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Strategy to Select and Grade Efficient Dyes for Enhanced Photo-Absorption

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Abstract

In this paper, a simple strategy to select and grade efficient natural dye-sensitizers for photo-absorption is developed. The selection criteria help to choose efficient dye for construction of solar cell. On the other hand, the dye-grade technique based on light and matter interaction parameters (absorbance, anthocyanin, and light harvesting efficiency) further reduce the number of dyes for efficient dye-sensitized solar cell (DSSC) production. The result shows that the dyes extracted from witch seed flower (*Striga hermonthica*), flamboyant flower (*Delonix regia*), and bitter gourd (*Momordica charantia*) have dye-grade 1, are the most efficient photo-absorber for enhanced DSSC fabrication while guava peel dye has grade 10 being the least efficient dye. The selection criteria and dye-grade techniques provide surer way of getting promising dyes for effective DSSC production than choosing the dyes randomly based on some features like their colors and abundance.

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Keywords: Selection criteria, Dye-grade, Absorbance, Anthocyanin, Photo-absorber

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1. Introduction

The first generation of natural dyes available to mankind were derived from natural resources based on their source of origin broadly classified as plant (leaves, berries, roots, wood, bark, flowers, fruit, seed), animal, mineral, and microbial (fungi, lichens) dyes until the discovery of the second generation, the synthetic dyes in 1856 [1]. The plants are known as the major sources of natural dyes. The different regions of the world have different natural resources of

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these natural dyes, that is, they are not evenly distributed across the surface of the earth. Dyes have majorly found applications in coloration of textile materials (as decorations, wears). Also natural dyes are used in the coloration of food, medicines, handicraft items and toys, and in leather processing. Furthermore, natural dyes unlike synthetic dyes are considered eco-friendly, as they are renewable and biodegradable. Consequently, natural dyes are used in the fabrication of solar cells to generate electricity [2, 3]. In the early nineteen century, rapid research strides of the chemistry of natural dyes supported by the industrialization of Dye Sensitive solar Cells (DSSCs) production have led to the development of commercial solar cells in many countries of the world today which may likely push the present conventional electricity generation into oblivion. However, environmental issues in the production and application of synthetic dyes once again revived consumer interest in natural dyes during the last decades of the twentieth century [4]. Electricity generation with natural dyes is preferred by environmentally conscious consumers and today there is a suitable market for such DSSCs for electricity generation. But the share of natural dyes in the electricity sector is insignificant due to certain technical and sustainability issues involved in the production and application of these dyes such as non-availability in ready-to-use standard form, unsuitability for DSSC use, and limited and non-reproducible shades [5]. Natural dyes are suitable as they are renewable and biodegradable but they cannot fulfill the huge demand from power sector in view of the preferential use of land for food and feed purposes. Also, over exploitation of natural resources to obtain dyes may result in deforestation and threaten endangered species. For these reasons, the Global Organic Textiles Standard (GOTS) permits the use of safe synthetic dyes and prohibits the use of natural dyes from endangered species [1]. Various research efforts have been undertaken all over the world to address the shortcomings of natural dyes in view of the tremendous environmental advantage they offer. Some of the problems encountered in the use of natural dyes include non-availability because of difficulty of collection, bulk isolation, standardization of dyeing procedure, color yield, complexity of dying process, and reproducibility of shade.

This paper attempts to look at the current status of the availability, screening, and grading of plant natural dyes-based on absorbance parameters to enhance efficient future dye-sensitized solar cell (DDSC) production.

The sensitization of wide band gap semiconductor using natural dyes is largely attributed to anthocyanin, which belongs to a natural group that gives color to the flowers, leaves and fruits of plants. In addition, it is responsible for several colors in the purple-red range [6, 7]. Furthermore, anthocyanin can also be obtained in other plant parts, such as tubers, roots, seeds, and stems [8]. Figure 1 depicts the molecular structure of anthocyanin. Anthocyanin molecule have carbonyl and hydroxyl groups bound to the semiconductor titanium dioxide (TiO_2) or zinc oxide (ZnO) surface which excite electron transfer from the anthocyanin molecules (sensitizer) to the conduction band of porous TiO_2 or ZnO film [9, 10]. Anthocyanin extracted from different plants provides various sensitizing performances of DSSC [11].

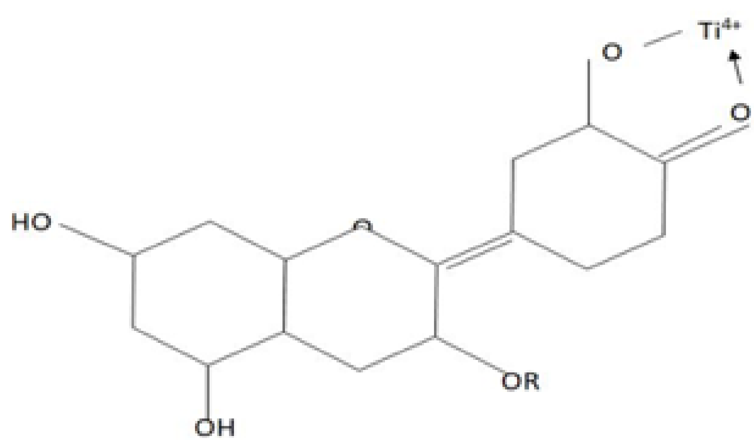

Figure 1. Structure and binding of a typical anthocyanin molecule with Ti^{4+} [12].

Khwanchi et al reported that anthocyanin dyes have various absorption spectra and provide even more synergistic effect than the chlorophyll dye [13-15]. Also, it has been reported that anthocyanin dye is a better DSSC sensitizer than chlorophyll dye [9, 16, 17]. Therefore, it is imperative to have basis for selection of dyes for photo-absorption activities in solar cells. We extracted the dyes from flowers and fruits and determined the concentration of anthocyanins and their photoactivities. Grading from 1 to 10 of the extracted dyes was based on their respective photoactivities.

2. Materials and Methods

In this paper, three experiments were carried out viz: collection and screening of plant dyes, extraction of dyes, and measurement of anthocyanin concentration of plant dyes.

2.1. Collection and Screening of Dye Plants

The flowers were collected from wild forest or flora of Bauchi state, Northeastern Nigeria and the fruits were purchased from Bauchi main market. Because the plant species are many, some criteria were adopted in the collection and screening of the flowers and fruits as good source of natural dye as follows:

a). Plants that grow in abundance were collected, taking care that rare or protected species were not collected.

b). Fresh flowers and fruits that yielded much dye with small quantity of plant material were collected.

c). The flowers were squeezed between the fingers and if the discharge was colored, it was accepted as good source of natural dye.

d). If the color were retained on the fingers even after washing the hand with water, it was considered a good source of natural dye with probably good wash fastness.

e). The flowers were crushed in pestle-mortar and each of the crushed paste was smeared on filter paper, if the color was retained on the paper, it was accepted to be a good source of natural dye.

f). The smeared filter paper was placed under table lamp for 3-4 hours, and the color that remained the same without fading off was considered a good source of natural dye with good light fastness properties.

Therefore, the dyes from the flowers and fruits that satisfied the criteria for screening were considered promising photosensitizers for the fabrication of DSSCs.

2.2. Extraction of Dyes

Nine flowers (sunflowers, witch seed, Red cockscomb, rose flower, hibiscus, flamboyant, bougainvillea, wild merigold flower, and lantana camera) and five fruits (bitter guard, guava, orange, tomato, and mango) which have met up the requirements of a good dye were earmarked. Sufficient quantities of the selected plant flowers and fruits were collected and dried on shade for two weeks. After drying, the samples were grinded into fine powder with the help of a blender (BLSTVB-RVO-000 from Walmat). Specific amount of each of the powdered samples were collected in sterile 50 *ml* falcon tubes and proportionate amount of solvents (HCl or ethanol or distilled water) were then added and the solutions were vortexed. The solutions were sonicated using a sonicator (Branson SFX250) for one hour at 4 $^{\circ}C$. The solutions were then centrifuged at 1500 rpm at 4 $^{\circ}C$ for ten minutes. The solid residues were filtered out while the supernatant of the clear dry solutions were collected, and stored at 4 $^{\circ}C$ before use. The containers were covered with aluminum foil to prevent damage from light exposure. The different formulations of selected plants pigments were extracted using ethanol with a fix amount of 0.1 *mole* of hydrochloric acid. The ethanol solvent with $0.1M\ HCl$ was taken as control.

2.3. Measurement of Anthocynin Concentration of Dyes

UV-VIS Spectrophotometer (6305 JENWAY) was used to measure the absorbance of fourteen selected plant pigments at different wavelengths in the range 200-800 *nm* (at interval of 50 *nm*) at Skanda Life Sciences Bangalore and College of Engineering Bangalore, India. The anthocyanin content of a dye for a given wavelength was calculated using the Equation 1 [18],

$$Anthocyanin\ content = \frac{A_{\lambda} \cdot MW \cdot DF \cdot 10^{8}}{\epsilon \cdot l}, \tag{1}$$

where A_λ is the absorbance at $(A_{520\ nm} - A_{700\ nm})pH_{1.0} - (A_{520\ nm} - A_{700\ nm})pH_{4.5}$, MW is the molecular weight equals to 449.2 $g/mole$ for cyaniding-3-glucose, which is the most abundant anthocyanin in nature, DF is dilution factor such that 0.2 ml sample diluted to 2 ml gives DF equals to 10, E is the extinction coefficient ($Lxcm^{-1}mol^{-1}$) which is equal to 26.9 for cyaniding-3-glucose and L is the path length in cm which is equal to 1. The same extinction coefficient was used for standards to calculate the concentration of each anthocyanin and hence the results reported should be seen as expressed in cyanadin-3-glucose equivalents. Also, the light harvesting efficiency (LHE) of a dye obtained using Equation 2 [19, 20],

$$LHE = (1 - 10^{-A_\lambda}) \times 100\%, \tag{2}$$

where A_λ is the absorbance at a specific wavelength λ.

3. Results and Discussion

Out of hundreds of the flora available in Bauchi State in Northeastern Nigeria, nine flowers (sunflowers, witch seed, Red cockscomb, rose flower, hibiscus, flamboyant, bougainvillea, wild marigold flower, and lantana camera) and five fruits (bitter guard, guava, orange, tomato, and mango) were used as source of dyes and represented in Table 1.

Table 1 contains the measured values of the absorbance of natural dyes extracted from nine flowers and five peels of fruits/fruits. Also the calculated values of the concentration of anthocynin (mm/mg) and the Light Harvesting Efficiency (LHE) in percentage are recorded in Table 1. The results show that the values of the absorbance, anthocynin concentration, and LHE lie in the ranges 0.08 - 4.00, 0.08 - 6.68 mm/mg, and 10.26 - 99.9 % respectively. Also the results show that witch seed flower, flamboyant flower and bitter gourd have the highest absorbanc of 4 corresponding to anthocynin concentration of 6.68 mm/mg and LHE of 99.99 %.Furthermore, the results reveal that bougainvillea and red cockscomb have absorbance 3.98 corresponding to anthocynin concentration of 6.64 mm/mg and LHE of 99.90 %. On the other hand, orange peel and tomato fruit have the least absorbance of 0.09 and 0.08 corresponding to anthocynin concentration of 0.82 mm/mg and 1.40 mm/mg, and LHE of 67.64 % and 85.54 % respectively.

In another perspective, Table 1 also depicts the dye grades as superscripts of the values of absorbance, anthocyanin concentration, and LHE in columns 3, 4, and 5 respectively. The dye grades: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11 are in descending order of the magnitudes of absorbance, anyhocyanin content, and LHE. That is, the largest magnitude of a quantity corresponds to the least grade 1 and vice versa. The average grade for each dye in column 5 lies in the range 1.00 - 10.00 from which we obtained the final dye grade. The result shows that witch seed flower, bougainvillea flower, and bitter gourd fruit dyes with dye grade 1 are the most promising dyes and guava peel dye with dye grade 10 is the least promising dye for DDSC fabrication. This grading technique in conjunction with the criteria of dye selection, can be employed to identify dyes that would provide high efficiency and cost effective rather than choosing the dyes at random for DSSC fabrication.

The absorbance of different dyes extracted from flowers and peel of fruits/fruits are depicted in Figure 2. The figure shows that the absorbance of the natural dyes depends on the type of natural dye sources [21]. In particular, the result shows that natural dyes from flowers have higher absorbance than those obtained from fruits except that of *Celosia cristata*.

The anthocyanin concentration of various dyes extracted from flowers and peel of fruits/fruits are depicted in Figure 3. The figure shows that the anthocyanin concentration of the natural dyes depends on the type of natural dye sources. In particular, the result shows that natural dyes from flowers that have high anthocyanin concentration are more than those obtained from fruits and the result is in agreement with previous report [15]. This entails that the pattern of the dependence of absorbance and anthocyanin concentration of natural dyes are in good agreement.

Figure 4 depicts the light harvesting efficiency of some natural dyes extracted from the flowers and peel of fruits/fruits of plants obtained from the flora of Bauchi state, northeastern Nigeria. The figure reveals that all the natural dyes from flowers have LHE greater than 99 % except that of Hibiscus with 85.5 % while for fruits only that of red cockscomb has $LHE > 99$ % and guava peel has the least 25.9 %. This clearly indicates that in addition to absorbance and anthocyanin concentration LHE is another good signature or indicator of a promising good dye.

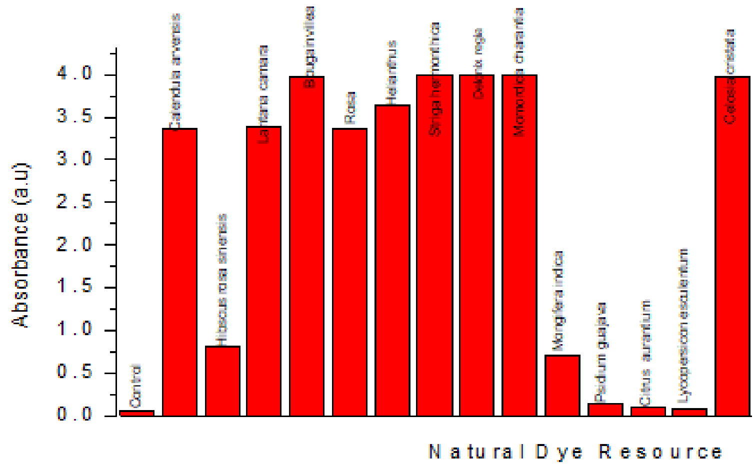

Figure 2. Absorbance of natural dyes.

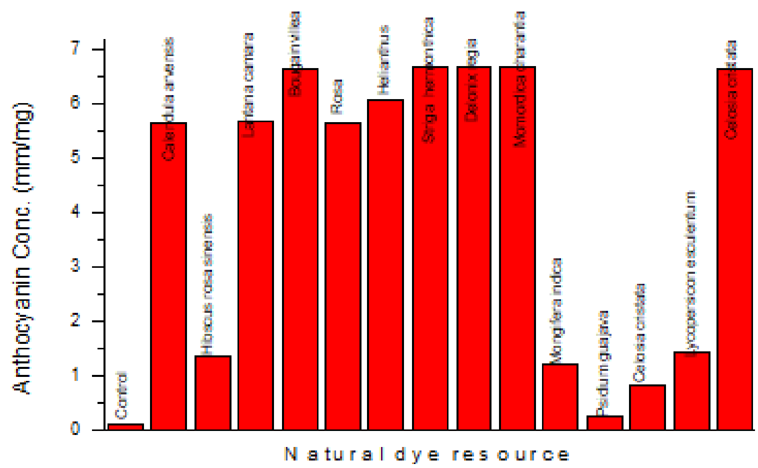

Figure 3. Anthocynin concentration of natural dyes.

4. Conclusion

A simple selection criteria and dye-grade method for knowing efficient dye-sensitizers for production of DSSC were developed. The selection and dye-grade methods were used to obtain promising dyes to be used to fabricate efficient DSSCs. These techniques overcome the difficulties associated with random method of selection of dyes for DSSC fabrication. The result shows that the dyes extracted from *Striga hermonthica*, *Delonix regia* and *Momordica charantia* with dye-grade 1, are the most efficient dye-sensitizers for enhanced DSSC fabrication while *Psidium guajava* dye has dye-grade 10 being the least efficient.

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Table 1. Concentration of Anthocyanin in plant natural dyes at 550 *nm*.

Source of natural dye					
English Name	**Scientific Name**	**Absorbance (a.u)**	**Anthocyanin conc. (mm/mg)**	**LHE (%)**	**Average grade**
Control		0.05	0.08	10.26	-
Wild marigold	*Calendula arvensis*	3.36^{5}	5.61^{5}	99.90^{3}	$4.33^{(5)}$
Hibiscus	*Hibscus rosa sinensis*	0.81^{6}	1.35^{7}	84.50^{6}	$6.33^{(6)}$
Lantana	*Lantana camara*	3.39^{4}	5.66^{4}	99.80^{4}	$4.00^{(4)}$
Bougainvillea	*Bougainvillea*	3.98^{2}	6.64^{2}	99.90^{3}	$2.33^{(2)}$
Rose flower	*Rosa*	3.36^{5}	5.61^{5}	99.90^{3}	$4.33^{(5)}$
Sun flower	*Helianthus*	3.63^{3}	6.06^{3}	99.97^{2}	$2.66^{(3)}$
Witch seed flower	*Striga hermonthica*	4.00^{1}	6.68^{1}	99.99^{1}	$1.00^{(1)}$
Flamboyant	*Delonix regia*	4.00^{1}	6.68^{1}	99.99^{1}	$1.00^{(1)}$
Bitter gourd	*Momordica charantia*	4.00^{1}	6.68^{1}	99.99^{1}	$1.00^{(1)}$
Mango peel	*Mongifera indica*	0.71^{7}	1.18^{8}	80.50^{7}	$7.33^{(8)}$
Guava peel	*Psidium guajava*	0.13^{8}	0.22^{10}	25.87^{9}	$9.00^{(10)}$
Orange peel	*Citrus aurantium*	0.09^{9}	0.82^{9}	67.64^{8}	$8.66^{(9)}$
Tomato	*Lycopersicon esculentum*	0.08^{10}	1.40^{6}	85.54^{5}	$7.00^{(7)}$
Red cockscomb	*Celosia cristata*	3.98^{2}	6.64^{2}	99.90^{3}	$2.33^{(2)}$
1-grade 1; 2-grade 2;	3-grade 3; 4- grade 4;	5-grade; 6-grade 6;	7-grade 7; 8-grade 8;	9-grade 9;	10-grade 10

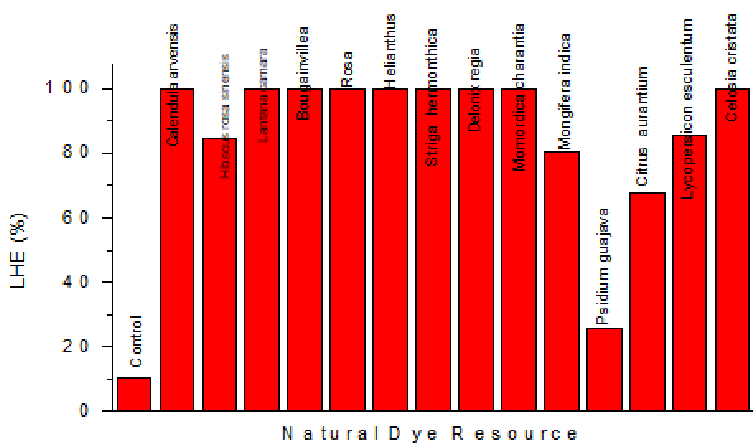

Figure 4. Light harvesting efficiency of natural dyes.

References

[1] S. Saxena & A. S. M. Raja In S.S. Muthu, "Roadmap to Sustainable Textiles and Clothing || Natural Dyes: Sources, Chemistry, Application and Sustainability Issues", Textile Science and Clothing Technology, (2014) (Chapter 2), pp 37–80. https://doi.org/10.1007/978-981-287-065-0_2

[2] A.N. Ossai, A. B. Alabi, S. C. Ezike & A. O. Aina, "Zinc oxide-based dye-sensitized solar cells using natural and synthetic sensitizers", Current Research in Green and Sustainable Chemistry, **3** (2020) 100043. https://doi.org/10.1016/j.crgsc.2020.100043

[3] U. I. Ndeze, J. Aidan, S. C. Ezike & J. F. Wansah, "Comparative performances of nature-based dyes extracted from Baobab and Shea leaves photo-sensitizers for dye-sensitized solar cells (DSSCs)", Current Research in Green and Sustainable Chemistry **4** (2021) 100105. https://doi.org/10.1016/j.crgsc.2021.100105

[4] A.N. Ossai, S. C. Ezike, P. Timtere & A. D. Ahmed, "Enhanced photovoltaic performance of dye-sensitized solar cells-based Carica papaya leaf and black cherry fruit co-sensitizers", Chemical Physics Impact **2** (2021) 100024. https://doi.org/10.1016/j.chphi.2021.100024

[5] P. H. Wante, J. Aidan & S. C. Ezike, "Efficient dye-sensitized solar cells (DSSCs) through atmospheric pressure plasma treatment of photoanode surface", Current Research in Green and Sustainable Chemistry **4** (2021) 100218. https://doi.org/10.1016/j.crgsc.2021.100218

[6] H. Chang & Y. J. Lo, "Pomegranate leaves and mulberry fruit as sensitizers for dye-sensitized solar cell", Solar energy **84** (2010) 1833.

[7] O. M. Andersen & M. Jordheim, "The Anthocyanins In: Andersen OM, Markham KR editors Flavonoids chemistry, biochemistry and applications", Boca Raton USA CRC Press,Taylor and Francis group (2006) 471.

[8] A. O. T. Patrocinio, S. K. Mizoguchi, L. G. Paterno, C. G. Garcia, N. Y. M. Iha, "Efficient and low-cost devices for solar energy conversion, efficiency and stability of some natural dye-sensitized solar cells", Synth. MET. **159** (2009) 2342.

[9] S. Hao, J. Wu, W. Haung & J. Lin, "Natural dyes as photosensitizer for dyesensitized solar cell", Solar Energy **80** (2006) 209.

[10] A. N. Ossai, S. C. Ezike & A. B. Dikko," Bio-synthesis of zinc oxide nanoparticles from bitter leaf (vernonia amygdalina) extract for dye-sensitized solar cell fabrication", Journal of Materials and Environmental Sciences **11** (2020) 444.

[11] P. Luo, H. Niu, G. Zheng, X. Bai, M. Zhang & W. Wang, "From salmon pink to blue natural sensitizer for cells. Canna indica L. Salvia splendens, cowberry and Solanum nigrum L", Spectrochim Acta A **74** (2009) 936.

[12] A. P. Attanayake, K. A. P. W. Jayatilaka, C. Pathirana & L. K. B. Mudduwa, "Phytochemical Screening and In Vitro Antioxidant Potentials of Extracts of Ten Medicinal Plants used for the Treatment of Diabetes Mellitus in Sri Lanka", Afr J Tradit Complement Altern Med. **12** (2015) 28.

[13] W. Khwanchit, V. Meeyoo & S. Chavadej, "Dye-sensitized solar cell using natural dyes extracted from rosella and blue pea flowers", Solar energy matter solar cell **91** (2006) 566.

[14] T. Frank, "Pharmacokinetics of anthocyanidin-3-glycosides following consumption of hibiscus sabdariffa I extract", J Clin. pharmacol **45** (2005) 203.

[15] S. C. Ezike, C. N. Hyelnasinyi, M. A. Salawu, J. F. Wansah, A. N. Ossai & N. N. Agu, "Synergestic effect of chlorophyll and anthocyanin Co-sensitizers in TiO_2-based dye-sensitized solar cells", Surfaces and Interfaces **22** (2021) 100882. https://doi.org/10.1016/j.surfin.2020.100882.

[16] S. Kishiomoto, T. Maoka, K. Sumitomo & A. Ohmya, "Analysis of carotenoid composition in petals of calendula (Calendulaofficianalis I)" BioSci Biotech Bioch **69** (2005) 2122.

[17] Y. Li, S. H. Ku, S. M. Chen, M. A. Ali & F. M. A. Alhemaid, "Photoelectronchemistry for red cabbage extract as natural dye to develop a dye-sensitized solar cells", Intl. J Electrochem Sci. **8** (2013) 1237.

[18] W. A. Shehata, Md. S. Akhtar & T. Alam, "Extraction and Estimation of Anthocyanin Content and Antioxidant Activity of Some Common Fruits", Trends in Applied Sciences Research **15** (2020) 179. https://dx.doi.org/10.3923/tasr.2020.179.186

[19] K. E. Jasim, In: Leonid A. Kosyachenko (editors), "Dye sensitized solar cells-working principles challenges and opportunities, solar cells-dye sensitized devices", ibsn 9789533077352. InTech, Available from http//www.intechopen.com/books/solar-cells-dye-sensitized-devices/dye-sensitized-solar-cellsworking-principles-challenges-and-opportunities.

[20] H. Kyung-jun, P. Ju-Young, J. Sungho, O. K. Sang & W. C. Dae, "Light-penetration and light-scattering effects in dye-sensitized solar cells", New J. Chem, Royal Society of Chemistry (2014).

[21] R. M. Selvam, G. Athinarayanan, A. U. R. Nanthini, A. J. A. R. Singh, K. Kalirajan, P. M. Selvakumar, "Extraction of natural dyes from Curcuma longa, Trigonella foenum graecum and Nerium oleander, plants and their application in antimicrobial fabric", Industrial Crops and Products **70** (2015) 84. https://doi.org/10.1016/j.indcrop.2015.03.008