PRINT ISSN 1119-8362
Electronic ISSN 1119-8362

Full-text Available Online at
https://www.ajol.info/index.php/jasem
http://www.bioline.org.br/ja

J. Appl. Sci. Environ. Manage.
Vol. 26 (5) 943-948 May 2022

Matrix Method of Determining Optical Energy Bandgap of Natural Dye Extracts

[1*] YERIMA, JB; [1,2]BABANGIDA, A; [1*]EZIKE, SC; [3]DUNAMA, W; [1]AHMED, AD

[*1]*Department of Physics, ModibboAdama University Yola, Adamawa State, Nigeria*
[2]*Department of Physics, Aminu Saleh College of Education Azare, Bauchi State, Nigeria*
[3]*Department of Mathematics, ModibboAdama University Yola, Adamawa State, Nigeria*

**Corresponding Author Email: sabastine.ezike@mautech.edu.ng; bjyerima@gmail.com*
Other Authors Emails: bgalkali2@gmail.com; dunamakadiri@gmail.com; adahmed19@mautech.edu.ng

ABSTRACT: In this paper, a total of fourteen dye extracts from different plants' parts (flowers and fruits) were extracted. Absorbance of light by dye extracts with 5%, 10% and 20%concentrationsweremeasured using a UV-Vis spectrophotometer at different wavelengths. A system of linear equations in terms of wavelength and absorbance without film thickness was developed and solved using MATLAB software. Also, optical energy bandgap (E_g) obtained experimentally are at range of 1.77- 2.76 eV. From the solutions of the system of equations, the $E_g$of the natural dyes were obtained. The results show all the dye extracts have E_g in the range 1.34-2.09 eV which falls within the range of UV and IR portions of the electromagnetic spectrum. Also, the results reveal that sunflower (*Helianthus*) dye has the smallest E_g of 1.34 eV and guava (*Guajava*) peel dye with the higherE_g of 2.09 eV. This means *Helianthus* dye absorbs more light over a wider part of the electromagnetic spectrum and the easier electron transfer from its valence band to the conduction band. The values obtained via matrix method are in agreement with the experimental values with slight deviation, hence this validates the matrix method of obtaining optical energy bandgaps.

DOI: **https://dx.doi.org/10.4314/jasem.v26i5.22**

Impact factor: **http://sjifactor.com/passport.php?id=21082**

Google Analytics: https://www.ajol.info/stats/bdf07303d34706088ffffbc8a92c9c1491b12470

Dates: Received: 13 March 2022; Revised: 13 April 2022; Accepted: 11 May 2022

Keywords: Absorbance, Energy bandgap, Natural dyes, Matrix technique, MATLAB software

In semiconductor industries, TiO_2 (Ezike, 2020; Ndeze *et al*., 2021) simply called titania is added as an ingredient to coatings. TiO_2 is known to enhance the internal trapping of light by scattering (redirecting) the light reflected from the metallic electrode in the active layer and also to improve the transport of charge carriers through the active layer (Banwell, 1983). The optical band gap of active layer is very important. The optical energy bandgap (E_g) properties of a semiconductor can be controlled or enhanced by using semiconductor alloys or natural dye-sensitizers (Sharma *et al*., 2018). An alternative technique is to employ layers of various materials coated unto the silicon base materials. This is used in the solar industry in the construction of photovoltaic solar cells. The E_g is useful as it controls the part of the solar spectrum a photovoltaic cell absorbs. A larger portion of the solar radiation reaching the earth is composed of wavelengths with energies greater than the $E_g$of silicon (Rhodes, 2010). These higher energies will be absorbed by the solar cell, but the difference in energy is converted into heat energy rather than useful electrical energy. As a result, except the E_g is controlled, the efficiency of the solar cell will be poor. Using layers of various materials with various E_g properties is known to give maximum efficiency of the solar cells. In other to improve the performance of photosensitizers for energy sustainability and efficiency, several scientists have used different materials such as ZnO/CdS (Repins *et al*., 2008), Dye-Sensitized Colloidal TiO_2 Films (O'Regan and Grätzel, 1991; Wante *et al*., 2021; Salawu *et al*., 2022), Sb_2S_3-Sensitized Nanoporous TiO_2 Solar Cells (Itzhaik *et al*., 2009), Photoelectrochemical Cell with Mesoscopic Electrodes Sensitized by Lead-Halide Compounds (Kojima *et al*., 2008), Tris (2-(1H-pyrazol-1-yl)pyridine)cobalt (III) as p-Type Dopant

**Corresponding Author Email: sabastine.ezike@mautech.edu.ng; bjyerima@gmail.com*

for Organic Semiconductors and Its Application in Highly Efficient Solid-State Dye-Sensitized Solar Cells (Burschka *et al*., 2011) and Perovskites (Snaith, 2013; Ezike *et al*., 2021a) amongst many others. We report fourteen different dye extracts obtained from different plant parts (flowers and fruits) prepared at concentrations of 5%, 10% and 20%, and their absorbance were measured using UV-Vis spectrophotometer. System of linear equations in terms of wavelength and absorbance were developed and solved using matrix method to obtain E_g via MATLAB software. The E_g obtained using set of equations solved using MATLAB corresponded with the earlier reports on E_g of the extracts.

MATERIALS AND METHODS

Sample Collection: Various plant parts: flowers [sunflower(*helianthus*), Witchweed (*Strigahermonthica*), red cockscomb (*celosiaagentea*), rose (*rosaceous*), hibiscus (*Hibiscus rosa Sinensis*), flamboyant (*Delonix regia*), bougainvillea(*bougainvillea*), wild marigold (*Calendula arvensis*), and lantana (*lantana camera*)]; five fruits [bitter guord (*mormodicacharantia*), guava peel (*Psidium guajava*), orange peel (*citrus sinensis*), tomato (*Lycopersicon esculentum*), and mango peel (*mongifera indica*)] were used as source of natural dyes. The plant parts were dried on shade for two weeks. The dried samples were grinded into fine powder with the help of a blender (BLSTVB-RVO-000 from Walmat). 2g of each of the powdered samples was collected in sterile 50 ml falcon tubes and 20 mL of ethanol was then added and the solutions were vortexed. The solutions were sonicated using a sonicator (Branson SFX250) for one hour at 4 ℃. The solutions were then centrifuged at 1500 rpm at 4 ℃ for ten minutes. The residues were filtered using filter paper while the filtrate was collected, and stored at 4 ℃ for further use. The different formulations of selected plants' pigments were extracted using ethanol with a fixed amount of 0.1 moles of hydrochloric acid. The ethanol solvent with 0.1M HCl was taken as control. The containers were covered with aluminium foil to prevent damage from light exposure (Babangida *et al*., 2022). The absorption spectra of extracted dyes were obtained in the wavelength range of 200 - 800 nm using a UV–VIS spectrophotometer.

Estimation of Optical Band Gap Energy: The optical band gap energy in the photo-absorbers (the plant parts extracted dyes) were estimated using various theories that requires the measurement of the absorbance spectrum without the need for extra information such as the film thickness or reflectance spectra (Souri and Shomalian, 2009; Alarcon *et al*., 2007). The relationship between the absorption coefficient α(ν) and photon energy ($h\upsilon$) is given by Equation (1) (Uyanga *et al*. 2020;Ossai *et al*., 2020; Ezike, 2018; Mott and Davis, 1979; Tauc and Menth, 1972; Ghobadi, 2013)

$$\alpha(\upsilon)h\upsilon = B\left(h\upsilon - E_g\right)^m \qquad (1)$$

Where B is a constant, ν is the frequency of photon, and m depends on the nature of the electron transition and is equal to 0.5 or 2 for the direct and indirect transition band gaps (Chopra *et al*., 1990). According to Beer-Lambert's law, the absorption coefficient (Equation 2) can be written as (Ezike *et al*., 2020; Ezike, 2020; Balogun *et al*., 2018)

$$\alpha(\upsilon) = \frac{2.303A(\lambda)}{t} \qquad (2)$$

Where t is the film thickness and A (λ) is the film absorbance. For more accurate measurement or evaluation of α (ν), it is required corrections to the absorption due to reflectance are done. To obtain the E_g from absorption spectrum measurements using MATLAB software technique we started by combining Equations (1) and (2) to get Equation (3)

$$\left(\frac{1240A}{\lambda}\right)^{\frac{1}{m}} = \left(\frac{Bt}{2.303}\right)^{\frac{1}{m}}\left(\frac{1240}{\lambda} - E_g\right) \qquad (3)$$

Since m, t, and B are constants, we set the term $\left(\frac{Bt}{2.303}\right)^{\frac{1}{m}}$equals to another constant, say A_0, so that Equation (3) can be written as

$$\left(\frac{1240A}{\lambda}\right)^{\frac{1}{m}} = A_o\left(\frac{1240}{\lambda} - E_g\right) \qquad (4).$$

Now, for $m = 0.5$ or 2, Equation (4) is linear representing a straight line if the term on the left-hand side is replaced by Y and the $\frac{1240}{\lambda}$ at the right hand of Equation (4) is replaced by X so that the resulting equation (5) takes the form

$$Y = A_oX - C \qquad (5)$$

Where the slope, $S = A_0$ and the intercept, $C = A_0E_g$

Finally, Equation (5) can be solved using MATLAB software which requires system of linear equations to be solved. In this case, any n set of pairs of Y and X values substituted into Equation (5) yields n set of linear equations in A_0 and C in the form $Y_i = A_oX_i - C$ (i=1, 2, 3, …., n)which can be solved for A_0 and C such that $E_g = \frac{C}{A_o}$can be calculated.

RESULTS AND DISCUSSION

Table 1 contains the absorbance of light by dye extract with concentrations of 5%, 10%, and 2% measured using a UV-Vis spectrophotometer. The peak absorbance values are reported in Table 1 obtained at specific wavelength range. The peak absorbance values obtained lie at visible range of em spectrum. Absorption of the extract at visible region indicates that they are potential photo-absorber in solar cells. Bitter gourd (*Momordica charantia*), Orange peel (*Citrus sinensis*), Mango peel (*Mongifera indica*), Guava peel (*Psidium guajava*) (20%), Tomato peel (*Lycopersicon esculentum*), *Bougainvillea*, *Striga* flower, Hibiscus, *Rosaceous* (20%), *Helianthus* flower and Wild marigold (*Calendula arvensis*) have peak absorbance value of 4 at visible region. The E_g can be calculated using Equation (6)

$$E_g = \frac{1240}{\lambda_p} \qquad (6)$$

Where λ_p is the corresponding wavelength at peak absorbance.

The E_g calculated using equation (6) for all the dye extracts are at range of 1.77-2.76 eV. The calculated E_g agree with previous reports (Syafinar *et al*., 2015; Safie *et al*., 2017)

Table 1: Peak absorbance value of dye extracts with corresponding wavelength obtained at varying concentrations

Dye extract	Concentration (%)	Peak absorbance Value (a.u)	Wavelength (range) (nm)
Wild marigold (*Calendula arvensis*)	5	4.00	450
	10	4.00	450-550
	20	4.00	450-550
Sunflower (*Helianthus*)	5	4.00	600-650
	10	4.00	600-700
	20	4.00	600-700
Rose flower (*Rosaceous*)	5	3.83	550
	10	3.85	550
	20	4.00	550
Hibiscus (*Hibiscus rosa Sinensis*)	5	4.00	450/550
	10	4.00	450-600
	20	4.00	450-600
	5	3.66	550
Lantana (*Lantana Camera*)	10	3.72	550
	20	3.79	550
Red Cockscomb (*Celosia cristata*)	5	3.58	550
	10	3.62	550
	20	3.85	550
Witch seed flower (*Striga hermonthica*)	5	4.00	600
	10	4.00	600-650
	20	4.00	600-700
Bougainvillea (*Bougainvillea*)	5	4.00	550
	10	4.00	550/650
	20	4.00	550-700
Flamboyant (*Delonix regia*)	5	3.87	650
	10	3.96	650
	20	3.94	700
Tomato peel (*Lycopersicon esculentum*)	5	4.00	550
	10	4.00	450/550
	20	4.00	450/550
Guava peel (*Psidium guajava*)	5	3.68	450
	10	3.74	450
	20	4.00	550
Mango peel (*Mongifera indica*)	5	4.00	550
	10	4.00	450/550
	20	4.00	450/550
Orange peel (*Citrus sinensis*)	5	4.00	550
	10	4.00	550
	20	4.00	550
Bitter gourd (*Momordica charantia*)	5	4.00	600-700
	10	4.00	600-700
	20	4.00	600-700

In this case, to obtain the solution to Equation (5) using the matrix method, we substitute values of both wavelength (λ) and absorbance (A) in Table 1 to generate a system of linear equations of the form of Equation (7)

$$Y_1 = A_o X_1 - C$$

$$Y_2 = A_o X_2 - C$$
$$Y_{13} = A_o X_{13} - C$$

The matrix solution of Equation (7) gives the values of A_o and C from which the value of E_g is calculated from $E_g = \frac{C}{A_o}$. The absorbance data for other photo-absorbers were reported elsewhere. Similarly, the procedure is performed for all the other samples and the corresponding E_g values are recorded in Table 2. The result shows that E_g lie in the range 1.34-2.09 eV which is within the photon energy range 1.55-3.1 eV of the visible spectrum. The sunflower, rose flower, Latana, Red cockscomb, Striga, Bougainvillea, flamboyant and Bitter gourd extend their absorption towards near infrared region. This behavior is closely matched to the absorption behavior of silicon with bandgap of 1.1 eV. Tomato peel, Guava, mango, hibiscus flower, Orange and marigold have E_g range of 1.89 – 2.09 eV. The concentrations of the active materials have no or little effect on the optical performance of the natural dye. The obtained $E_g s$ correspond with earlier reports (Babangida *et al*., 2022; Ossai *et al*., 2021a,b) suggesting that natural dyes absorb within visible and near infrared regions of em spectrum, hence can be deployed as photo-absorber in solar cells. This implies all the dye samples can absorb light energy from both UV and Vis portions of the electromagnetic (em) spectrum which they can convert into usable electrical energy without extra to convert to heat energy.

Table 2: Optical energy bandgap of natural dyes obtained via matrix method

Dye	% Extract concentration	E_g (eV)	*Photon Energy
Calendula arvensis	5	2.05	Vis
	10	1.90	
	20	2.09	
Helianthus	5	1.35	IR
	10	1.34	
	20	1.37	
Rosaceous	5	1.42	IR
	10	1.41	
	20	1.41	
	5	1.96	Vis
	10	1.93	
Hibiscus rosa Sinensis	20	1.89	
	5	1.54	IR
	10	1.56	
Lantana Camera	20	1.43	
Celosia cristata	5	1.51	IR
	10	1.61	
	20	1.60	
Striga hermonthica	5	1.72	Vis-IR
	10	1.62	
	20	1.55	
Bougainvillea	5	1.39	IR
	10	1.44	
	20	1.45	
Delonix regia	5	1.40	IR
	10	1.41	
	20	1.40	
Lycopersicon esculentum	5	2.05	Vis
	10	2.02	
	20	2.01	
Psidium guajava	5	2.09	Vis
	10	2.09	
	20	2.04	
Mongifera indica	5	2.02	Vis
	10	1.95	
	20	1.97	
Momordica charantia	5	1.53	IR
	10	1.46	
	20	1.44	
Citrus sinensis	5	2.04	Vis
	10	2.03	
	20	2.01	

**Photon energy range: UV: 124-3.10 eV; VIS: 3.10 -1.77 eV; IR: 1.77 eV - 1.24 meV*

Therefore, these dyes are good photosensitizers that can be employed in the fabrication of dye-sensitized solar cells (DSSCs) fabrication. It is worthy to note that the smaller the E_g, the easier the electrons transfer from the valence band to the conduction band, and hence the dye is a better photosensitizer (Ezike *et al*., 2021b).

The results show that sunflower (*Helianthus*) dye with 10% concentration has the least E_g of 1.34 eV which indicates that the dye absorbs light over a broader portion (UV-Vis, and IR) of the electromagnetic spectrum while the dye extract from guava (*Psidium guajava*) peel with 5% and 10% concentration has the highest value of E_g of 2.09 eV suggesting that the dye absorbs light in lesser portions (UV and Vis) of the em spectrum. These portions of the em spectrum are designated as UV-Vis and UV-IR in Table 2. This further confirms that the smaller the E_g of a material, it absorbs light from a wider portion of the em spectrum and hence the better photosensitizer it will be.

The values of E_g obtained using matrix method are in agreement with the experimental optical energy bandgaps from Equation (6). The values obtained $E_g$via matrix method deviated slightly from experimental values. However, the matrix method of obtaining optical energy bandgaps is valid.

Conclusion: Matrix method was deployed to solve linear system of equations to obtain optical band gap energy (E_g) of photo-absorbers (dyes) using MATLAB software. The result showed that E_g of the dyes lie at the range of 1.34-2.09 eV. Among the dyes, dye extract from sunflower (*helianthus*) has the smallest E_g=1.34 eV while guava (*guajava*) peel has E_g=2.09 eV which lies in the visible region of the electromagnetic spectrum. The experimental values of optical energy bandgaps and the values obtained via matrix method are in agreement. Hence, matrix method of obtaining E_g is valid.

REFERENCES

Alarcon, LE; Arrieta, A; Camps, E; Muhl, S; Rudil, S; Santiago, EV (2007). Comparison and semiconductor properties of nitrogen dopped carbon thin films grown by different techniques. *Appl. Surf. Sci.* 254: 412.

Babangida, A; Yerima, JB; Ahmed, AD; Ezike, SC (2022). Strategy to Select and Grade Efficient Dyes for Enhanced Photo-Absorption. *Afr. Sci. Rep.* 1: 16–22

Balogun, SW; Ezike, SC; Sanusi, YK; Aina, AO (2017). Effects of thermal annealing on optical properties of poly (3-Hexyithiophene): [6, 6]-Phenyl C6o-butyric acid methyl ester blend thin film, *JPMT* 3: 14-19

Banwell, CN (1983). Fundamental of molecular spectroscopy, University of Sussex, 3rd edition

Burschka, J; Dualeh, A; Kessler, F; Baranoff, E; Cevey-Ha, NL; Yi, CY; Nazeeruddin, MK; Gratzel, M (2011). Tris(2-(1H-pyrazol-1-yl)pyridine)cobalt(III) as p-Type Dopant for Organic Semiconductors and Its Application in Highly Efficient Solid-State Dye-Sensitized Solar Cells. *J. Am. Chem. Soc.* 133:18042−18045.

Chopra, N; Mansingh, A; Chadha, G.K (1990). Electrical, optical and structural properties of amorphous V_2O_2 blown films. *J. Non-cryst Solids*194**:** 126.

Ezike, S (2020). Effects of concentration variation on optical and structural properties TiO_2 thin films. *J. Mod Mater* 7: 1-6.

Ezike, SC (2018). Stability Improvement of Perovskite Thin Films Through Surface Modifications for Perovskite Solar Cells Fabrication. Thesis, Kwara State University

Ezike, SC; Alabi, AB; Ossai, AN; Aina, AO (2020). Effect of tertiary butylpyridine in stability of methylammonium lead iodide perovskite thin films. *Bull. Mater. Sci.* 43: 40

Ezike, SC; Alabi, AB; Ossai, AN; Aina, AO (2021a).Stability-improved perovskite solar cells through 4-tertbutylpyridine surface-passivated perovskite layer fabricated in ambient air. *Opt. Mater*. 112: 110753.

Ezike, SC; Hyelnasinyi, CN; Salawu, MA; Wansah, JF; Ossai, AN; Agu, NN (2021b). Synergestic effect of chlorophyll and anthocyanin Co-sensitizers in TiO_2-based dye-sensitized solar cells. *Surf. Interfaces* 22: 100882

Ghobadi, N (2013). Bandgap determination using absorption fitting (ASF) spectrum. *Int. Nano Lett* 3: 2.

Itzhaik, Y; Niitsoo, O; Page, M; Hodes, G (2009). Sb_2S_3-Sensitized Nanoporous TiO_2 Solar Cells. *J. Phys. Chem. C* 113: 4254−4256.

Kojima, A; Teshima, K; Shirai, Y; Miyasaka, T (2008). Novel Photoelectrochemical Cell with

Mesoscopic Electrodes Sensitized by Lead-Halide Compounds. 214th ECS Meeting, Honolulu, Hawaii, Oct. 12−17.

Mott, NF; Davis, EA (1971). Electronic process in non-crystalline materials. Oxford University Press

Ndeze, UI; Aidan, J; Ezike, SC; Wansah, JF (2021). Comparative performances of nature-based dyes extracted from Baobab and Shea leaves photo-sensitizers for dye-sensitized solar cells (DSSCs). *CRGSC* 4: 100105.

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.

Ossai AN, Ezike SC, Timtere P, Ahmed AD (2021a) Enhanced photovoltaic performance of dye-sensitized solar cells-based Carica papaya leaf and black cherry fruit co-sensitizers. *Chem. Phy. Impact* 2: 100024.

Ossai AN; Alabi AB; Ezike SC; Aina AO (2021b). Zinc oxide-based dye-sensitized solar cells using natural and synthetic sensitizers. *CRGSC* 3**:** 100043.

Ossai, AN; Ezike, SC; Dikko, AB (2020). Bio-synthesis of zinc oxide nanoparticles from bitter leaf (vernonia amygdalina) extract for dye-sensitized solar cell fabrication. *J. Mater. Environ. Sci*. 11: 444-451.

Repins, I; Contreras, MA; Egaas, B; DeHart, C; Scharf, J; Perkins, CL; To, B; Noufi, R (2008). 19.9%-Efficient $ZnO/CdS/CuInGaSe_2$ Solar Cell with 81.2% Fill Factor. *Prog. Photovoltaics* 16: 235−239.

Rhodes, CJ (2010). Solar energy: principles and possibilities. *Sci. Prog.* 93: 37–112

Safie, NE; ludin, NA; Hamid, NH; Sepeai, S; Teridi, MAM; Ibrahim, MA; Spiano, K; Arakawa, H (2017). Energy levels of natural sensitizers extracted from rengas (*Gluta* spp.) and mengkulang (*Heritiera elata*) wood for dye-sensitized solar cells. *Mater Renew Sustain Energy* 6: 5.

Salawu, MA; Ayobami, AA; Adebisi, A; Ezike, SC; Saheed, YO; Alabi, AB (2022). Characterization of Eosin red and hibiscus sabdariffa-based dye-sensitized solar cells. *Opt. Mater.* 127: 112177

Sharma, K; Sharma, V; Sharma, SS (2018). Dye-Sensitized Solar Cells: Fundamentals and Current Status. *Nanoscale Res. Lett.* 13: 381.

Snaith, HJ (2013). Perovskites: The Emergence of a New Era for Low-Cost, High-Efficiency Solar Cells. *J. Phys. Chem. Lett.* 4: 3623−3630.

Souri, D; Shomalian, K (2009). Bandgap determination by absorption spectrum fitting (ASF) method and structural properties of different compositios of $(60\text{-}x)V_2O_5\text{-}40TeO_2\text{-}xSb_2O_3$ glasses, *J. Non-cryst. Solids* 355: 1597-1601.

Syafinar, R; Gomesh, N; Irwanto, M; Fareq, M; Irwan, YM (2015). Chlorophyll Pigments as Nature Based Dye for Dye-Sensitized Solar Cell (DSSC). *Energy Procedia* 79: 896-902

Tauc, J; Menth, A (1972). States in the gap. *J. Non-cryst Solids* 569: 8-10

Uyanga, KA; Ezike, SC; Onyedika, A; Kareem, AB; Chiroma, TM (2020). Effect of acetic acid concentration on optical properties of lead acetate based methylammonium lead iodide perovskite thin film. *Opt. Mater.* 109:110456

Wante, HP; Aidan, J; Ezike, SC (2021). Efficient dye-sensitized solar cells (DSSCs) through atmospheric pressure plasma treatment of photoanode surface. *CRGSC* 4: 100218