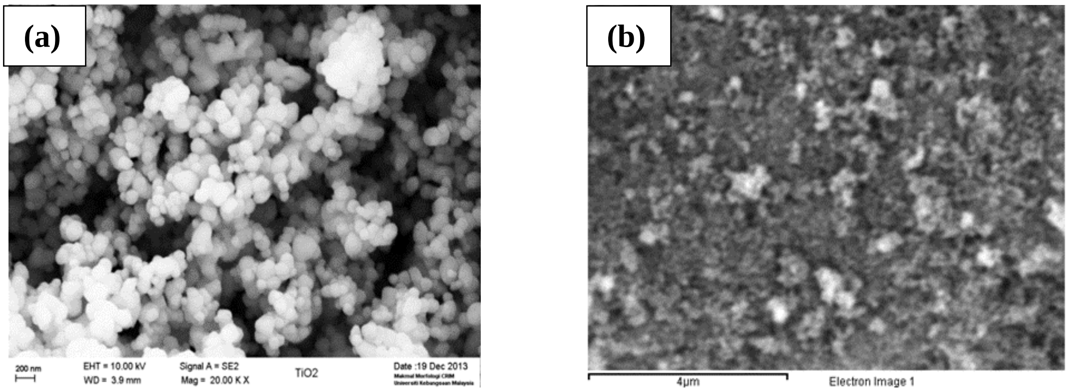
Figure 10. Effects of different pH on the dye concentration of *C. ternatea*

3.2 Applications of the extracted dyes

A photosensitiser is a molecule (dye) that produces a formal change in TiO_2 particles in a photochemical process. To validate the applicability of chlorophyll and anthocyanin dyes as sensitisers in DSSCs, solar cells were designed using the chlorophyll extracted from *Z. officinale* leaves and anthocyanin from *C. ternatea* flower petals. The surface morphological properties of the deposited TiO_2 thin-film electrode were studied through SEM and EDX spectra.

3.2.1 Surface morphology of TiO_2

The SEM images shown in Figure 11 revealed that the TiO_2 particles aggregated into nanoclusters (Figure 11a). Aggregation behaviour is affected with the photo material of the DSSCs [38]. The SEM images of the adsorbed chlorophyll from *Z. officinale* and anthocyanin from *C. ternatea* on TiO_2 particles are presented in Figures 11b and 11c respectively.



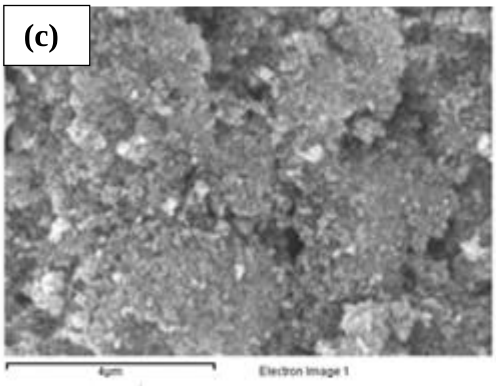
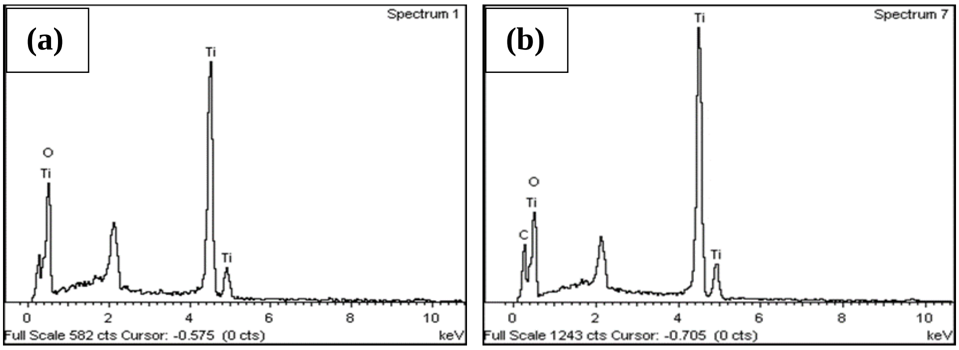


Figure 11. Scanning electron microscope images of (a) pure TiO_2, (b) TiO_2–*Z. officinale* dye and (c) TiO_2– *C. ternatea* dye

These figures indicated that the aggregation of TiO_2 particle increased after dye adsorption. The particles shapes of TiO_2 also slightly changed after dye adsorption (Figures 11a, 11b and 11c). The aggregation of TiO_2 particles due to the ability of the dyes molecules to cover surfaces of TiO_2 particle, thereby causing the surfaces to attach together [39].

3.2.2 EDX spectroscopy analysis

The EDX spectra of the TiO_2 particles are shown in Figure 12a. The spectra exhibited distinct Ti and O peaks. As shown in Table 1, the weight contributions of Ti and O were 57.24% and 42.76% respectively, which confirmed the high purity of TiO_2 particles as photo materials with natural dyes. The EDX spectra of TiO_2 covered by chlorophyll from *Z. officinale* and TiO_2 covered by anthocyanin from *C. ternatea* are illustrated in Figures 12b and 12c, respectively. In addition to the Ti and oxygen peaks, the spectra of the TiO_2–dye complexes showed prominent peaks that were attributed to the functional groups of the dyes. The weight contributions of *Z. officinale* and *C. ternatea* dyes functional groups were 16.32% and 6.67% respectively (Table 1). This result indicated the existence of natural dye functional groups on the surfaces of the TiO_2 particles [40].



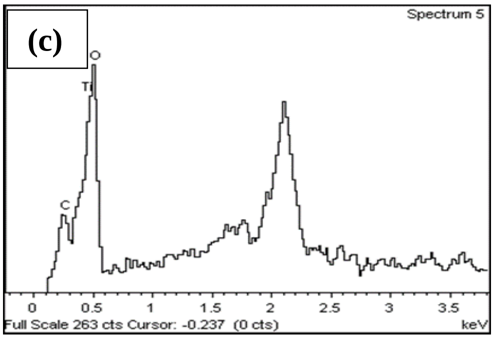


Figure 12. Energy dispersive X-ray (EDX) spectra of (a) pure TiO_2, (b) TiO_2–*Z. officinale* dyes and (c) TiO_2–*C. ternatea* dyes

Table 1. EDX data of pure and dyed TiO_2

Sample	Element	Wt. (%)	At. (%)
Pure TiO_2	Ti	57.24	30.89
	O	42.76	69.11
TiO_2- *Z. officinale* dye	Ti	43.65	19.10
	O	40.03	52.42
	C	16.32	28.48
TiO_2- *C. ternatea* dye	Ti	46.62	21.88
	O	46.71	65.64
	C	6.67	12.48

3.2.3 Performance of DSSC sensitised with the extracted natural dyes

DSSCs were fabricated using dyes extracted from *Z. officinale* leaves and *C. ternatea* flowers as photosensitisers. The *I–V* characteristic curves of the DSSCs prepared with natural dyes were obtained through photovoltaic tests under AM 1.5 solar illuminations. The corresponding *I–V* curves for *Z. officinale* and *C. ternatea* dyes are shown in Figure 13. The photoelectrochemical parameters of the DSSCs fabricated using natural dyes are listed in Table 2. The DSSC prepared using chlorophyll extracted from *Z. officinale* leaves and anthocyanin extracted from *C. ternatea* flowers exhibited the maximum energy conversion efficiencies of 0.30% and 0.13% and the FFs of 57.93% and 81.82% respectively. Generally, natural dyes used as photosensitisers in DSSCs demonstrate lower conversion efficiencies than those of synthetic dyes given the absence of specific functional groups [41].

As shown in Figures 1 and 2, the *Z. officinale* dye displayed broader absorption range than that of the *C. ternatea* dye. The conversion efficiency of a DSSCs fabricated with natural dyes as sensitisers strongly dependent on the presence of available bonds between the dyes molecules and particles of TiO_2; these bonds facilitate the transfer of excited electrons from the dyes molecules to TiO_2 layer [42]. The UV–Vis spectra and *I–V* curves obtained in the present study are agreement with those obtained in previous studies [43, 44]. The DSSCs prepared with chlorophyll from *Z. officinale* and anthocyanin from *C. ternatea* demonstrated a Voc of 0.56 and 0.54 V and I_{sc} of 0.8 and 0.3 mA, respectively. Extensive dye adsorption on the TiO_2 surface causes high numbers of photons to convert to electrons rapidly, thereby causing rapid electron injection [45].

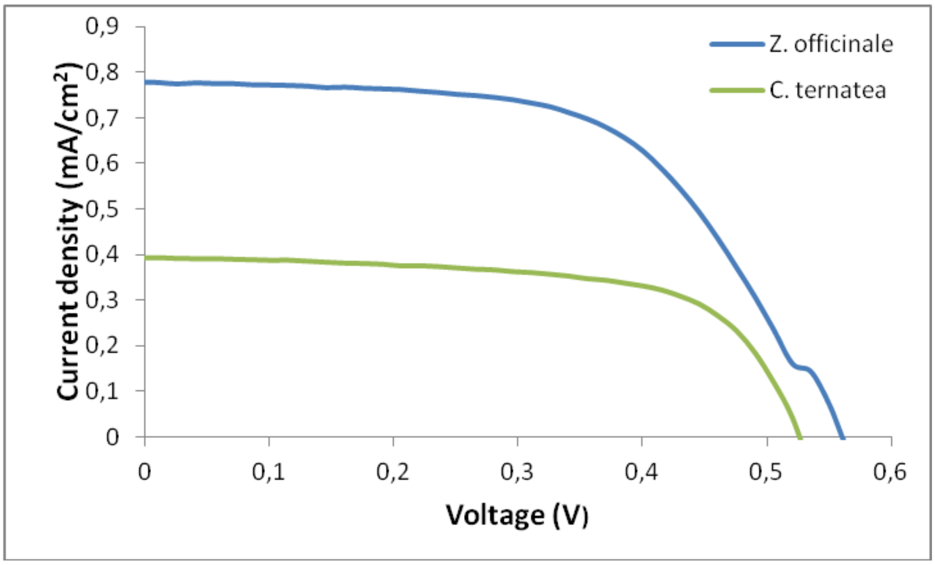


Figure 13. Current–voltage curves of dye-sensitised solar cells (DSSCs) sensitised with dyes from *Z. officinale* leaves and *C. ternatea* flowers

Table 2. Photoelectrochemical parameters of DSSCs sensitised with dyes from *Z. officinale* leaves and *C. ternatea* flowers

Dye	*Voc* (v)	*Isc* (mA)	*Jsc* (mA/cm^2)	*Vm* (v)	*Im* (mA)	*Pmax* (W)	*η* (%)	*FF* (%)
Z. officinale	0.56	0.8	0.8	0.385	0.7	0.3	0.30	57.93
C. ternatea	0.54	0.3	0.3	0.436	0.3	0.1	0.13	81.82

4. CONCLUSIONS

The extracts from *Z. officinale* leaves and *C. ternatea* flowers were studied as natural dyes to prepare photosensitisers for DSSCs. In addition to other components, the extracted dyes contained chlorophyll and ternatin as dyes. The effects of solvent, temperature and pH on natural extract yield were investigated. Results showed that the optimum conditions of natural dye extraction were achieved using ethanol as the polar organic solvent at temperatures of 80 °C for *Z. officinale* leaf extract and 70 °C for *C. ternatea* flower extract. These results indicated the stability of pigments at relatively high temperature and acidic extraction solution, specifically at pH 4. The absorption spectrum peaks and functional groups of extracted natural dye were assigned using UV–Vis spectroscopy and FTIR analysis. To identify the adsorption of natural dye on the surface of TiO_2, SEM and EDX analyses were performed. Under the same extraction, preparation and irradiation conditions, the performance parameters of the DSSC sensitised with chlorophyll from *Z. officinale* leaves were higher than those of the DSSC sensitised with anthocyanin from *C. ternatea* flowers. Various photovoltaic parameters, such as *Isc*, *Voc*, *Pmax*, *FF* and *η*, were evaluated. Higher energy conversion efficiency of 0.30% and *FF* of 57.93% were obtained from fabricated DSSC sensitised with chlorophyll extracted from *Z. officinale* leaves than those of DSSC based on anthocyanin extracted from *C. ternatea* flowers which showed 0.13% and 81.82%, respectively.

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References

1. M.A. Green, K. Emery, Y. Hishikawa, and W. Warta, *Prog. Photovoltaics Res. Appl.*, 19 (2011)84-92.
2. B.E. Hardin, H.J. Snaith and M.D. McGehee, *Nat. Photonics,* 6 (2012)162–169.
3. B. O'Regan, D.T. Schwartz, S.M. Zakeeruddin and M. Gratzel, *Adv. Mater.*, 12 (2000)1263-1267.
4. M. A. M. Al-Alwani, A.B. Mohamad, N.A. Ludin, A.A.H. Kadhum and K. Sopian, *Renewable Sustainable Energy Rev.,* 65 (2016)183–213.
5. U.Bach, Y.Tachibana, J.-E. Moser, S. A. Haque, J.R. Durrant, M. Grätzel, and D.R. Klug, *J. Am. Chem. Soc.,* 121(1999)7445-7446.
6. L. Giribabu, S.V. Kumar, V.K. Challuri, S. Yarasi, G.R. Veerannagari and Y.R. Paidi, *Adv. Optoelectron,* (2011) 8 pp.
7. M.A. Khan, S. M. Khan, M. A. Mohammed, S. Sultana, and J.M.I.J. Uddin, *American Academic & Scholarly Research Journal*, 4(2012)1-10.
8. M. Toivola, F. Ahlskog and P. Lund, *Sol. Energy Mater. Sol. Cells,* 90(2006)2881-2893.
9. E.M. Abdou, H.S. Hafez, E. Bakir, and M.S.A. Abdel-Mottaleb, *Spectrochim. Acta, Part A,* 115(2013)202-207.
10. S. Kishiomoto, T. Maoka, K. Sumitomo and A. Ohmya, *Biosci. Biotechnol. Biochem.,* 69(2005)2122–8.
11. S. Keka, P.D. Saha and S. Datta, *J. Dyes Pigment.,* 94(2012)212–6.
12. M.R. Nishantha, Y.P.Y.P. Yapa and V.P.S. Perera, *Proceed Tech. Sess.*, 28(2012)54–8.
13. M.A.M. Al-Alwani, A.B. Mohamad, A.A.H. Kadhum, N.A. Ludin, N. E. Safie, M. Z. Razali, M. Ismail and K. Sopian, *Int. J. Electrochem. Sci.,* 12 (2017) 747 – 761.
14. H.Chang, M.-J. Kao, T.-L. Chen, C.-H. Chen, K.-C. Cho, and X.-R. Lai, *Int. J. Photoenergy,* 2013: 1-8.
15. M.A.M. Al-Alwani, A.B. Mohamad, A.A.H. Kadhum and N.A. Ludin, *Spectrochim. Acta, Part A,* 138 (2015) 130.
16. A. Oluwaseun, T. Kamil, and A.Y. Oladiran, *Int. J. Eng. Tech.,* 2(2016)34-41.
17. B.C. Mphande and A. Pogrebnoi, *J. Energy Nat. Res.*, 3(2014)38-45.
18. J. Rhode, S. Fogoros, S. Zick, H. Wahl, K.A. Griffith, J. Huang, and J.R. Liu, *BMC Complementary & Alternative Medicine,* **7(**2007)44.
19. P.K. Mukherjee, V. Kumar, N.S. Kumar, and M. Heinrich, *J. Ethnopharmacol.*, 120(2008) 291–301.
20. M.A.M. Al-Alwani, N.A. Ludin, A.B. Mohamad, A.A.H. Kadhum and K. Sopian, *Spectrochim. Acta, Part A*, 179(2017)23–31.
21. X. Wang, X. Min, Z. Fan, D. Bin, F. Hao and Z. Zhengtao, *Nano Energy,* 12 (2015) 794–800.
22. E. Yamazaki, M. Murayama, N. Nishikawa, N. Hashimoto, M. Shoyama, and O. Kurita, *Sol. Energy,* 81(2007)512-516.
23. N. Kumara, P. Ekanayake, A. Lim, M. Iskandar, and L.C. Ming, *J. Sol. Energy Eng.,* 135(2013)031014.

24. K. Wongcharee, V. Meeyoo, and S. Chavadej, *Sol. Energy Mater. Sol. Cells*, 91(2007) 566-571.
25. S.A. Minicante, E. Ambrosi, M. Back, J. Barichello, E. Cattaruzza, F. Gonella, E. Scantamburlo and E. Trave, *J. Phys. D Appl. Phys.*, 49(2016)295601-295608.
26. R.M. Silverstein, G.C. Bassler, and T.C. Morrill, *John Wiley & Sons*, 2014, 8th Edition, London.
27. R. Syafinar, N. Gomesh, M. Irwanto, M. Fareq and Y.M. Irwan, *ARPN J. Eng. Appl. Sci.*, 10(2015)1-8.
28. H. Chang, & Y.J. Lo, *Sol. Energy*, 84(2010)1833-1837.
29. F. Anwar, M. Manzoor and J.R. Bajwa, *Pak. J. Ana. Environ. Chem.*, 5(2004)28-37.
30. W. Peschel, F. Sánchez-Rabaneda, W. Diekmann, A. Plescher, I. Gartzía, D. Jiménez, R. Lamuela-Raventós, S. Buxaderas and C. Codina, *Food Chem.*, 97(2006)137–150.
31. S.A.S. Chatha, F. Anwar, M. Manzoor and J.R. Bajwa, *Grasas y Aceites*, 57(2006)328-335.
32. N. Abd Razak, S. M. Tumin and R. Tajuddin, *Am. J. Appl. Sci.*, 8(2011)45-49.
33. M.A.M. Jinasena, A.D.U.S. Amarasinghe, B.M.W.P.K. Amarasinghe and M.A.B. Prashantha, *J. Natl. Sci. Found.*, 44(2016)11–21.
34. J.E. Cacace and G. Mazza, *J. Food Eng.*, 59(2003)379–389.
35. N.E. Durling, O.J. Catchpole, J.B. Grey, R.F. Webby, K.A. Mitchell and L.Y. Foo, *Food Chem.* 101(2007)1417–1424.
36. P.S. Devi, M. Saravanakumar, and S. Mohandas. *Afr. J. Food Sci.*, 24(2012)567-573.
37. S.K. Reshmi, K.M. Aravindhan, D.P. Suganya, *Asian J. Pharm. Clin. Res.*, 5(2012)107-110.
38. M.M. Noor, M.H. Buraidah, S.N.F. Yusuf, M.A. Careem, S.R. Majid, and A.K. Arof, *Int. J. Photoenergy*, 2011 (2011) 5 pages.
39. G. Sepulveda-Jimenez, P. Rueda-Benitez, H. Porta, M. Rocha-Sosa, *Physiol. Mol. Plant Pathol.*, 64 (2004) 125-133.
40. H.M.C. Azeredo, *Int. J. Food Sci. Technol.*, 44 (2009) 2365-2376.
41. G. Calogero, G.D. Marco, *Sol. Energ. Mater. Sol. Cells*, 92 (2008) 1341-1346.
42. A. S. Polo and N.Y.I. Murakami, *Sol. Energ. Mater. Sol. Cells*, 90(2006)1936-1944.
43. H. Hug, M. Bader, P. Mair and T. glatzer, *Appl. Energy*, 115 (2014) 216-225.
44. M. Bhogaita, A. D. Shukla and N.R. Pratibha, *Sol. Energ.*, 137(2016) 212.
45. H. Zhou, W. Liqiong, G. Yurong, M. Tingli, *J. Photochem. Photobiol. A Chemistry*, 219 (2011) 188-194.