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Research Article

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Analysis of UV Spectra of Some Natural Plant Dyes Applicable in Fabrication of Grätzel Cells

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Abstract Natural dye-sensitized solar cells, also known as Grätzel cells are considered to be non-toxic and low cost solar cells useful for electrical energy generation. Anthraquinones, flavonoids, and chlorophyll among others are phytoconstituents necessary for good photosensitization in these solar cells. Seven plants were randomly selected from tropical environs, Ota, Nigeria. Preliminary screening was carried out on them via chemical detection assay for secondary metabolites known for exhibiting chromophores at useful UV-visible regions. The phytochemical screening proved that three plant species were promising, namely: *Mangifera indica* leaf, *Syzygium samarangense* leaf, and *Bougainvillea spectabilis* flower. Successive extraction via cold maceration was carried out on each of the selected plants with hexane, ethyl acetate and methanol based on polarity scale. The partitioned extracts were subsequently subjected to UV-visible spectral detection for useful chromophores. The ethyl acetate fraction of the dyes had the highest concentration of activity of compounds. *M. indica* had UV absorptions at 272 nm, 317 nm, 410 nm, and 665 nm, indicating the presence of anthraquinones, flavonoids and chlorophyll. *S. samarangense* had UV/visible absorptions at 317 nm, 410 nm, 431 nm, and 665 nm, indicating the presence of anthraquinones, flavonoids and chlorophyll. *B. spectabilis* had UV/visible absorptions at 407 nm, 470 nm, and 665 nm, signifying the presence of flavonoids and chlorophyll. The UV-Vis results showed that *M. indica* leaf, *S. samarangense* leaf and *B. spectabilis* flower absorb photons in the visible region of the electromagnetic spectrum, hitherto fulfilling an important criterion for their use as sensitizers in Grätzel cells.

Keywords *Bougainvillea spectabilis*, *Mangifera indica*, *Syzygium samarangense*, phytochemical screening, UV/visible absorption

1. Introduction/Background

The Grätzel cell also known as the dye sensitized solar cell (DSSC) which was developed by Grätzel and colleagues [1] in 1991 operates in a manner similar to nature's photosynthetic process [2]. Photosynthetic plants convert light to chemical energy; Grätzel cells convert light to electrical energy. A Grätzel cell comprises a fluorine-doped or indium-doped tin oxide layer, a mesoporous nanocrystalline semiconductor oxide electrode, a photosensitizer, an electrolyte, and a counter electrode as shown in Figure 1. The dye being a major component of the Grätzel cell (also known as the photo-sensitizer) plays a very crucial role in the operation of the cell [3, 14, 15]. The cell's performance relies on the capacity of the dye to inject photo-excited electrons into the conduction band of a semiconductor oxide [4] such as TiO_2. The rate of electron injection in Grätzel cells is influenced by how well the dye molecules are immobilized to the TiO_2 surface and this is dependent on the

anchoring groups present in the dye molecule [15]. Secondary metabolites such as phenols, tannins, flavonoids and anthraquinones, based on their structure, can aid in the determination of useful chromophores present in the plant from which the dye is obtained [8]; these chromophores aid charge transport in the cells [5]. A very important pigment found in most photosynthetic plants, useful for dye sensitization is the chlorophyll pigment [6]. The fraction of sunlight that can be absorbed is specific for each dye and varies with its chemical structure. The molecules of each dye can only oscillate at frequencies corresponding to certain wavelengths of radiant energy. It is such energy that is absorbed by the dye molecules. Due to the chemical structure of secondary metabolites and the chromophores present in dye molecules, useful information is provided concerning the activities of compounds contained in dye extracts of plants. The chromophore is the portion of the molecule responsible for absorption of UV or visible radiation. The performance of a Grätzel cell depends on the type of photosensitizer used [7]. An efficient photosensitizer should have an intense absorption in the visible region, must possess very good adsorption quality to the surface of the semiconductor oxide, must be well able to inject electrons into the conduction band of the semiconductor oxide [12], and should possess as much hydroxyl or carbonyl groups as possible for the proper anchoring of the dye on the surface of the TiO_2 film, also providing easy electron transfer from the dye molecule to the conduction band of the semiconductor oxide [19].

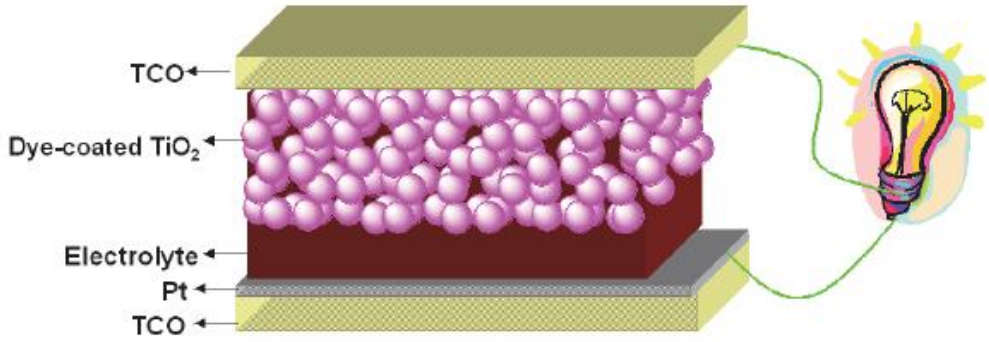

Figure 1: Schematic diagram of a DSSC in operation [18]

In this work, seven plants randomly selected from tropical environs were screened via chemical detection assay, the selected ones were successively extracted with solvents based on scale of polarity, and the partitioned extracts were subsequently subjected to UV-visible spectral detection for useful chromophores.

2. Materials and Methods

2.1. Harvesting of samples and phytochemical screening

Samples of *M. indica* leaf, *T. stans* flower, *S. samarangense* leaf, *C. odorata* leaf, *B. spectabilis* flower, *T. procumbens* leaf and *N. laevis* leaf were harvested in few quantity from tropical environs, Ota, Nigeria, and subjected to preliminary phytochemical screening. They were tested for tannins, phenols, flavonoids, and anthraquinones using the methods of Olugbuyiro [9].

2.2. Dye extraction from selected samples

The species of *M. indica* leaf, *S. samarangense* leaf, and *B. spectabilis* flower shown in Figures 2.1, 2.2, and 2.3 respectively were selected from the screened seven plants. The samples were harvested and air-dried for two weeks until constant weight was assumed by each. The samples were blended with with a Nakai Japan magic blender and weighed with a Radawag AS 310/C/2 electronic beam balance. Dyes were extracted from the blended samples by successively soaking in hexane, ethyl acetate and methanol respectively. The solvents were purchased from Fanor Chemicals, Ojota, Lagos, Nigeria. 232.773 grams of *M. indica* leaf was soaked in 1 litre of hexane, 104.421 grams of *S. samarangense* leaf was soaked in 1 litre of hexane, and 14.325 grams of *B. spectabilis* flower was soaked in 200 ml of hexane. The three samples were soaked in hexane inside TLC tanks and covered for 40 hours. The hexane extracts were collected and filtered with cotton wool. The residue of each sample after collecting the hexane extract was soaked with ethyl acetate for 40 hours. The ethyl acetate extract was collected and filtered with cotton wool. The filtrate of each sample was collected in big beakers and left

uncovered to obtain the ethyl acetate dye extracts. After the ethyl acetate solvent evaporated completely, the dye extracts were transferred into small beakers and covered with foil paper. The residue of each sample after obtaining the ethyl acetate extracts was soaked in methanol for 5 days. The extracts were collected, filtered and poured into beakers. The beakers were left uncovered for a week. In the beaker containing *B. spectabilis* flower filtrate, methanol got completely evaporated and the dye extract was transferred into a smaller beaker and covered with foil paper. In the other two beakers containing the filtrates of *M. indica* leaf and *S. samarangense* leaf respectively, methanol evaporated to a very large extent but due to incomplete evaporation, a rotary evaporator was employed to remove the methanol solvent totally from the solutions. The dye extracts were transferred into clean beakers.

Figure 2.1: M. indica

Figure 2.2: S. samarangense

Figure 2.3: B. spectabilis

2.3. UV-Visible Spectrometry of Dye Extracts

The partitioned extracts for each of the selected samples were subsequently subjected to UV-visible spectral detection for useful chromophores within 200 nm to 700 nm scanning range using Genesys spectrophotometer (model ID- 2L7J355002); this is known to be the range of measurement for coloured compounds [16]. Dye extracts with top ranked optical properties were marked as light harvesting material in Grätzel cell construction.

3. Results and Discussion

3.1. Phytochemical Screening

Table 3.1 shows the results of screened seven plants using the Olugbuyiro's techniques [9] of detecting dye containing plant metabolites. The useful classes of secondary metabolites were found absent in *T. stans* flower, *C. odorata* leaf, *T. procumbens* leaf, and *N. laevis* leaf; hence, they were subsequently screened out. The phytochemical test indicated three species as dye containing candidates namely, *M. indica* leaf, *S. samarangense* leaf, and *B. spectabilis* flower. Thus, the three selected plant samples were extracted and the extracts were further screened by using UV-visible spectrophotometer.

Table 3.1: Screened secondary metabolites inplant samples

Phytochemicals	MIL	SSL	BSF	TSF	COL	TPL	NLL
Tannins	+++	++	-	-	-	-	-
Phenols	+++	+++	+++	-	-	-	-
Flavonoids	++	+++	+++	-	-	-	-
Free Anthraquinones	++	-	++	-	-	-	-
Combined Anthraquinones	-	-	++	-	-	-	-

Keys: (+++) Intense, (++) Moderate, (+) Mild, (-) Absent

MIL = *Mangifera indica* leaf, SSL = *Syzygium samarangense* leaf, BSF = *Bougainvillea spectabilis* flower, TSF = *Tecoma stans* flower, COL = *Chromolaena odorata* leaf and TPL = *Tridax procumbens* leaf, NLL = *Newbouldia laevis* leaf

The wavelength regions of the spectral absorbance peaks could also be used to identify the pigments present in the plants. The UV-Vis spectra of anthraquinones have absorption bands in the wavelength range of 220–

350 nm [10]. Flavonoids in standardized UV-Vis spectroscopy reveal two characteristic UV absorption bands with maxima in the 240 to 285 and 300 to 550 nm range [11]. Chlorophyll pigments strongly absorb wavelengths corresponding to the blue and red regions of the visible spectrum, the light that is not absorbed is in the green region [13].

The hexane extracts of *Mangifera indica* in Figure 3.1 had UV absorptions at 410 nm, 443 nm, 473 nm and 668 nm; this indicated the presence of flavonoid and chlorophyll pigments. *Syzygium samarangense* in Figure 3.4 had UV absorptions at 278 nm, 317nm, 407 nm and 668 nm, indicating the presence of flavonoids and chlorophyll pigments. In Figure 3.7, *Bougainvillea spectabilis* had UV absorption at 224 nm, signifying the presence of anthraquinones. The ethyl acetate extracts of *Mangifera indica* leaves, *Syzygium samarangense* leaves, and *Bougainvillea spectabilis* flower in Figures 3.2, 3.5, and 3.8 had the best absorbance peaks during the UV-visible spectrophotometric scanning. In Figure 3.2, *Mangifera indica* had UV absorptions at 272 nm, 317 nm, 410 nm, and 665 nm, indicating the presence of anthraquinones, flavonoids and chlorophyll. In Figure 3.5, *Syzygium samarangense* had UV/visible absorptions at 317 nm, 410 nm, 431 nm, and 665 nm, also suggesting the presence of anthraquinones, flavonoids and chlorophyll. In Figure 3.8, *Bougainvillea spectabilis* had UV/visible absorptions at 287 nm, 407 nm, 470 nm, and 665 nm, signifying the presence of anthraquinones, flavonoids and chlorophyll.

Comparing the chlorophyll pigment of *M. indica* in Figure 3.1 with that of Figure 3.2, a hypsochromic shift from wavelength 668 nm to 665 nm was observed. This blue shift could be ascribed to the ethyl acetate solvent being more polar than hexane. For *S. samarangense*, a bathochromic shift from 407 nm to 410 nm was observed in the violet regions of Figures 4.4 and 4.5 respectively while for the red (chlorophyll) region of the same respective figures, a hypsochromic shift similar to that of *M. indica* in Figures 3.1 and 3.2 was observed. This shift to shorter wavelength could be due to a reduction in conjugation, influenced by an extraction solvent of increased polarity.

According to [17], ultraviolet and visible spectroscopy could be used in the identification of multiple bonds and aromatic conjugations existing within molecules of organic compounds. The absorption peaks within the spectra could suggest what type of bonds exists within molecules and also, the kind of electronic transition taking place. Based on the interest of this study, it was observed that within the 400 nm – 700 nm spectra ranges of Figures 3.1 to 3.9, there were π to π* and n to π* electronic transitions. For instance, at 410 nm wavelengths of Figures 3.1 and 3.2, π to π* electronic transitions were observed. This observation predicts the presence of unsaturated centres in the compounds of *M. indica* leaf. An important unsaturated compound necessary for effective photosensitization in Grätzel solar cells is the carbonyl compound. The lower absorption peaks observed at longer wavelengths (lower energies) depict the n to π* electronic transition. The occurrence of an n to π* electronic transition predicts the presence of saturated aliphatic ketones [17]. This also signifies the presence of the carbonyl group. In Figure 3.7, no electronic transition was observed within the visible region; this indicates the absence of the carbonyl group and as such, the dye extract will not work as photosensitizer in a Grätzel solar cell.

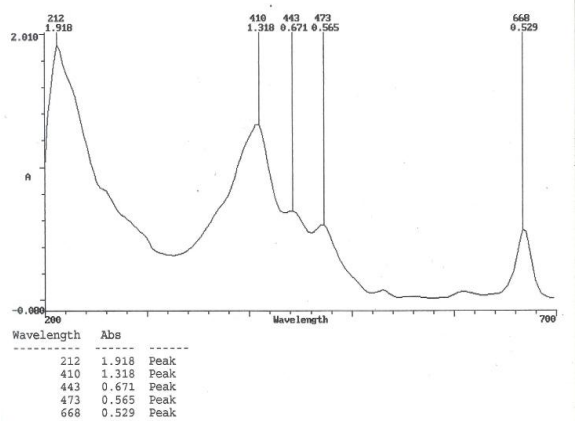

Figure 3.1: UV-vis spectrum of hexane dye extract of Mangifera indica leaf

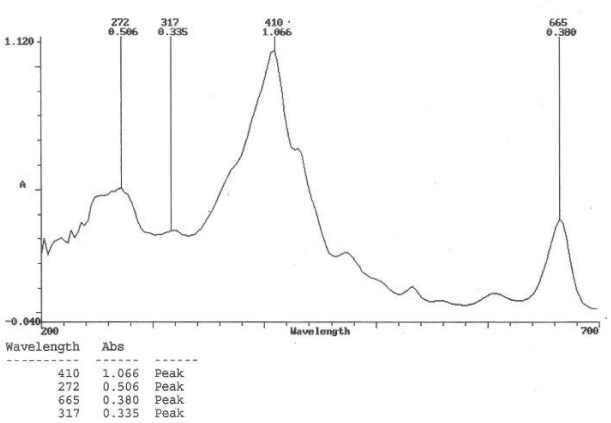

Figure 3.2: UV-vis spectrum of ethyl acetate dye extract of Mangifera indica leaf

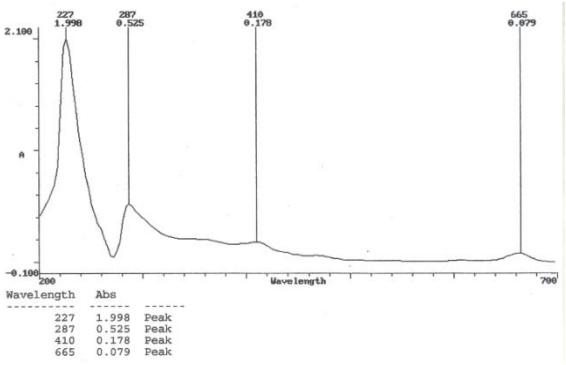

Figure 3.3: UV-vis spectrum of methanol dye extract of Mangifera indica leaf

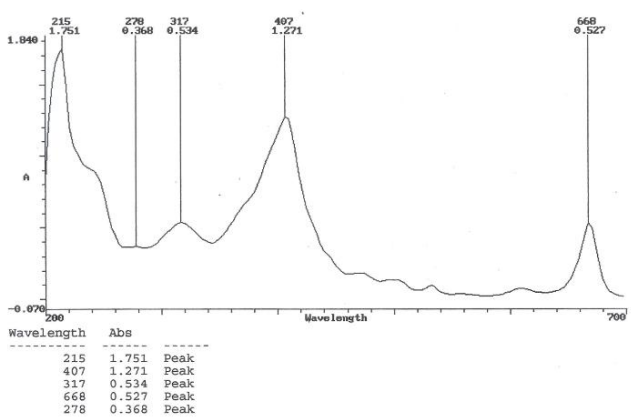

Figure 3.4: UV-vis spectrum of hexane extract of Syzygium samarangense leaf

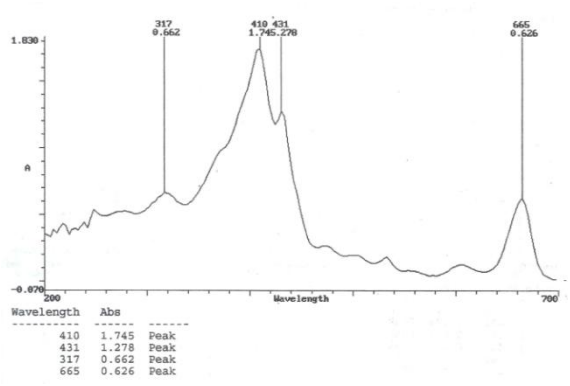

Figure 3.5: UV-vis spectrum of ethyl acetate dye extract of Syzygium samarangense leaf

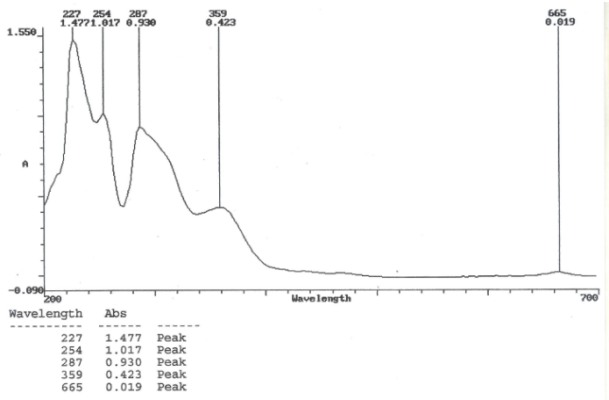

Figure 3.6: UV-vis spectrum of methanol dye extract of Syzygium samarangense leaf

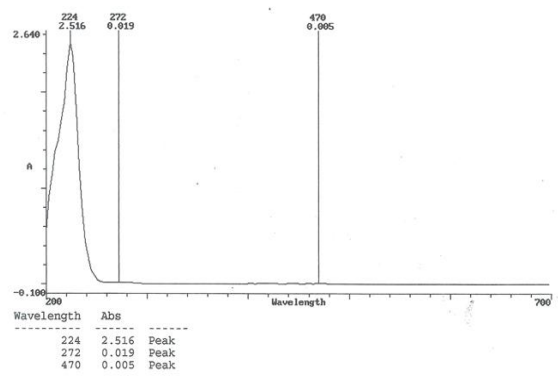

Figure 3.7: UV-Vis spectrum of hexane dye extract of Bougainvillea spectabilis flower

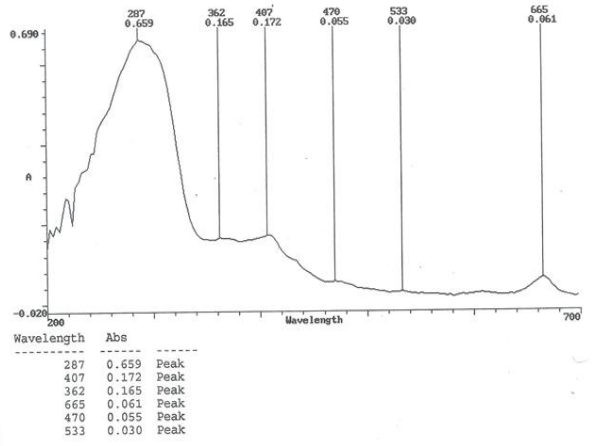

Figure 3.8: UV-Vis spectrum of ethyl acetate dye extract extracts of Bougainvillea spectabilis flower

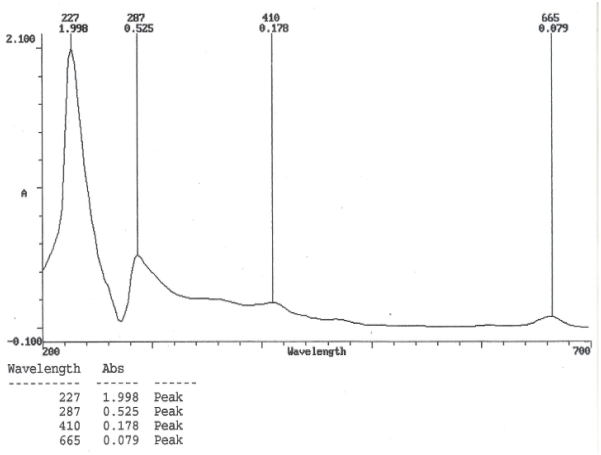

Figure 3.9: UV-VIS spectrum of methanol dye extract of Bougainvillea spectabilis flower

4. Conclusion

Three plant species namely, *M. indica* leaf, *S. samarangense* leaf and *B. spectabilis* flower, were selected out of seven plants which were screened for natural dye sensitized solar cell application on the basis of chemical detection assay. Secondary metabolites such as phenols, tannins, flavonoids, and anthraquinones, in reasonable amounts were confirmed present in the selected plant species. Natural dyes for use as sensitizer in Grätzel cells were successively extracted from the leaves and flowers of the plants. Confirming with UV-Visible spectroscopic analysis, the presence of these pigments indicated that the extracted dyes will be useful as photosensitizer in the construction of Grätzel cells. The UV-Vis results showed that *M. indica* leaf, *S. samarangense* leaf and *B. spectabilis* flower absorb photons in the visible region of the electromagnetic spectrum, hitherto fulfilling an important criterion for their use as sensitizers in Grätzel cells.

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References

[1]. O'Regan, B. & Grätzel, M. (1991). A low-cost, high-efficiency solar cell based on dye- sensitized colloidal TiO_2 films. *Nature, 353*, 737-740.

[2]. Loos, J. (2012). Polymers. In G.V. Tendeloo, D.V. Dyck, & S.J. Pennycook (Eds.), *Handbook of Nanoscopy* (pp.1247-1272). Weinheim, Germany: Wiley-VCH Verlag.

[3]. Hemmatzadeh, R. & Mohammadi, A. (2013). Improving optical absorptivity of natural dyes for fabrication of efficient dye-sensitized solar cells. *Journal of Theoretical and Applied Physics*, *7*(57), 1-7. doi: 10.1186/2251-7235-7-57

[4]. Narayan, M.R. (2012). Review: Dye sensitized solar cells based on natural photosensitizers. *Renewable and Sustainable Energy Reviews, 16*, 208-215. doi: 10.1016/j.rser.2011.07.148

[5]. Boyo A.O., Shitta, M.B., Oluwa, T. & Adeola, S. (2012). Bitter Leaf (*Vernonia amygdalin*) for Dye Sensitized Solar Cell. *Trends in Applied Sciences Research, 7*(7), 558-564. doi: 10.3923/tasr.2012.558.564

[6]. Taya, S.A, El-agez, T.M, Elrefi, K.S., & Abdel-latif, M.S. (2015). Dye-sensitized solar cells based on dyes extracted from dried plant leaves. *Turkish Journal of Physics, 39*, 24-30. doi: 10.3906/fiz-1312-12

[7]. Suhaimi, S., Shahimin, M.M., Alahmed, Z.A., Chysky, J., and Reshak, A.H. (2015). Materials for Enhanced Dye-sensitized Solar Cell Performance: Electrochemical Application. *International Journal of Electrochemical Science, 10*, 2859-2871.

[8]. Delgado-Vargas, F., Jiménez, A.R., & Paredes-López, O. (2000). Natural Pigments: Carotenoids, Anthocyanins, and Betalains — Characteristics, Biosynthesis, Processing, and Stability. *Critical Reviews in Food Science and Nutrition, 40*(3), 173–289

[9]. Olugbuyiro, J.A.O. (2012). Phytochemical Guides. Laboratory manual for natural products Research. Department of Chemistry, Covenant University.

[10]. Anour, E.H., Osman, C.P, Weber, J.F., & Ismail, N.H. (2014). UV/Visible spectra of a series of natural and synthesized anthraquinones: experimental and quantum chemical approaches. *SpringerPlus, 3*(233). doi: 10.1186/2193-1801-3-233

[11]. Bohm, B.A. (1998). *Introduction to Flavonoids.* Singapore: Harwood academic publishers.

[12]. Narayan, M.R. (2012). Review: Dye sensitized solar cells based on natural photosensitizers. *Renewable and Sustainable Energy Reviews, 16*, 208-215. doi: 10.1016/j.rser.2011.07.148

[13]. Matthews, P. (1992). *Advanced Chemistry.* Cambridge, United Kingdom: Cambridge University Press.

[14]. Susanti, D., Nafi, M., Purwaningsih, H., Fajarin, R., & Kusuma, G.E. (2014). The preparation of Dye Sensitized Solar Cell (DSSC) from TiO_2 and Tamarillo Extract. *Procedia Chemistry, 9*, 3-10. doi: 10.1016/j.proche.2014.05.002

[15]. Nazeeruddin, M.K., Zakeeruddin, S.M., Lagref, J.J., Liska, P., Comtea, P., Barolo, C., Viscardi, G., Schenk, K., and Grätzel, M. (2004). Stepwise assembly of amphiphilic ruthenium sensitizers and their applications in dye-sensitized solar cell. *Coordination Chemistry reviews, 248*, 1317-1328.

[16]. Harborne, J. B. (1973). *Phytochemical methods: A guide to modern techniques of plant analysis*. London: Chapman and Hall.

[17]. Kalsi, P.S. (2004). *Spectroscopy of Organic Compounds*. New Delhi: New Age International Publishers

[18]. Chen, Z., Tian, Q., Tang, M., and Hu, J. (2011). The Application of Inorganic Nanomaterials in Dye-Sensitized Solar Cells. In L. A. Kosyanchencko, Ed. Solar Cells: Dye Sensitized Devices

[19]. Ayalew, W.A. and Ayele, D.W (2016). Dye-sensitized solar cells using natural dye as light-harvesting materials extracted from Acanthus sennii chiovenda flower and Euphorbia cotinifolia leaf. *Journal of Science: Advanced Materials and Devices,1*, 488-494. doi:10.1016/j.jsamd.2016.10.003