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Characterization of Dye Sensitized Cells Using Natural Dye from Oil Bean Leaf (*Pentaclethra macrophylla*): The Effect of Dye pH on the Photoelectric Parameters

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Abstract

Fresh leaves of oil bean (*P. macrophylla*) were used as sensitizers for fabrication of dye sensitized solar cells (DSSCs) at four dye pH values of 2.58°C at 23.7°C, 2.62°C at 22.2°C, 2.65°C at 22.3°C and 3.61°C at 22.1°C. The methanol extracts of *P. macrophylla* were extracted and used as sensitizers for the development of dye sensitized solar cells. The solar cells sensitized by *P. macrophylla* leaf extracts realised up to short circuit current (J_{sc}) 0.16 mA/cm², open circuit voltage (V_{oc}) 0.045 V, P_{max} 0.031 mW/cm² and fill factor (FF) 0.50. The energy conversion efficiency (η) of the DSSCs is 0.43%. Phytochemical screening of *P. macrophylla* leaf extract shows the presence of flavonoids and anthraquinones. The nanostructured dye shows conversion of solar energy into electricity using low cost natural dyes as wide band-gap semiconductor sensitizers in DSSCs. This will provide economically viable substitute to silicon p-n junction photovoltaic (PV).

Keywords

Dye-Sensitized Solar Cells, Dye Sensitizer, *P. macrophylla* Leaf, Anthraquinones, Conversion Efficiency

1. Introduction

The concept of dye sensitization of wide band gap mesoporous metal oxide semiconductors began by the work

of [1] [2] in 1960 with collaboration of their co-workers; they used several dyes as photo sensitizers and zinc oxide (ZnO) as semiconductor. ZnO is a compound of group II, VI elements. Its unique applications and semiconductor properties are drawing attention from researchers because of its diverse uses in everyday life. ZnO has high electron mobility [3], strong-luminescence at room temperature and good transparency. Efficiencies observed were very low for many years [4]. In 1991, progress was made when [5] [6] obtained efficiency higher than 7% from using TiO₂ with a Ruthenium based sensitizer as semiconductor material [6]. DSSC research increased its impact worldwide [7] after Ruthenium-based dye was used and a higher efficiency; 11% was recorded in a cell made with TiO₂ nanoparticles in a photoelectrochemical cell (PEC) device. Nanocrystalline TiO₂ existed in five different forms; TiO₂ (anatase) was used because it was abundant, safe and very stable. TiO₂ has a wide band gap ($E_{g_{\text{rutile}}} = 3.0 \text{ eV}$; $E_{g_{\text{anatase}}} = 3.3 \text{ eV}$). DSSC technology based on PEC holds out the promise of cheaper solar cells significantly less than customary silicon cells. The PEC is an electrolyte-based semiconductor device that generates photovoltage when illuminated and it is photocurrent when external circuit is closed. The short circuit current is a linear function of intensity of illumination, so the device does not need external bias. Investigations revealed cheaper manufacturing costs and faster process of producing DSSC modules.

Transport and light absorption in DSSC are separated unlike in silicon solar cells where the sensitizer harvesting the light is attached to a wide band semiconductor surface [6]. At the boundary, charge separation through light induced electron transmission from the into the semi-conductor conduction band of the dye to the charge collector [8]-[12]. At present, ruthenium polypyridyl complex manufactured from heavy transition metal compound is most commonly used because of its good absorption, long excitation lifespan, highly efficient metal-to-ligand charge transfer (MLCT) [13] and strong charge-transfer (CT) absorption in the visible spectrum of light. Complexes of Ruthenium are however difficult to prepare as well as expensive; this restricts their applications on a large-scale in solar cells, creating a need for cheaper alternatives like organic cells [14]. DSSC's with efficiencies of up to 9% using organic cells that have properties like Ruthenium have been investigated [15]-[17]. Organic dyes used as dye sensitizers in DSSC's are from fruits, plants, leaves, pulp and other natural sources [18]-[20]. Most leaves, flowers and fruits contain different pigments that are used in DSSC's. Green leaves are usually rich in chlorophyll; its application as dye sensitizers has been researched by many scientists [9] [17]. Anthocyanins are responsible for the colour of plants and fruits, the red colour of petals, purple-red color of autumn leaves and the rich olive green of the oil bean leaf. In this paper, flavonoid and anthocyanin extracts of the hexane fraction of *P. macrophylla* were used as dye sensitizer at different pH in DSSC's.

P. macrophylla Benth (Oil Bean) tree is a member of the "Fabaceae" family [21], Leguminosae-Mimosoideae sub family, of genus *Pentaclethra*. It has some local names: African oil bean, Atta bean, Congo acacia, Ngazi (English), Owala, Mubala, Owala oil tree, arbre à acacia cu Congo (French), and Sucupira, Marróne (Poland). *P. macrophylla* provides food for West Africans, all through the rain forest belt. Its seeds are roasted or boiled; when fermented, the seed is served as a meaty flavoured snack, "Ugba". The dry empty pod is used as a source of fuel. *P. maloba* also belongs to the same genus and family, but it is found in temperate regions of the world. *P. macrophylla* seed oil can be extracted for fuel, used in cooking, food preservation, spices and condiment. The leaves, when they fall, improve soil fertility. *P. macrophylla* wood "mubala" or "ovala" is suitable for making charcoal and fuel. Ash from its pods, wood or tannins is used as a mordant for dyeing in Ghana. Household utensils and decorations are carved from its wood in Nigeria and Ghana. Its seeds are decorative and are used in beads, rosaries and necklaces. It is nitrogen-fixing plant and so enriches the soil nutrient content [22]. Two years after cultivation, *P. macrophylla* develops a measure of resistance to fire and when lopped; it sprouts easily. Species grow relatively fast and attain a height of about 1.5 metres in first year after on good soil and favourable weather conditions. The wood is strong and hard, but difficult to work.

2. Experimental Details

2.1. Extraction of *P. macrophylla* Leaf Dye

Leaves of *P. macrophylla* were dried in air until it crumbled dry crisply. It was milled to coarse particles, and spread out to dry to prevent it from becoming moldy. A phytochemical screening was done on the leaf sample to identify the active chromophores. *P. macrophylla* was soaked in methanol for eleven days to extract the dye. This dyesol (dye solution) mixture was separated using plastic funnels and cotton wool. The filtrate was collected in large sample bottles and covered. This was then poured periodically into a rotary evaporator, to separate the dye from the mother liquor for future use in the laboratory.

2.2. Batch Separation of Dye

A separating funnel was used to purify the feedstock. The crude extract (dye) was mixed with 40 ml Hexane and 20ml Ethyl Acetate [23] [24]. This mixture was thoroughly mixed and poured into the flask of the separating funnel to obtain the different sections. The four portions obtained were:

- The crude;
- Aqueous;
- Hexane;
- Ethyl Acetate factions.

The dry crude and hexane portions had the largest percentage; the aqueous and ethyl acetate factions were very small.

Test for Flavonoids

The solution of the extract was tested with the following reagents:

Shinoda Test: 3 ml of extract was added to a small quantity of magnesium turnings, and then a few drops of concentrated hydrochloric acid were run down the side of the test tube. At the upper phase, the appearance of three colour bands; orange, pink, reddish indicated the presence of flavonoid (Table 1).

Test for Anthraquinones

Free Anthraquinones: About 0.5 g of the extract was shaken with 5 ml of chloroform for ten minutes and filtered. The filtrate was shaken with 5 ml of ammonia solution. Presence of a pink colour in the ammoniacal phase indicated the presence of free anthraquinones (Table 1).

Combined Anthraquinones: 1 g of powdered extract was boiled with 5 ml of 10% hydrochloric acid for five minutes and filtered while hot. The cool filtrate was partitioned against equal volume of chloroform (two volumes), avoiding vigorous shaking. A clean pipette was then used to transfer the chloroform layer to a test tube taking care not to include the aqueous layer. An equal volume of 10% ammonia was added to the chloroform extract. A pink, red or violet colour in the aqueous layer indicates the presence of combined anthraquinones (Table 1).

2.3. Preparation of DSSC

Commercial TiO₂ powder (Assay 98% min) variety was used. The TiO₂ film was prepared by smoothening 12 g TiO₂ in 20 ml of concentrated nitric acid for about 1hour and sintered in the oven to properly fuse the TiO₂ molecules and to enhance its absorption performance. The whitish paste was spread on Fluorine doped tin oxide (FTO) conducting glass with dimensions: 50 mm × 50 mm × 22 mm and surface resistivity 7 Ω/m² (735140-5EA. ALDRICH). Screen printing method and rigid squeegee was used to deposit TiO₂ paste on the FTO. TiO₂ nanoparticles thus produced had an average particle size of 20 nm. The DSSC's active area was 6.25 mm² (≈ 2.5 mm × 2.5 mm).

The sintered TiO₂ was immersed in *P. macrophylla* dye, allowing the dye to be adsorbed on TiO₂ nanoparticles. Methanol was used to clean off any dye trickle on the FTO. After cleaning the DSSC's, the photoelectrode was assembled. Soot was coated on the conducting side then, each unit of DSSC was held firmly with crocodile clips; Allowing a little space at the edges to enable injecting the dye sensitizers or electrolyte.

2.4. Current Voltage Characterization

The performance of the DSSC under AM1 atmosphere was measured using a multimeter (Voltcraft; M-3850 series). Results obtained was plotted to obtain an I-V curve, from which the open circuit voltage V_{oc} (V), short-circuit current density J_{sc} (mA/cm²), fill factor (FF) and conversion efficiency η% was determined.

3. Results and Discussion

Figure 1 shows the Fourier Transform Infrared spectroscopy (FTIR) spectrograph of *P. macrophylla* leaf dye

Table 1. Phytochemical analysis of *P. macrophylla*.

Analysis	<i>P. macrophylla</i>	
	Anthraquinones	Flavonoids
	++	++

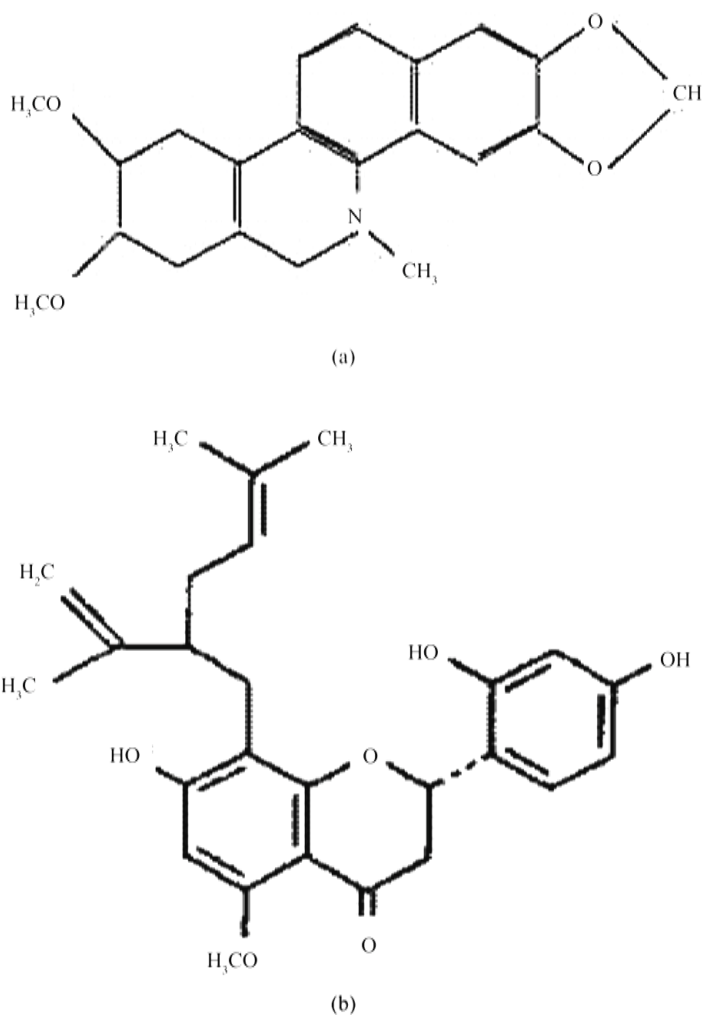


Figure 1. Chemical structure of two allotropes of *P. macrophylla*. (a) <http://journal.9med.net/upload/Image/4QT23.jpg@21/03/15;> 3:48 p.m; (b) <http://www.plant-expert.com/upload/structures/34981-26-5.gif @ 21/03/15 by 3;> 50 p.m.

extract used as dye sensitizer on sintered TiO₂ nanoparticle. It reports [25] functional groups and types of bonds present in an organic compound from a list of absorption frequency and peaks shown by its wave number.

FTIR is very useful in the analysis of metal complexes and fluoromanganates contained in organic compounds. A detailed analysis of compounds present in *P. macrophylla* is shown in **Table 2**.

An absorption peak (A.P) 426.28 cm⁻¹ indicates any iodoalkane-type bond (C-X), its appearance is medium to strong. 673.18 and 731.05 (cm⁻¹) reveals any chloroalkane (C-X) whose presence is medium to strong. A.P of 835 cm⁻¹ tells of strong para-disubstituted aromatic benzene. 1041.60, 1078.24 and 1163.11 (cm⁻¹) specifies (C-X) ordinary and trifluoromethyl fluoroalkanes respectively having two strong broad bands. A.P 1240.27 cm⁻¹ conveys presence of aromatic ethers (C-O). Alkyl (C-H) bonds are expressed by 1377.22 cm⁻¹, 2852.81 cm⁻¹ and 2926.11 cm⁻¹; methyl-type of weak, medium to strong appearance respectively. Three or four Aromatic C=C bonds of weak to strong appearance is indicated by 1458.23 cm⁻¹ A.P. Strong aliphatic nitro compounds (N-O) is contained in 1535.30 cm⁻¹. A.P of 1618.33 cm⁻¹ and 1664.62 cm⁻¹ reveals C=N bond with similar conjugation effects to C=O. 1712.85 cm⁻¹ and 1735.99 cm⁻¹ shows carboxylic acids (C=O) derivatives of saturated type, esters and lactones (influenced by conjugation and ring size) respectively. A.P 2727.44 cm⁻¹ communicates any medium sized aldehyde bond (C-H). Multiple broad peaks of ammonium ions is shown by 2956.97 cm⁻¹.

Table 2. FTIR analysis of compounds in *P. macrophylla*'s leaf extract.

<i>P. macrophylla</i>	FTIR analysis		
	Absorption peak (cm ⁻¹)	Type of bond	Appearance
	426.28	Unidentified	
	673.18 - 731.05	C-H (Cis-disubstituted alkenes and monosubstituted benzene)	Strong
	835.21 - 1041.6	C-H (trisubstituted alkenes; aliphatic amines)	Medium to strong; often overlapped
	1078.24 - 1163.11	C-X (fluoroalkanes)	Two strong broad bands
	1240.27 - 1377.22	C-O (aromatic ethers and carboxylic acids) N-O (aliphatic nitro compounds)	Weak
	1458.23 - 1535.39	Aromatic C-C	About 3 to 4
	1618.33 - 1664.62	Conjugated C-C with benzene ring (dienes)	Strong
	1712.85 - 1735.99	C=O (saturated carboxylic acids); esters and lactones	
	2727.44 - 3392.9	N-H (ammonium ions)	Multiple broad peaks

FTIR analysis of *P. macrophylla*'s constituents.

Figure 3 shows an absorption range of *P. macrophylla* dye from 702 - 774 nm with an absorption peak at 670 nm and absorbance of 0.053 au without any electrolyte sensitizer. The absorption spectra reveal the transition between the ground state and excited state of the *P. macrophylla* dye and the absorption width of solar energy wavelength.

Figures 4-6 show the absorption spectra of *P. macrophylla* with potassium iodide (KI), potassium bromide (KBr) and mercury chloride (HgCl₂) electrolytes respectively compared with *P. macrophylla* dye having no sensitizer for dye. The KI sensitized DSSC (**Figure 4**) had an absorption in the frequency range 408 - 1086 nm with an absorption peak at 408 nm and absorbance of 0.592 au. A series of interesting events unfold: between 300 nm to 400 nm a π to π^* transition occur at 0.592 au. Recombination occurs between 408 nm and 470 nm. Another π to π^* transition occur between 470 nm and 520 nm. Consequent loss of energy follows recombination at 570 nm to 620 nm. A third π to π^* jump occurs at 700 nm to 750 nm, 750 nm to 800 nm witnesses a loss of energy due to recombination. Finally, it attains stability after 800 nm [26]. The chlorophyll dye extract with the KBr and HgCl₂ as sensitizer also had absorption peaks at 408 nm but at 0.851 and 0.634 absorbance respectively. Chlorophyll has its highest absorbance within the blue and red bands of the absorption spectra. **Figure 5** has similar features as **Figure 4**. Its first transition occurs at 320 nm to 400 nm at 0.851 au. However, recombination is longer 408 nm to 480 nm. At 500 nm to 504 nm wavelength, a small jump π to π^* occurs at 0.151 au. A higher jump π to π^* happens at 669 nm at 0.360 au before a consequent recombination [27] and resulting stable state. HgCl₂ reveals an initial boost as energy level of *P. macrophylla* starts at a good peak of 0.628 au absorbance, a drop due to recombination of holes with electrons occur from 300 nm to 330 nm. A π to π^* transition occurs at 330 nm to 408 nm at 0.634 au. Recombination and resulting energy drop follow before a final stable state. **Figures 4-6** show absorption peak of 408 nm which indicates that the dye has same colour composition but different absorbances due to differences in the compositions of the electrolytes [26] [27]. The weak absorption of the *P. macrophylla* in the red region is a disadvantage, this affects the DSSC efficiency. The optimum use of dye sensitizers, solution of electrolyte and surface morphology of metal oxide will improve on DSSC performance.

Operational parameters like open circuit voltage V_{oc} , short circuit current I_{sc} , current and voltage at maximum power point of a solar cell are obtained from the current-voltage (J-V) curves of the solar cell. **Figure 7** shows the J-V characteristics of the fabricated DSSC using *P. macrophylla* leaf extract and KI, KBr and HgCl₂.

Table 3 shows data obtained from determining the photoelectric conversion efficiency of DSSC's *P. macrophylla*.

Conversion efficiency of DSSCs sensitized with *P. macrophylla* dye and KI electrolyte is 0.21%, with V_{oc} of 0.032 V, J_{sc} of 0.2 mA/cm² and fill factor (FF) of 0.480. Conversion efficiency for DSSC sensitized with *P. macrophylla* and KBr is 0.43%, V_{oc} is 0.045 V, J_{sc} is 0.16 mA/cm² and FF of 0.28. The conversion efficiency for DSSC sensitized with HgCl₂ is 0.36% , with V_{oc} of 0.043 V, J_{sc} of 0.12 mA/cm² and FF of 0.23. The equation used for determining the efficiency is:

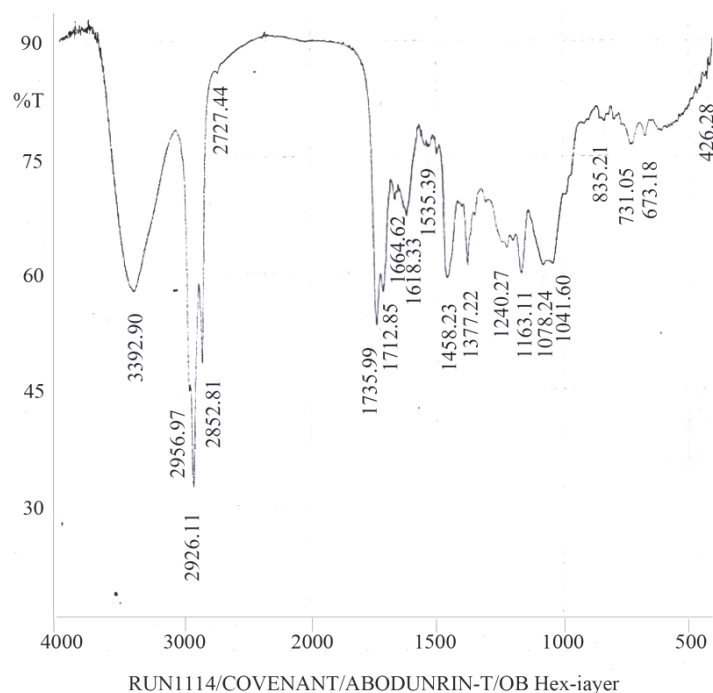


Figure 2. Fourier transform infrared spectrograph of hexane fraction of *P. macrophylla* dye.

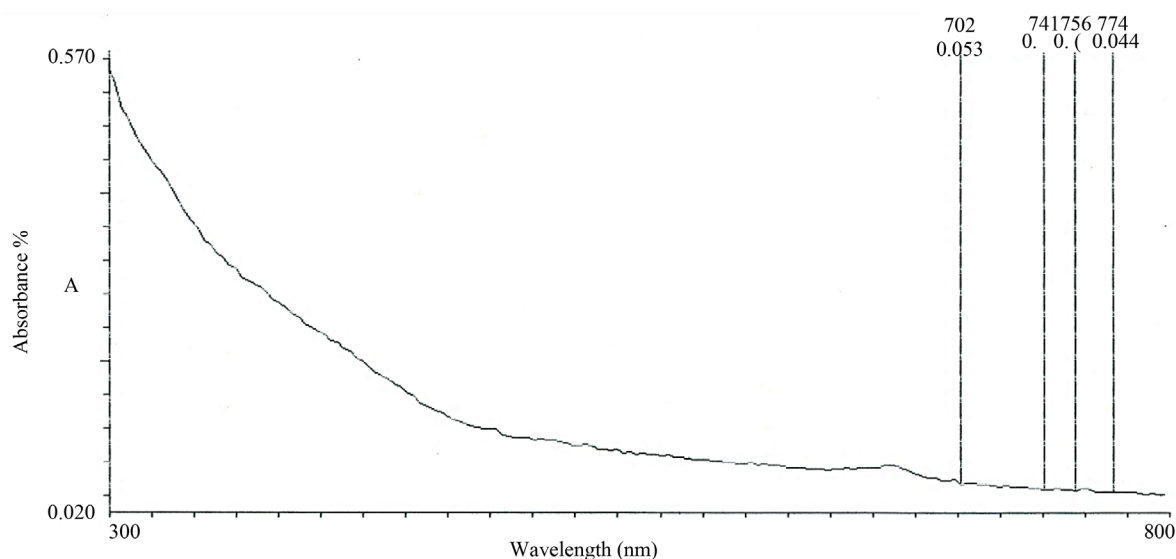


Figure 3. UV/Vis of *P. macrophylla* without dye sensitizer.

$$\eta = \frac{FF \times J_{sc} \times V_{oc}}{P_{in}} \times 100\%$$

P_{in} is power intensity of incident radiation [28].

The result in **Table 3** shows the DSSC sensitized with $HgCl_2$ had the highest efficiency while that sensitized with KI had the least photoelectric conversion efficiency. The V_{oc} of *P. macrophylla* dye was less than ruthenium dye this could be due to the functional groups present in the organic dye; typically O and OH ligands which do not have-COOH ligand that combine readily with TiO_2 's hydroxyl particles forming esters which cause an increased rate of electron-transport [29]. These values are close to those for DSSCs of frozen Blackberries [14] where V_{oc} was reported as 0.33 V and 0.4 V and 0.59 V as V_{oc} for Jabticaba's skin and dye extracts of

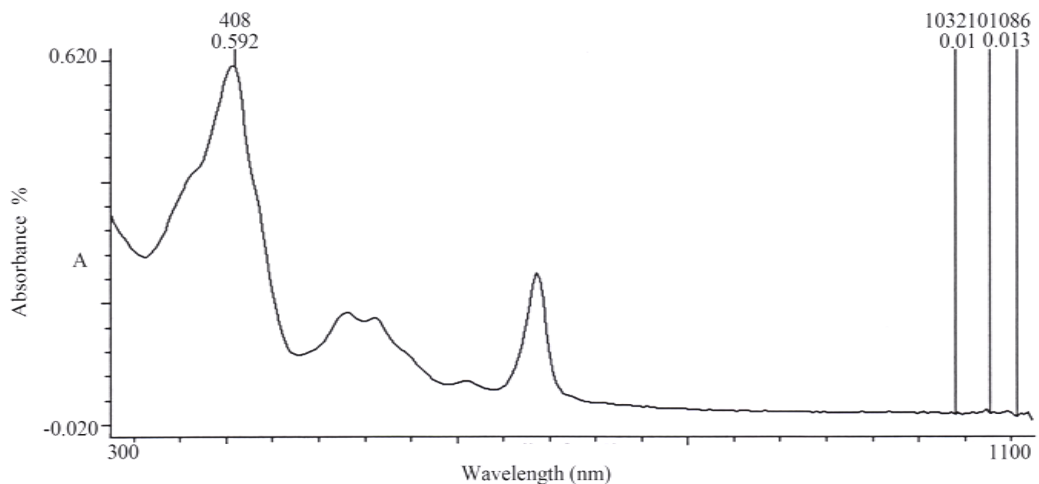


Figure 4. UV/Vis spectrograph of *P. macrophylla* with KI dye sensitizer.

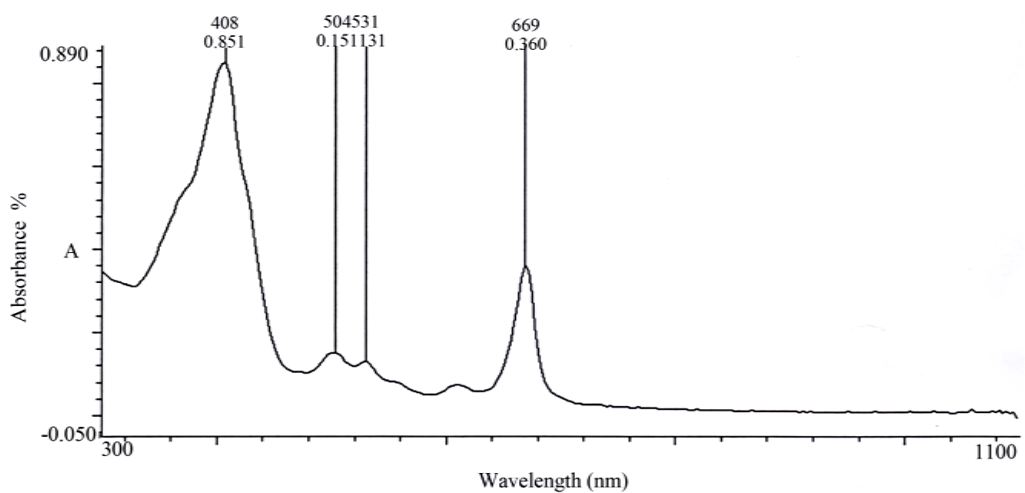


Figure 5. UV/Vis spectrograph of *P. macrophylla* with KBr dye sensitizer.

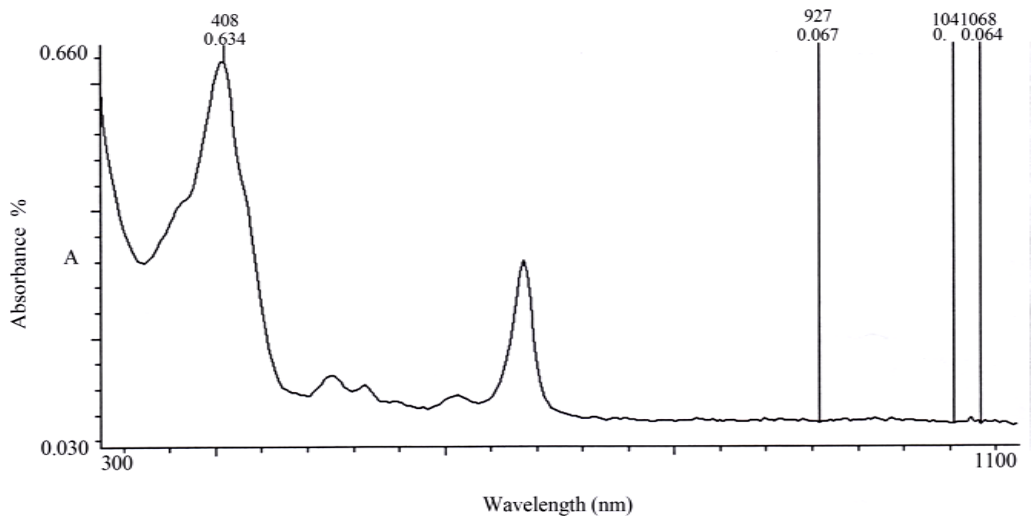


Figure 6. UV/Vis spectrograph of *P. macrophylla* with HgCl₂ dye sensitizer.

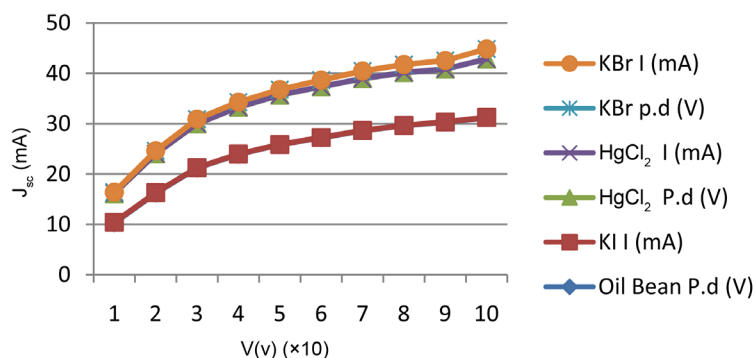


Figure 7. J-V characteristics of DSSCs with KI, KBr and HgCl₂ dye sensitizers with *P. Macrophylla* extracts dye.

Table 3. Characteristics of *P. macrophylla* dye-sensitized solar cells.

DSSC	Photoelectric parameters of <i>P. macrophylla</i> DSSCs				
	Dye-sensitizer	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF	$\eta\%$
	KI	0.20	0.032	0.48	0.21
	KBr	0.16	0.045	0.28	0.36
	HgCl ₂	0.12	0.043	0.23	0.43

Photoelectric parameters of *P. macrophylla* DSSCs.

blueberries respectively [30].

4. Conclusion

Dye sensitized solar cells were prepared from anthocyanin extracts of *P. macrophylla* and a mixture of dye sensitizers; KI, KBr and HgCl₂. The photoelectric conversion efficiency with HgCl₂ attained 0.43%, while the conversion efficiency with KI as dye sensitizer was only 0.21%. The DSSC with HgCl₂ in this study gives a higher incident photon-to-electron conversion. Sustaining the visible high peaks, less recombination of holes with electrons ejected from electrolytes is subject to future research. Dye substrates enclosed in substances like plasma gel and centrifugal paste are a quest for prospective research, as the effect of dye sensitizers on DSSCs photoelectric conversion efficiency continues to be further researched.

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