Confluence Journal of Pure and Applied Sciences (CJPAS)
Faculty of Science, Federal University Lokoja, Kogi State, Nigeria

Vol. 1, No. 2, Nov. 2018
ISSN: 2616-1303 | **Web:***www.cjpas.fulokoja.edu.ng*

ANTHOCYANIN DYES AS ALTERNATIVE PHOTOSENSITIZERS FOR TiO_2 DYE-SENSITIZED SOLAR CELLS (DSCs)

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ABSTRACT

*Natural dyes from Hibiscus sabdariffa, Delonix regia, Acalypha wilkesiana and Ixora coccinea have been extracted employing the simple solution aqueous method without any chemical treatment. Their pH values were measured using TechmelpH meter and their optical properties before and after adsorption ontoTiO_2 photoelectrodes were investigated employing UV-Visible spectrophotometer (model UV-750) in the wavelength range 210nm to 1100nm. Our choice is tied to the fact that natural dyes have better molar extinction coefficient and are environmentally benign. In this study, we present the results obtained from pH measurement and optical characterization before and after adsorption onto TiO_2 photoelectrodes.T****he measured pH values for the dye extracts extends up to about 5.0 revealing the dye molecules to possess more OH groups with long bond lengths.*** *Absorption maxima were observed in the region332nm to 455nmfor the dye extracts,but upon sensitization, there was reduction in absorption intensity which broadened towards the longer wavelengthsdue to weak bonding of anthocyanin molecules in the dye extracts to the oxide surface.* ***The light harvesting efficiency values for the dye extracts are almost close to unity but gradually reduce after adsorption onto TiO_2photoelectrodes with the bandwidth in the range of 150nm to 200nm. The calculated molar extinction coefficients were found to be high with values ranging between 102,902M^{1} cm^{-1}to159,837$M^{1}cm^{-1}$with Delonix regia having the highest value. Finally, it was discovered that TiO_2band gap was reduced upon sensitization with the extracted dyes. The value ranges between 2.03eV to 2.40eVwith the least difference occurring for Delonix regia sensitized TiO_2photoelectrode.***

Keywords: *Anthocyanin dyes, light harvesting efficiency, molar extinction coefficient, optical band gap, TiO_2-DSC.*

1. INTRODUCTION

Naturallyoccurring dyes have found application as photosensitizers for the wide band gap semiconductor such as TiO_2 in Dye-sensitized Solar Cells (DSCs) (Grätzel, 2003).In DSCs, they serve as energy absorbers which control the light harvesting efficiency and the overall photoelectric conversion efficiency (Garcia *et al.,* 2003).An ideal sensitizer for a DSC should absorb all light below a threshold wavelength of about 920 nm, inject electrons into conduction band with quantum yield of unity, possess sufficiently high redox potential so that it can be regenerated rapidly via electron donation from the electrolyte and be stable under illumination for about 20 years (Grätzel, 2005, Fernando *et al.,* 2008).Natural dyeshave become a viable alternative to the expensive and rare organic sensitizers

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How to cite this paper: AHMED, T. O., ALU, N and ADEBAYO, A. A. (2018).
Anthocyanin Dyes As Alternative Photosensitizers For Tio_2 Dye-sensitized Solar Cells (Dscs)
Confluence Journal of Pure and Applied Sciences (CJPAS), 1 (2), 150-160.

because of its low cost, availability, abundance in supply of raw materials and no environmental threat (Hao*et al.,* 2006). They are usually extracted from various components of a plant such as flowers, petals, leaves and bark via simple solution aqueous method, complicated solvent system method, ultrasonic extraction using a sonicator and supercritical fluid extractor method as sensitizers for DSCs (Wongcharee*et al.,* 2007). Although the power conversion efficiencies obtained for these DSCs have been less than 1%. Early researchers in this field used chlorophyll and other naturally occurring dyes as the sensitizer (Tributsch, 1971). Although quantum efficiencies of up to 10% were recorded, the measured photocurrents were very small due to the small light harvesting efficiency of a dye monolayer. Today, the most widely used dyes are based on inorganic ruthenium compounds which are the first sensitizers for nanoporous TiO_2 electrodes (O'Regan*et al.,* 1991). This was followed closely by the discovery of N3 dye in 1993 (Nazeeruddin, *et. al,* 1993).Organic sensitizers such as polyene-diphenylaniline(commonly known as D5) (Boschloo, *et. al.,* 2008) and indoline known commercially as D149 (Ito, *et. al.,* 2006) dyes have also been reported. These dyes have demonstratedgood light harvesting efficiency and are promising sensitizers due to their easier and simpler synthesis routecompared to the dyes based on ruthenium metal complexes.Althoughruthenium-based complexes work well and have been the mostwidely used dyes over the past two decades, it seems that increased improvements in dye design and the promise of removing expensivemetals will result in not only increased power-conversion efficienciesbut also greater potential to scale beyond 19 GW per year,which is the limit set by the availability of ruthenium(Horiuchi*et al.,* 2004, minerals.usgs.gov, 2010).In view of this, investigation on low cost, readily available natural dyes as efficient sensitizers for DSCs still remains the present challenge to the scientific community globally.As such, naturally occurring organic plant based dyes have also been studied as photosensitizers (Cherapy, *et. al.,* 1997; Deb, *et. al,* 1997; Tennakone, *et. al.,* 1997; Smestad, 1998).Complexation studies on anthocyanin pigments have shown that the pigment chelates with metal ions of aluminum, iron, titanium and chromium (Cherapy, *et. al.,* 1997) where the metal ions compete with the dye's protons displacing them and hence shifting the anthocyanin equilibrium from quinoidal to flavilium state. The shift between the two chemical states corresponds to the shift in the absorption peak towards longer wavelengths that is observed on the absorption spectrum (Polo, *et. al.,* 2006). It is known that low efficiency observed in natural sensitizers is due to poor complexation between the dye and the semiconductor, but the change in absorption characteristics when the pigment attaches to TiO_2 is not reported.

It is in this context that we carried out investigation on the optical characteristics of anthocyanin dye pigments as alternative sensitizers for TiO_2 dye-sensitized solar cell with emphasis on the optical characteristics before and after anchorage of the dye molecule on the TiO_2 semiconductor.Therefore, the study of alternative photosensitizers (mainly naturally occurring) at the microscopic level may yield cheaper, readily available yet efficient sensitizers which may give hope for large scale utilization.

2. MATERIALS AND METHODS

The major materials used for this study are the dried zobo leaves (*Hibiscus Sabdariffa),* the flame of the forest flower *(Delonix regia*), the copperleaf (*Acalypha Wilkesiana) and* the jungle flame flower (*Ixora coccinea*). Others are the Bunsen burner, distilled water, sieve, wire-gauze, tripod stand, laboratory glass wares (100ml beakers) andreagent bottles.The simple solution aqueous method was used for the extraction of natural dye from dried Zobo leaves (Hibiscus sabdariffa). The dried leaves of *Hibiscus Sabdariffa* were crushed into tiny bits and were washed repeatedly in distilled water to remove dust.Then, it was boiled in 100ml of distilled water for less than 1hr. The sample was slowly cooled down at room temperature. Then, the residue was removed by filtration and finally, the sample was filtered.The resulting extract was centrifuged to further remove any solid residue. Finally, the dye extract was filtered and stored in a reagent bottle.The same extraction method, procedure and condition were used for Flame of the forest flower *(Delonix Regia*),Copper leaf (*Acalypha Wilkesiana*) and Jungle flame flower (Ixora Coccinea).The pH values of the dye extracts were measured using a Techmel pH-meter having 0-14 as its range and buffer solution was used as reference. The measurement was done by dipping the pH meter probe into the dye extract and at the end of each measurement; the probe was washed and dipped into the buffer solution. A paste of titanium nanoxide in propanol in the ratio 1:3 by volume,was deposited on a soda lime glass substrate by doctor blading technique. It was then annealed for 40 minutes at 450°C. The annealed photoelectrode was allowed to cool to $80^{o}C$ and then soaked in the natural dye extracts for 12 hours overnight. Subsequently, the dye-sensitized photoelectrode were then removed using forceps, rinsed with acetonitrile and dried briefly on a hot plate.The dye's absorption characteristics were studied using UV-Vis spectrophotometer (AXION MEDICAL-UV753) within wavelengths 210 nm to 1100 nm. The absorption characteristics were recorded for anthocyanin dye in solution and also for photoelectrodes sensitized with anthocyanin pigment having different pH values. The empty cuvette was used as a reference for studies on dyes in solution while the unsensitized TiO_2 photoelectrode was used as reference for the dye sensitized film. The absorbance and wavelength values of the dye extracts and the dye-sensitized photoelectrodes were recorded automatically using LabVIEW software from National Instruments Inc., USA. In both cases the respective spectra recorded were subtracted from the reference spectra.The Light Harvesting Efficiency (LHE) for the dye extracts and dye-sensitized TiO_2photoelectrodes was calculated using:

$$LHE = \left(1 - 10^{-A(\lambda)}\right) \qquad (1)$$

Where *A(λ)* is the absorbance at any specific wavelength. Subsequently, the calculated values for the dye extracts and dye-sensitized photoelectrodes were plotted against wavelength. The graphical representations of this optical property are analyzed and discussed in section 3. The absorption coefficient (α) for the dye extracts and dye-sensitized TiO_2photoelectrodes was calculated using:

$$\alpha = \frac{2.303 \times A(\lambda)}{d} \qquad (2)$$

Where d is the path length of the cuvette for liquid sample and for thin film is the thickness of the film on glass substrate.In addition to this, the molar extinction coefficient (k) for the dye extracts and dye-sensitized TiO_2photoelectrodes was calculated using:

$$k = \frac{\alpha\lambda}{4\pi} \qquad (3)$$

Finally, the optical band gaps for the dye-sensitized TiO_2photoelectrodes were obtained from the absorbance spectra at the point of cut-off when spectra values are minimum. This was done by extrapolating these points to meet the wavelength axis and the energy gaps were calculated using the relation;

$$E_g = \frac{hc}{\lambda} \qquad (4)$$

Where Eg is the optical band gap in eV, *h* is the Planck's constant with numerical value given as

$6.626 \times 10^{-34}\ Js$, c is the speed of light given as $3 \times 10^{8}\ ms^{-1}$ 3X108 and λ is the wavelength under consideration.

3. RESULTS AND DISCUSSION

The measured pH values for the dye extracts are given in the table1. It is an established fact that the molecules of anthocyanin dyes are identified with two states; the more stable flavilium state and the unstable quinoidal state. These two states are known to exist at **two**different *pH* levels with flavilium being acidic while quinoidal form being basic(Cherapy, *et. al.,* 1997). In this work, t**he measured *pH* values for the dye extracts extend up to about *5.0*. The possibility of the dye molecules having more *OH* groups with long bond length is high, since *pH* values extends toward basicity.**

The absorbance of a dye upon

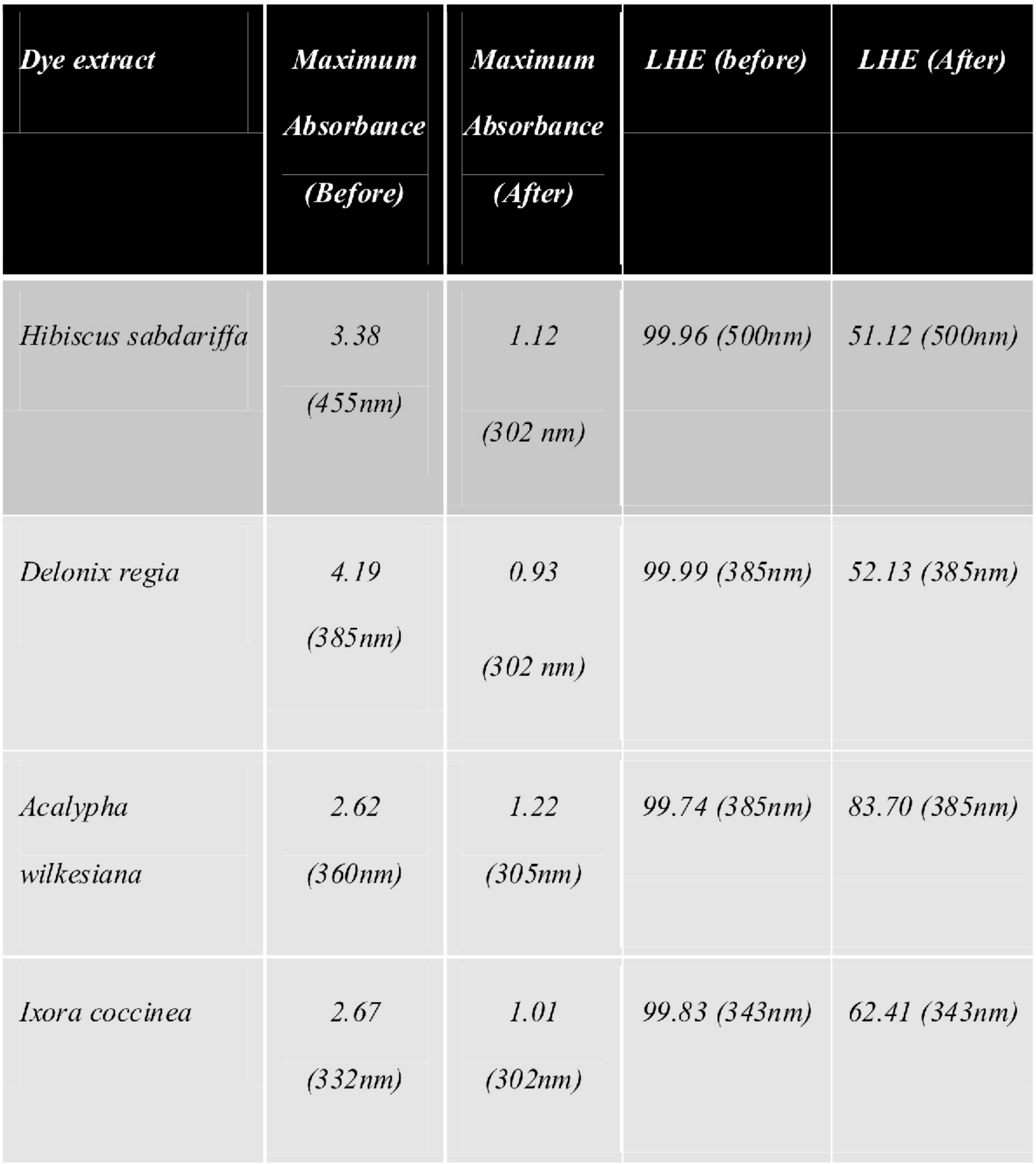
interaction with light defines its ability to absorb strongly or weakly at a specific wavelength. In view of this, the variation in absorbance with wavelength is presented for the dye extracts in figure 1.

Table 1: Measured *pH* values for the extracted dyes

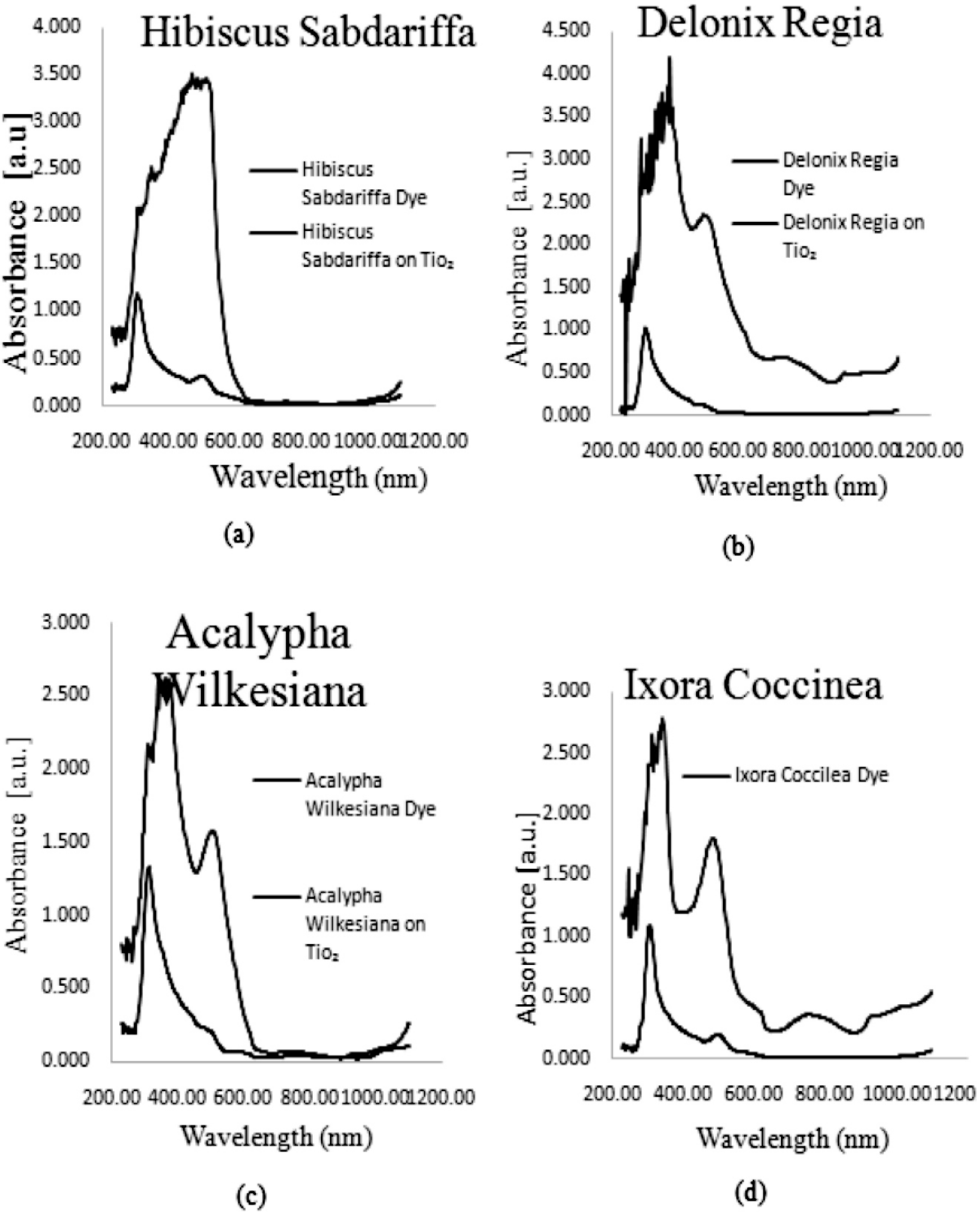
Dye Extract	*pH value*
Hibiscus sabdariffa	4.01
Delonix Regia	4.85
Acalypha Wilkesiana	3.78
Ixora Coccinea	3.20

The maximum absorbance and light harvesting efficiency (LHE) values for the dye extracts before and after adsorption on the TiO_2 photoelectrodes are given in table 2. In figure 1, absorption maxima were observed in the range*332nm* to *455nm*for the dye extracts but upon sensitization, there was reduction in absorption intensity which broadened towards the longer wavelength. The difference in the absorption intensity and broadening between the dye extract in solution and the one adsorbed on TiO_2 could be due to weak bonding of anthocyanin molecules in the dye extract to the oxide surface. Chemisorption of anthocyanins on TiO_2 has been reported by Hao*et al.,* 2006 to be as a result of alcoholic bound protons which condense with the hydroxyl groups present at the surface of nanostructured TiO_2. This attachment to the TiO_2 surface stabilizes the excited state, thus shifting the absorption maximum towards the lower energy of the spectrum. In our study, a shift in the absorption maximum towards the higher energy of the spectrum was observed. This observation suggests that there was no effective adsorption which could be attributed to the high *pH* value and the long bond length of the *OH* groups present in the dye extracts. These long *OH* groups may prevent anthocyanin from forming a bond with the oxide surfaceand also from arraying to the TiO_2film effectively. The shift may also be attributed to the changing of the anthocyanin molecule from the more stable flavilium state to the unstable quinoidal state upon chelation.

Since the cross section for photon absorption of most photosensitizers is much smaller than the geometric area occupied on the semiconductor surface, then the light absorption by a dye monolayer is small (Grätzel, 2005). However, to produce light harvesting efficiency close to unity requires thin film semiconductors. To avoid this, thin film TiO_2 photoelectrodes sensitized with dye extracts have been used. The light harvesting efficiency values obtained are plotted against wavelengths as shown in figure 2.



Dye extract	*Maximum Absorbance (Before)*	*Maximum Absorbance (After)*	*LHE (before)*	*LHE (After)*
Hibiscus sabdariffa	*3.38 (455nm)*	*1.12 (302 nm)*	*99.96 (500nm)*	*51.12 (500nm)*
Delonix regia	*4.19 (385nm)*	*0.93 (302 nm)*	*99.99 (385nm)*	*52.13 (385nm)*
Acalypha wilkesiana	*2.62 (360nm)*	*1.22 (305nm)*	*99.74 (385nm)*	*83.70 (385nm)*
Ixora coccinea	*2.67 (332nm)*	*1.01 (302nm)*	*99.83 (343nm)*	*62.41 (343nm)*



(a)

(b)

(c)

(d)

Figure 1: Absorbance for (a) Hibiscus sabdariffa, (b) Delonix regia, © Acalypha wilkesiana and (d) Ixora coccinea before and after adsorption on TiO$_2$

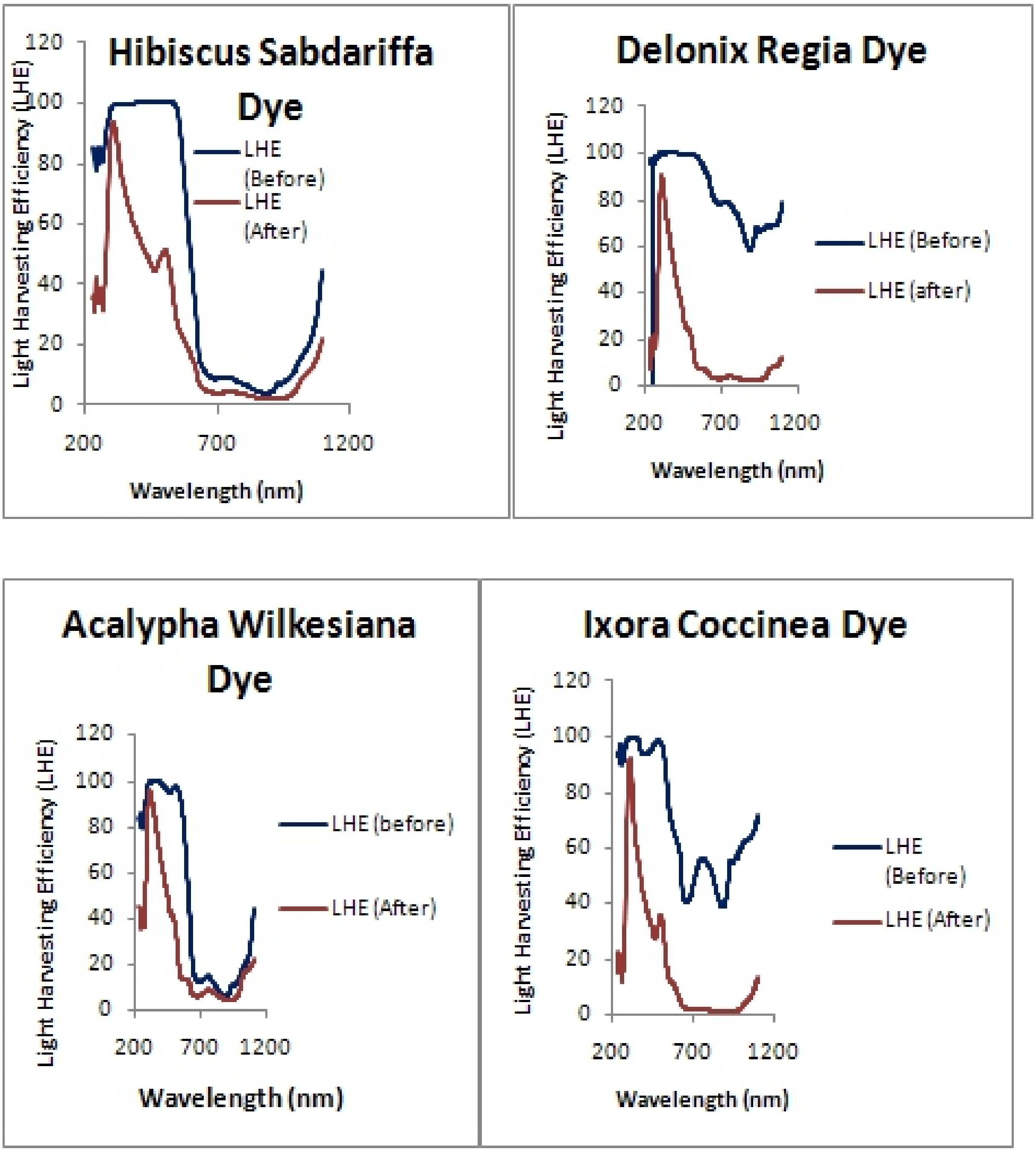
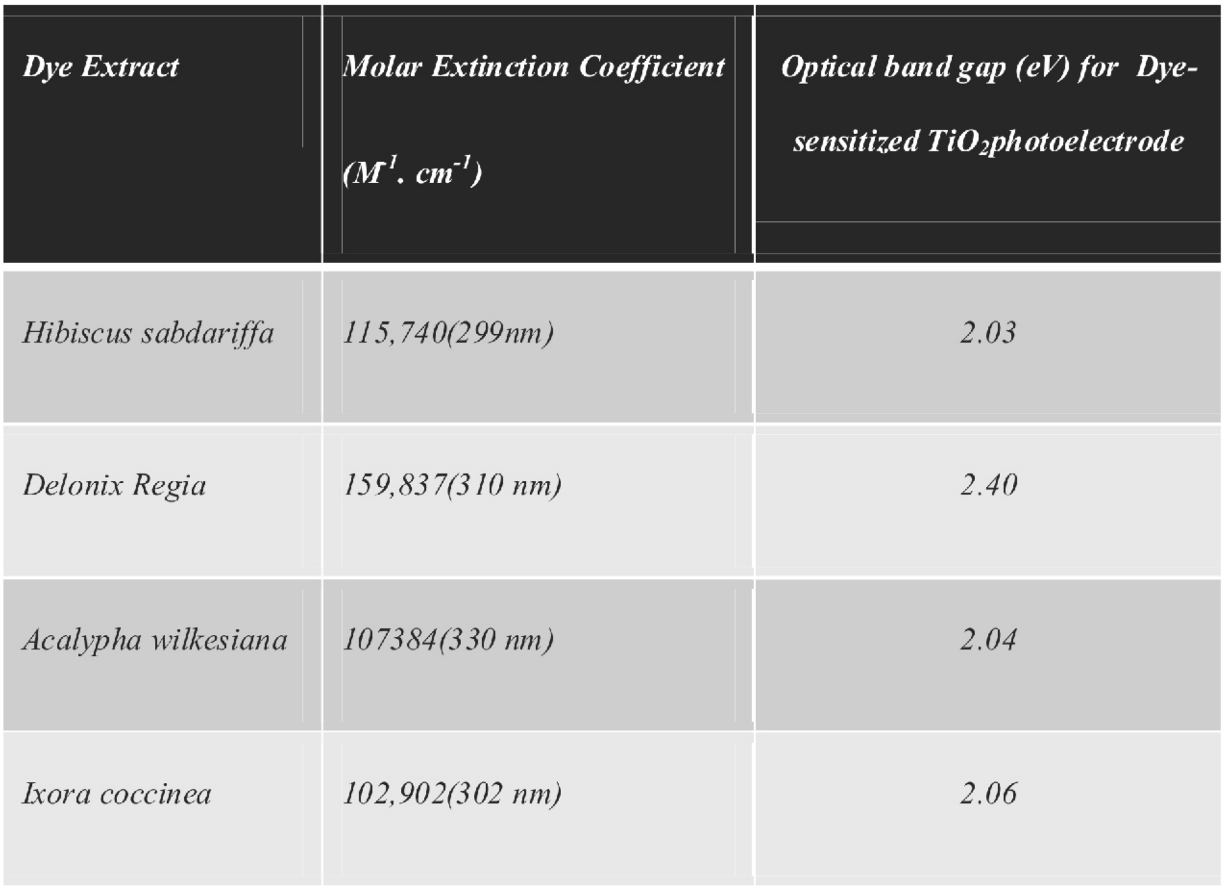


Figure 2: Light Harvesting Efficiency (LHE) before and after sensitization of TiO_2 PhotoelectrodesThe molar extinction coefficients were calculated using equation (3) and the values obtained are given in table 3. A major issue with light harvesting using anthocyanin dyes is that the absorption bands of the sensitizers are quite broad before sensitization and become a bit discrete after sensitization. Whilst the molar extinction coefficients in these absorption bands

can be very high, it turned out that only small areas are being covered by the solar irradiancespectrum.

Table 3: Calculated maximum molar extinction coefficient for the dye extracts and optical band gap for Dye-sensitized TiO_2Photoelectrodes



Dye Extract	*Molar Extinction Coefficient (M^1. cm^{-1})*	*Optical band gap (eV) for Dye-sensitized TiO_2photoelectrode*
Hibiscus sabdariffa	*115,740(299nm)*	*2.03*
Delonix Regia	*159,837(310 nm)*	*2.40*
Acalypha wilkesiana	*107384(330 nm)*	*2.04*
Ixora coccinea	*102,902(302 nm)*	*2.06*

Most notably, the bandwidth is within the range of *150nm* to *200nm*. Additionally, the region between *450nm* to *550nm* also has a low absorption of incident photons. This lack of absorption significantly constrains the photocurrent which can be obtained fromanthocyanin-based *DSC*.

It is a well-known fact that when TiO_2 is irradiated with ultraviolet light (wavelength less than *385nm*), electron-hole pairs are created but the electrons find it difficult to move to the conduction band because of the large band gap (*3.2eV*). In this work, it was discovered that TiO_2 band gap was reduced upon sensitization with the extracted dyes. For the sensitized TiO2 photoelectrodes, the optical band gaps were obtained at the point where spectra showed a strong cut off, when the absorbance values are minimum using equation (4). The band shifts could be attributed to the molecular transitions that take place when the dye molecule chelates with TiO_2. Anthocyanin dyes exhibit π - π*orbital transition which is attributed to the wavelength range between *500nm*to slightly above *600nm*. In this work, the cut off wavelength for spectra ranges between *522nm* to *610nm*. **The values obtained for the optical band gap are given in table *3*.**

4. CONCLUSION

In this work four different natural dyes were extracted using the simple solution aqueous method. Their *pH* values were measured using *TechmelpH* meter and their optical properties before and after sensitization on TiO_2 photoelectrodes were investigated employing *UV-V*isible spectrophotometer model *UV-750* in the wavelength range *210nm* to *1100nm*. In this work, t**he measured pH values for the dye extracts extend up to about 5.0. The possibility of the dye molecules having more *OH* groups with long bond length is high, since *pH* values extends toward basicity.** Absorption maxima were observed around*332nm* to *455nm*for the dye extracts but upon sensitization, there was reduction in absorption intensity which broadened towards the longer wavelength. The difference in the absorption intensity and broadening between the dye extract in solution and the one adsorbed on TiO_2 could be due to weak bonding of anthocyanin molecule in the dye extract to the oxide surface. **The light harvesting efficiency values before sensitization are almost close to unity but gradually reduce after sensitization. Most notably, the bandwidth is within the range of *150nm* to *200nm*. Additionally, the region between *450nm* to *550nm* also has a low absorption of incident photons. The calculated molar extinction coefficients were found to be high with values ranging between *102,902*M^{-1} cm^{-1}*to159,837*$M^{-1}cm^{-1}$*with delonix regia having the highest value*. In this work, it was discovered that TiO_2band gap was reduced upon sensitization with the extracted dyes. The value ranges between *2.03eV* to *2.40eV*with the least difference occurring for delonix regia sensitized TiO_2 photoelectrode.**It is highly recommended that stable dye mixtures should be engineered using organic reagents and acids that would significantly lower the *pH* values so as to extend the sensitizers absorption further towards the red end of the spectrum.

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