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The Effect of Electrolyte on Dye Sensitized Solar Cells Using Natural Dye from Mango (*M. indica* L.) Leaf as Sensitizer

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Abstract

Dye-sensitized solar cells (DSSC) were fabricated with mango leaf dye extracts as natural dye sensitizers at pH value of 5.20 and temperature of 18.1˚C. Methanol was used as dye-extracting solvent. DSSCs from dye extract of *M. indica* L. with $KMnO_4$ electrolyte had the highest photocurrent density of 1.3 mA/cm^2 and fill factor FF of 0.46 for the sun at its peak. Potassium permanganate ($KMnO_4$) had a photocurrent density of 1.3 mA/cm^2 and FF of 0.8 at sundown. Potassium Iodide (KI), Potassium Bromide (KBr) and Mercury Chloride ($HgCl_2$) electrolytes had 0.2 mA/cm^2, 0.08 mA/cm^2 and 0.02 mA/cm^2 photocurrent densities respectively. The fill factors of 0.09, 0.03 and 0.003 respectively for sun overhead while 0.08 mA/cm^2, 0.01 mA/cm^2 and 0.01 mA/cm^2 were the values of photocurrent densities respectively at sundown. The fill factors were 0.02, 0.0006 and 0.003 respectively at sundown. The maximum power P_{max} of the DSSCs were 0.5 mW/cm^2, 0.10 mW/cm^2, 0.01 mW/cm^2 and 0.012 mW/cm^2 respectively at 1300 h at 1630 h 0.9 mW/cm^2, 0.14 mW/cm^2, 0.005 mW/cm^2 and 0.0015 mW/cm^2 respectively.

Keywords

Dye-Sensitized Solar Cells, Dye Sensitizer, Electrolytes, *M. indica* L., Photocurrent Density, Fill Factor

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1. Introduction

Solar energy remains a foremost energy resource with unlimited capacity to solve man's numerous energy chal-

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lenges. Dye-sensitized solar cell (DSSC) discovered by Grätzel *et al*. [1] [2] has gained prominence because of its considerable low cost of production [2], no greenhouse gas emission, eco-friendliness and sustainability. Dye sensitizers perform a primary role of trapping solar energy and converting it to electricity through potential difference that exists between solar cell layers. Quality is a measure of efficiency and fill factor [3].

Anthocyanin, flavonoids from natural sources has been used as sensitizers in DSSCs and recorded low solar energy efficiency conversion [2] [4]-[6]. DSSCs change cheap energy from the sun to electricity established upon different sensitivities in band gap of dye sensitizers and electrolytes [7]. This process involves several subsystems whose work in cycle is in conjunction with the surface of adsorption of the dye deposited on a semiconductor surface that receives near IR photons and visible region of light. It pumps these incident electrons into the conduction band of the semiconductor. Performance of the DSSC is based on the band gap of materials like TiO_2, electrolytes and the dye sensitizer. TiO_2 is ideal because it has ability to withstand constant electron transfer under solar illumination in the ultraviolet range. Dye absorption performance on TiO_2 surface determines efficiency of DSSC [7]. DSSC efficiency of 10.4% has been observed for use of nanocrystalline TiO_2 films [8]. Ruthenium dye photosensitizers are one of the most efficient produced from heavy transition metallic compound, ruthenium polypyridyl complex widely used for its high charge-transfer absorption in the visible spectrum of light; long span of excitation time, good absorption, and high efficiency of metal-ligand charge transfer [9]. Ruthenium complexes are very difficult to make and costly, this limits their applications on large scale in solar cells, encouraging a search for suitable alternatives like organic dyes. However, organic dyes of higher absorption coefficients with similar characteristics and efficiencies up to 9% have been observed [9]-[11]. Higher absorption in organic dyes could mean thinner nanostructured metal oxide films that is most suitable for use of higher viscous materials and charge transport. Such materials include ionic liquids, solid electrolytes or hole conductors [12].

Leaves of most plants are rich in chlorophyll and its application as natural dye sensitizer has been experimented in many associated studies [3] [4] [13]. Anthraquinones are natural compounds that have medicinal properties as well as give colour pigments to plants [14].

Mango (*M. indica* L.) is a fairly large genus of Anacardiaceae family of evergreen trees [15]. It grows from 10 to 45 metres height, with a heavy dome-shaped crown and, a stout straight bole, thick bark, dark grey, rough, flaking off when old, with leaves linear, elliptic lanceolate or oblong, 10 - 30 cm long and 2 - 9 cm wide giving off an aromatic, resinous odour when crushed.

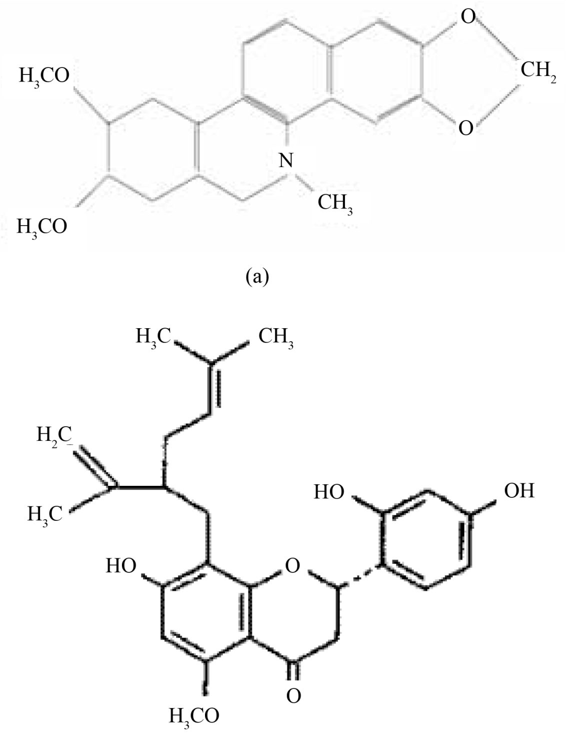
Anthraquinones and flavonoids from *M. indica* L. are composed of lupeol and certain tannins and saponnins pigments characteristic of Anacardiaceae family. They absorb visible radiation over a range 412 nm - 664 nm. Solar energy conversion efficiency a function of J_{sc}, open circuit voltage V_{oc}, and fill factor FF [17], suggest that their improvement is essential to increasing the conversion efficiency. Mangifera has several active triterpenoids [15] which have several medicinal benefits.

Lupeol's chemical structure is shown in **Figure 1** [16]; it contains functional carboxylic group which articulates with the TiO_2 surface bonding. In this paper, anthraquinone (**Table 1**) and flavonoid extracts of Mango (*M. indica* L.) mixed with iodine and four different electrolytes were used as natural dyes sensitizers in the preparation of DSSCs.

2. Experimental

The *M. indica* L. leaf pigments were extracted by crushing 317 g of *M. indica* L. in a milling machine and soaking it in 8000 ml of methanol. This mixture was filtered and a rotary evaporator used to recover the pigment from the mother liquor-methanol. The raw extracts of *M. indica* L. was divided into four and used as dye sensitizer at four different pHs. Two drops of Iodine (0.1 M) solution was added to all the samples then, two drops of $HgCl_2$ was added to a first sample of dye extract, a pH of 2.16 was recorded at 22.7˚C, two drops of KBr was added to a second sample, a pH of 1.78 was observed at 22.7˚C, a few drops of KI added to a third sample had a pH of 2.25˚C at 22.6˚C and lastly two drops of $KMnO_4$ was added to a fourth sample, a pH of 2.58 was recorded at 22.5˚C.

The transparent fluorine-doped tin oxide (FTO) conducting glass had the following dimensions 50 mm × 50 mm × 22 mm (ALDRICH) having surface resistivity of 7 Ω/m^2. The active area of DSSC was 0.54 cm^2. The TiO_2 paste was prepared by pounding 12 g of commercial TiO_2 (Assay) with 20 ml of concentrated nitric acid. The mixture was well blended and squeegee was used to screen-print the resulting TiO_2 paste onto the conduct-



(a)

(b)

Figure 1. Chemical structure of two allotropes of *P. macrophylla.* (a) http://journal.9med.net/upload/Image/4QT23.jpg at 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.

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

Anthraquinones	Flavonoids
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++ = highly present.

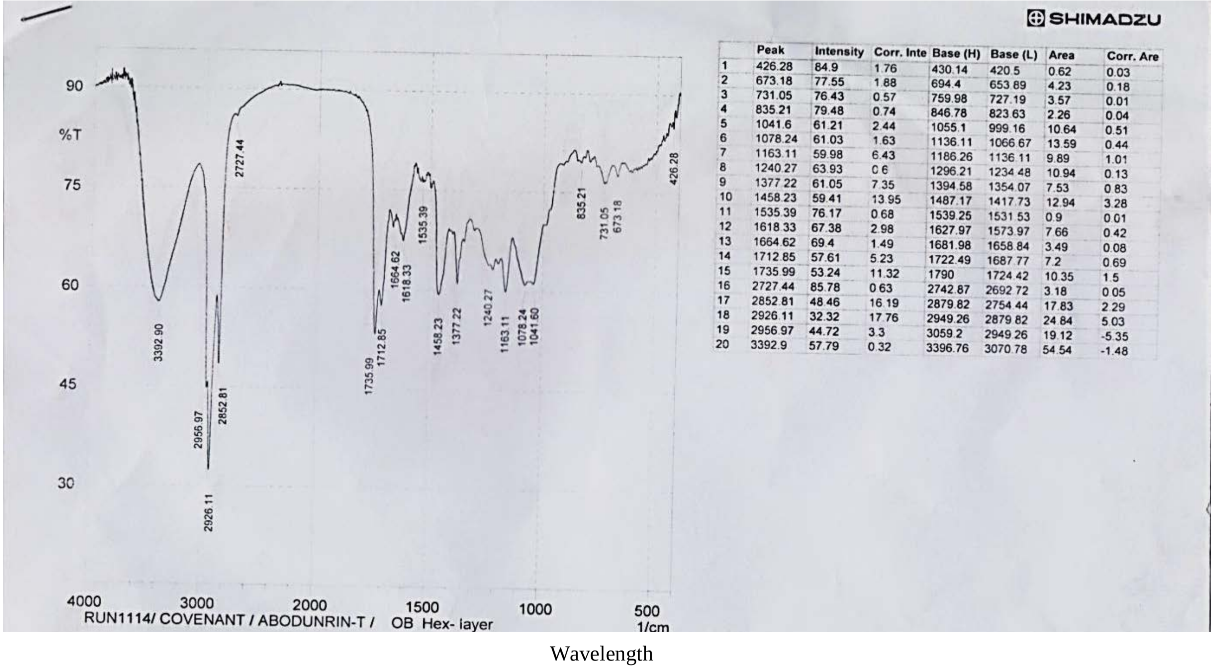
ing FTO. It was left for 30 min to allow the paste settle and even out the irregularities at the surface, then allowed to dry. Appropriate thickness of the TiO_2 working electrode is 9 µm. It was sintered at 450˚C for 45 min to enhance its absorption performance. Then the sintered thin film of TiO_2 was immersed 24 h in the *M. indica* L. prepared, t*hus a*llowing the dye pigment to be adsorbed *on the* TiO_2 nanoparticles surface. Glass insulation spacers were stuck on the edges of the base plate of conductive glass at the bottom. This space allows injection of the electrolyte. After cleaning the DSSCs photoelectrode, it is ready for testing.

3. Characterization

The absorption spectra of the *M. indica* L. dye was determined with Genesys 10 UV Scanning spectrophotometer an RC, 229,847 series model. Manufactured by Thermo Electron Corporation in USA. Aspex 3020 scanning electron microscope (SEM) was used at different magnification for specific wavelengths under the irradiation of 100 $mW \cdot cm^{-2}$. The current-voltage curves were recorded using a multimeter.

4. Results and Discussion

The FTIR image of hexane faction (**Figure 2**) of *M. indica* L. leaf extracts shows all the organic compounds present in the dye (**Table 2**). **Figure 3** shows the optical absorption spectra of *M. indica* L. leaf extracts for pH 2.16, pH 1.78, pH 2.25 and pH 2.58. Absorption spectra of a dye represents the probability of its transition between the ground state, excited state and the incident wavelength range of solar energy absorbed by the dye. All four dyes extract show absorption peaks centered at 303 and 350 nm in UV-range, with maximum peak at 350



	Peak	Intensity	Corr. Inte	Base (H)	Base (L)	Area	Corr. Are
1	426.28	84.9	1.76	430.14	420.5	0.62	0.03
2	673.18	77.55	1.88	694.4	653.89	4.23	0.18
3	731.05	76.43	0.57	759.98	727.19	3.57	0.01
4	835.21	79.48	0.74	846.78	823.63	2.26	0.04
5	1041.6	61.21	2.44	1055.1	999.16	10.64	0.51
6	1078.24	61.03	1.63	1136.11	1066.67	13.59	0.44
7	1163.11	59.98	6.43	1186.26	1136.11	9.89	1.01
8	1240.27	63.93	0.6	1296.21	1234.48	10.94	0.13
9	1377.22	61.05	7.35	1394.58	1354.07	7.53	0.83
10	1458.23	59.41	13.95	1487.17	1417.73	12.94	3.28
11	1535.39	76.17	0.68	1539.25	1531.53	0.9	0.01
12	1618.33	67.38	2.98	1627.97	1573.97	7.66	0.42
13	1664.62	69.4	1.49	1681.98	1658.84	3.49	0.08
14	1712.85	57.61	5.23	1722.49	1687.77	7.2	0.69
15	1735.99	53.24	11.32	1790	1724.42	10.35	1.5
16	2727.44	85.78	0.63	2742.87	2692.72	3.18	0.05
17	2852.81	48.46	16.19	2879.82	2754.44	17.83	2.29
18	2926.11	32.32	17.76	2949.26	2879.82	24.84	5.03
19	2956.97	44.72	3.3	3059.2	2949.26	19.12	-5.35
20	3392.9	57.79	0.32	3396.76	3070.78	54.54	-1.48

Figure 2. FTIR image of hexane faction of *P. macrophylla leaf dye*.

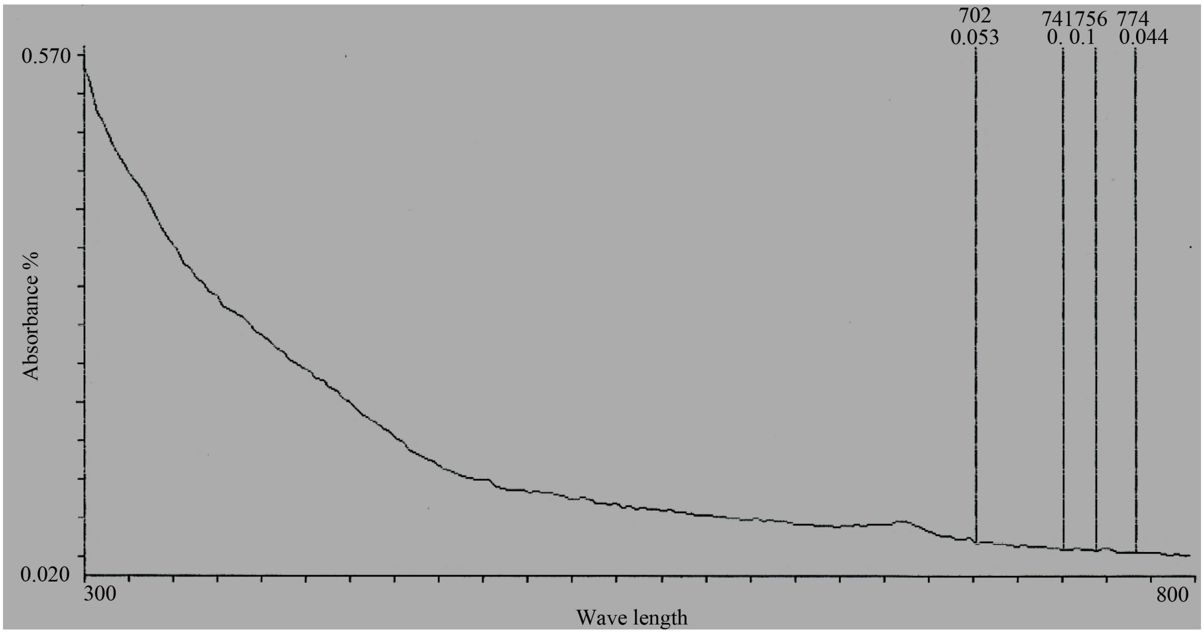


Figure 3. UV/Vis of *P. macrophylla* leaf dye without a sensitizer.

nm for pH 2.25, and pH 2.58, 312 nm for pH 1.78 and, 303 nm at pH 2.16 in range of short wavelength. The dye extracts at pH 2.25 and 2.58 have similar absorption intensity in long wavelength range. The highest intensity occurs at pH2.16 with a value of 2.936, which is higher than 2.880 at 220 nm for pH 5.20 at short wavelength range (**Figure 3**). The lowest absorption intensity in long wavelength is observed for dye at pH 2.16, indicating a degradation of the *M. indica* L. dye in strong acidic medium [18], at higher temperatures.

Dye extract at pH of 2.58 shows a broad absorption peak in the 303 - 400 nm range due to $\pi - \pi^*$ transitions due to the O-H phenolic bond [20], which has a high concentration with a specific absorbance peak of 3392.90 nm (**Figure 4**) and broad appearance. 426 - 731 nm indicates the presence of chloroalkanes whose appearance is

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

Absorption peak (cm)	Bond (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

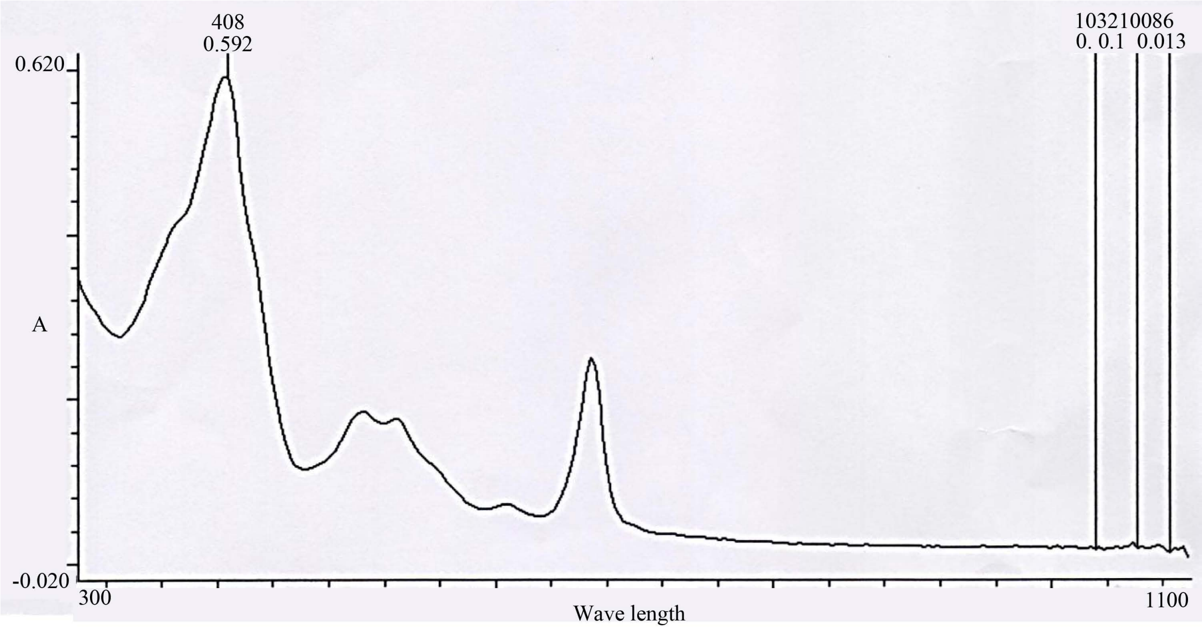
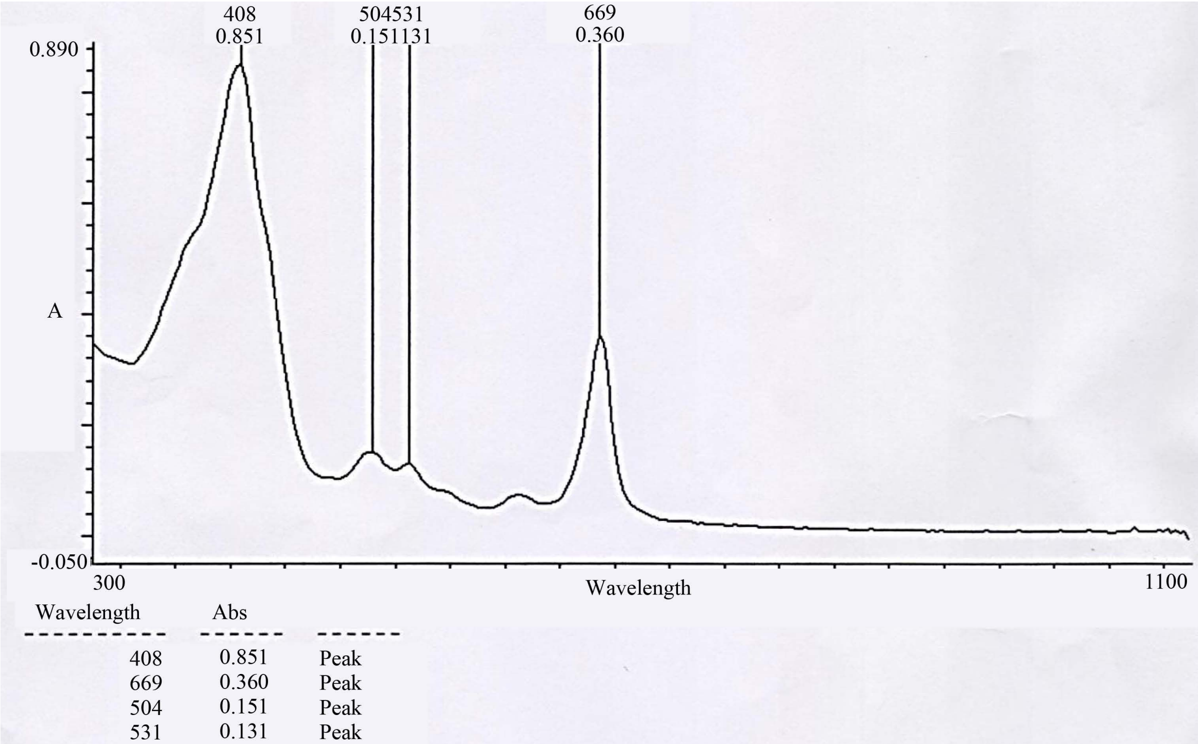


Figure 4. UV/Vis spectrograph of *P. macrophylla* leaf dye with KI electrolyte.

medium. 835.21 nm indicates the presence of the C-H bond, trisubstituted alkenes whose appearance is strong. 1041.6 - 1240.27 nm indicates presence of C-N bond, aliphatic amines which are often overlapped. 1377.22 nm indicates the presence of C-H, 1458.23 nm indicates 3 or 4 weak to strong aromatic C=C bond, 1535.39 nm indicates the presence of N-O bond, aliphatic nitro compounds which are stronger in appearance. 1618. 33 - 1664.62 nm indicates the presence of C=N with similar conjugation effects to C=O. 1712.85 - 1735.99 nm indicates the presence of C=O saturated carboxylic acids influenced by conjugation and ring size. 2727.44 - 2852.81 nm indicates the presence of C-H bond, aldehydes of medium appearance. 2926.11 - 2956.97 nm indicates the presence of the methyl group (**Figure 5** & **Figure 6**), medium in appearance.

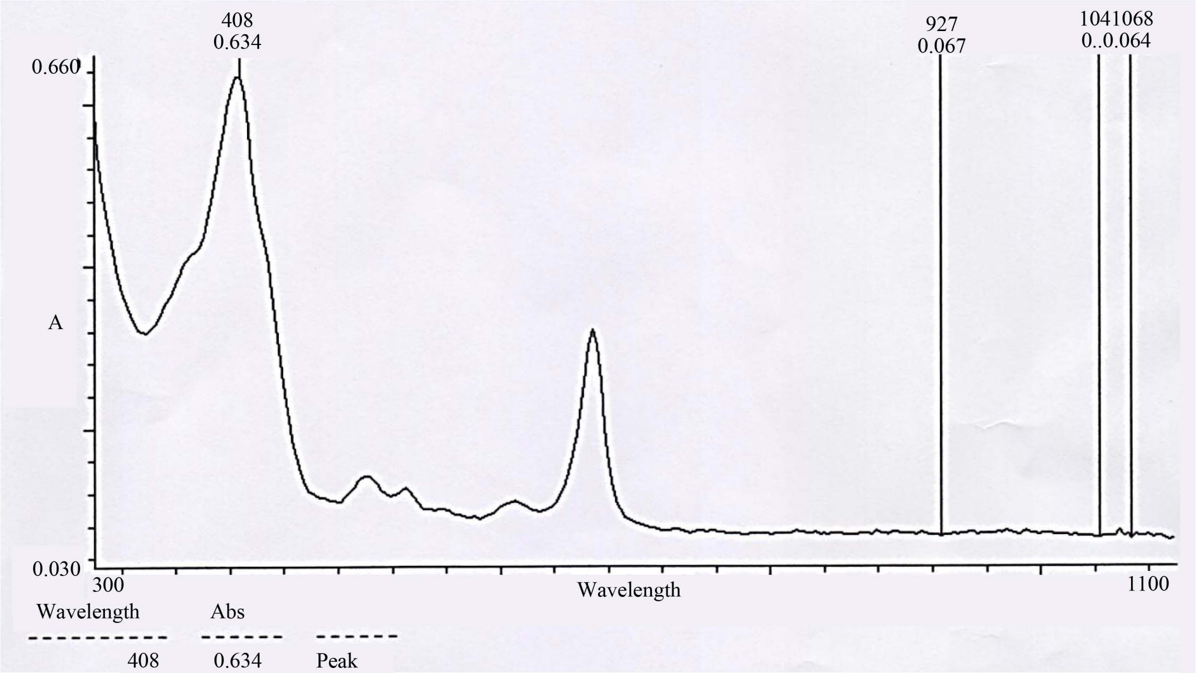
The combined J-V and P-V curves of the DSSCs at different pHs are shown in **Figure 7**. The open-circuit voltage V_{oc} of 0.38 is obtained for pH2.58 while at a pH of 2.25, and 2.16 the V_{oc} is 0.50; the least value is 0.13 when the pH is 1.78. The dye with pH2.58 has the highest J_{sc} of 1.30 mA/cm^2 and fill factor of 0.8.

The temperature increase reduced the J_{sc} of the dye at 2.16, the band gap is smaller as more electrons are excited and have high kinetic energy, and it also has the lowest fill factor, the resulting lupeol degradation in very strong acidic environment [18] causes poor harvesting of solar energy by the dye when injected on the TiO_2 [21]. The photoelectric parameters are shown on **Table 3**. Although J_{sc} of 20.5 mA/cm^2 and V_{oc} of 0.72 V are ob-



Wavelength	Abs	
408	0.851	Peak
669	0.360	Peak
504	0.151	Peak
531	0.131	Peak

Figure 5. UV/V is Spectrograph of *P. macrophylla* leaf dye with KBr electrolyte.



Wavelength	Abs	
408	0.634	Peak

Figure 6. UV/V is Spectrograph of *P. macrophylla* leaf dye with $HgCl_2$ electrolyte.

served under AM 1.5 [19] from the black dye, it is regarded as superior to all charge-transfer sensitizers. The J_{sc} 1.30 mA/cm^2 at dye sensitizer pH 2.58 is promising.

The Scanning Electron Microscope micrograph (**Figure 8**) of the *M. indica* L. shows the thickness of *M. indica* L. film. *The M. indica* L. film has a thickness of 9 µm and a mean particle size of 20 nm. The parallel veins

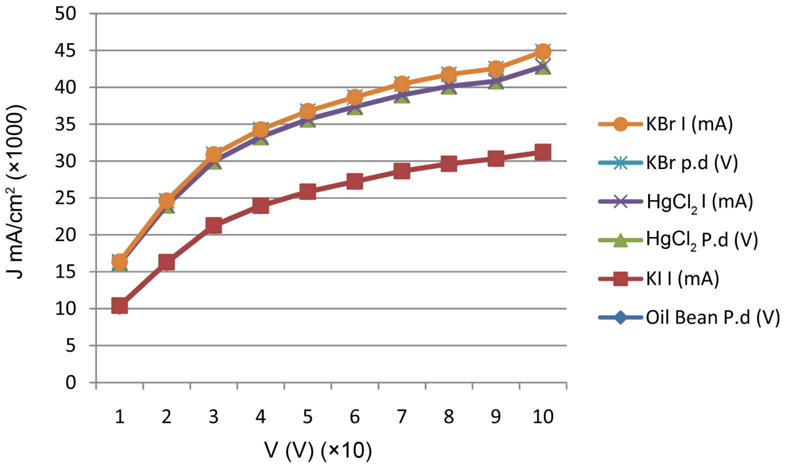


Figure 7. J-V characteristics of DSSCs with KI, KBr and $HgCl_2$ dye sensitizers with *P. macrophylla* extracts dye.

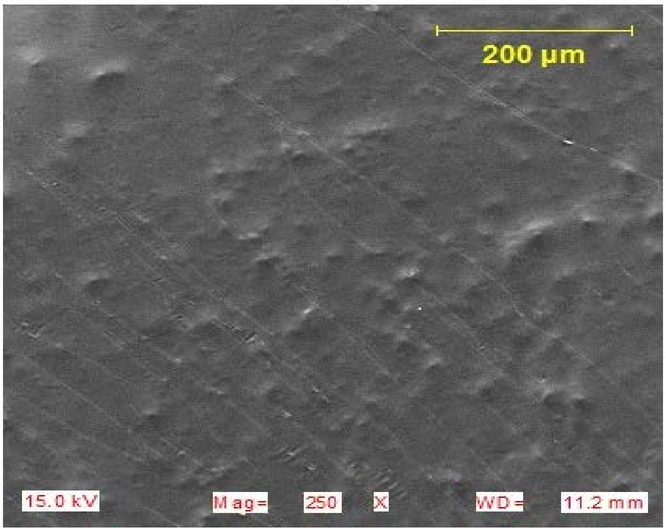


Figure 8. SEM micrograph of *M. indica* L.

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

Dye-sensitizer	J_{sc} (mA/cm^{-2})	V_{oc} (mV)	FF	η%
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

of the leaf is distinctly outlined in the chromophores of *M. indica* L.

5. Conclusion

Lupeol's crude extracts of *M. indica* L. were used as natural dye sensitizers for DSSCs for different pH values. The DSSC at pH 2.16 had the least parameter values due to degradation of lupeol at increased temperatures and strong acidic environment resulting in the leaching of the adsorbed dye from the TiO_2 surface. The dye sensitizer for DSSC at pH 2.58 recorded the highest J_{sc} of 1.3 mA/cm^2, a fill factor of 0.46, and highest p_{max} of 0.5 mW/cm^2. The low absorption of lupeol onto the titania surface at high pH led to decreased photochemical parameter of the cell at pH 2.16. These values are significantly less than that of black dye which is greater than all other charge-transfer sensitizers based on its performance under 1.5 AM at the moment, with a confirmed J_{sc} value of 20.5 mA/cm^2 and a V_{oc} of 0.72 V [19]. However, lupeol natural extract of *M. indica* L. represents an environmentally friendly, non-toxic, relatively cheap and available energy source, in dye sensitized solar cells.

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