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Fabrication and Characterization of Dye-Sensitized Solar Cell from Fruit and Leaf of *Discopodium peninervum* as Photosensitizers using Titanium dioxide Photoanode Material

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Abstract: Herein, we have studied dye sensitized solar cell (DSSC) from natural dyes extracted from fruit and leaf of *Discopodium peninervum* as photosensitizers based on TiO_2 photoanode material. The optical characterization were carried out using UV-Vis spectroscopy the as optical properties were studied. The photovoltaic performances of the as fabricated DSSC from fruit and leaf of *Discopodium peninervum* in terms of maximum current density (J_{max}), maximum voltage (V_{max}), maximum power (P_{max}), open circuit voltage (V_{OC}), short circuit current density (J_{sc}), fill factor (FF), and power conversion efficiency (η) were studied under sunlight approximately 100 mW cm^{-2} illumination. The recorded power conversion of the solar cells made from fruit of *Discopodium peninervum* were 1.201, 0.259, 0.311, 0.313, 1.56, 63.69, and 0.311 respectively and for leaf of *Discopodium peninervum* were 2.68, 0.550, 1.474, 0.650, 3.60, 62.99, and 1.474 respectively. Also the stability of the as prepared DSSC after their assembly for both fruit and leaf were studied, and as the duration of cell assembly increase the efficiency of the as prepared DSSC rapidly decreased. It shows the formation of fast degradation, and this may due to the nature of high volatility of liquid electrolyte used which may quench the dye solutions.

Keywords:. Dye-sensitized solar cells, Titanium dioxide, Natural dyes, Stability, *Discopodium peninervum*.

1 Introduction

Due to the rapid advancement of technology together with population and economic growth, the need of renewable energy resources has resulted in the rapid growth and much attention for dye sensitized solar cells (DSSCs) with time [1]. The low-cost nature of DSSCs proffers them as lucrative substitutes to the conventional silicon-based solar cells (SBSCs). Moreover, the future inspires us to build energy-sustainable buildings for future cities the as DSSC is a promising energy sources [2]. DSSCs are made up of photosensitizers, counter electrodes, redox electrolytes, and semiconductor electrodes, in which the photosensitizer is the critical part [3]. DSSCs have been taken as low-cost photovoltaic devices as compared to the first and second generation of solar cells called SBSCs and thin-film solar cell cells (TFSCs). They have got widespread attention in recent years; although much work is required to reach ideal device efficiencies. DSSCs are the third generation of photovoltaic system. SBSCs and thin-film technologies are the first and second generation of solar cells. As compared to SBSCs and TFSCs, DSSCs cells have low-cost, good absorbers of sunlight, easy operation, and environmentally benign or promise for reduction of CO_2.Natural plants such as fruits, leafs, flowers, roots, and seeds are the important parts of plants used for sensitization that can be extracted easily and becomes adsorbed on nano-crystalline, wide band gap metallic oxide, semiconductor porous material in order to play a key role in absorbing in coming photon, light energy in DSSC [4, 5]. The anthocyanin and chlorophyll pigments are widely found in fruits, leafs, flowers, and roots of plants responsible for several

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*Corresponding author e-mail: Chemmsc2010@gmail.com colors in the red-blue range and green respectively. They have anchoring groups, carbonyl (C=O) and hydroxyl (O -H), that make attachment to the oxygen site of TiO_2 film and allow electron injection. This paves the way to the electron transfer from the anthocyanin and chlorophyll molecule to the conduction band of TiO_2 [6]. The full structure for preparing DSSC shown in Figure 1 depicts the mechanism to convert solar energy into electrical energy. Since the role of the absorption of visible light and the conversion of photon energy into electricity is played by the dye and much attention paid in the identification of effective sensitizer.

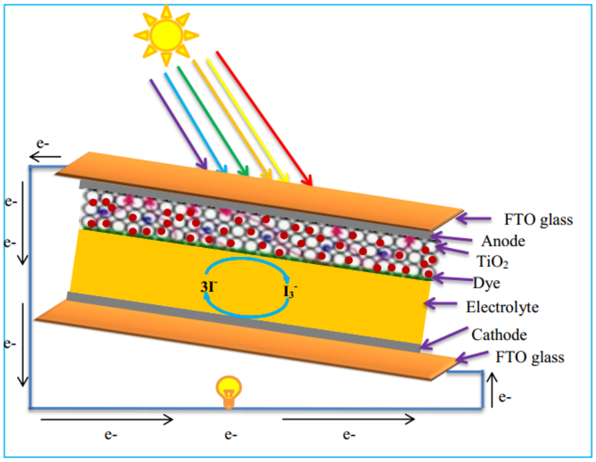

Fig. 1: A full structure of the as prepared DSSC.

Due to their cost, efficiency, availability, non-toxicity, and complete biodegradation, natural dyes from fruits, leafs, flowers, and roots get a wide attentions now a days. Alhamed et al. works homemade DSSC using natural dyes extracted from raspberries, shami-berries, grapes, hibiscus, and chlorophyll [7]. Another scholar Lai et al. also studied by using rhoeospathacea in DSSC as a dye sensitizer [8] and till now a lot effort is incorporated on the search of natural plant. However, in this work an alternative natural plant which is from fruit and leaf of Discopodium peninervum were used as photosensitizers for fabrication of DSSC. Fruit and leaf of Discopodium peninervum have both chlorophyll and anthocyanin pigments which can be used as light harvesting material for DSSC.

2 Experimental Sections

Chemicals used were; Triton-X 100 (India), ethylene glycol (99.0%, India), iodine (99.0%, India), Fluorine doped tin oxide (FTO, 2.5 cm × 2.5 cm, 15 Ω), glacial acetic acid (99.5%, SCR-India), TiO_2 powder, ethanol (99.0%, India), 2-propanol (99.0%, India), Acetone (99.0%), glass rod, Graphite of pencil (2B NATARAJ®, China), and natural dye that were extract from fruit and leaf of *Discopodium peninervum.*

2.1 Preparation of Natural Photosensitizers

Fresh fruits and leafs of *Discopodium peninervum* were collected then it washed with pipe water followed by distilled water to get ride off the dust particles and were allowed to dry using an electrical oven setting up a temperature at 40°C. Then, the samples were crushed with a pestle and mortar until homogenous powder obtained.

For a typical extraction of dyes, 2.0 g of powdered *Discopodium peninervum* leaf were mixed with 20 mL (1:10) of 99.0% ethanol by using a magnetic stirrer for 2 hrs. to disperse the powder completely and then kept for 48 hrs. in a dark place to prevent effect of light [9]. Then the extracted solution was filtrated out using filter paper to remove any precipitate presence in the crude extraction.

For *Discopodium peninervum* fruit the extraction procedure was same as [10] with some modifications. Fresh *Discopodium peninervum* fruits were peeled out and the juice extracted from the pulp coats using a fruit juice extractor while adding a few drop of distilled water. The extraction was then carried out by a sequence of filtration, centrifugation, and decantation to remove any precipitate present in the crude extract. The respective photographic images of *Discopodium peninervum* fruit and leaf of powdered and extracted dye solutions are shown below in Figure 2.

2.2 Preparation of TiO2 Electrode (Photoanode)

The TiO_2 film on the FTO glass (resistance of 15 Ω) was prepared using a doctor blade technique to obtain suitable thickness of TiO_2 film [11]. FTO glasses were cut with a dimension size of (2.5 cm × 2.5 cm) and were cleaned in a detergent solution using an ultrasonic bath each step for 20 minutes, rinsed with ethanol, acetone, 2-propanol, and then was allowed to dry for 15 minutes.

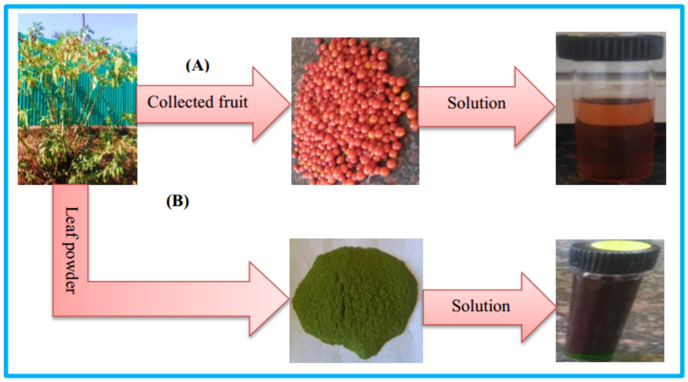

Fig. 2: A schematic diagram shows the as extracted sample dye solutions for (A) fruit and (B) leaf of *Discopodium peninervum*.

3.0 g of commercial TiO_2 powder was mixed with a small amount of distilled water (1 mL) containing 0.1 mL of glacial acetic acid to prevent aggregation of the particles**.** After the powder had been dispersed by the high shear forces in the viscous paste, it was diluted by slow stepwise addition of 4 mL distilled water and 1 drop of transparent surfactant (triton X-100) under continued mixing with in a porcelain mortar and pestle. The mixture was homogenized very well by using an ultrasonic bath for half an hour and the resulting paste was carefully spread over an FTO conductive glass plate by using scotch tape [11].

2.3 Preparations of Counter Electrode (Photo Cathode)

Here in, our work the counter electrode was prepared using an FTO coated glass as described elsewhere [12]. The FTO glass was ready and wiped with distilled water followed by ethanol and was dried at room temperature. Then the conductive side of the FTO glass was identified with digital multimeter and was coated the surface with graphite pencil then after as shown in Figure 3 and it was checked to ensure the homogeneity of coated.

2.4 Preparation of Electrolyte

The electrolyte in this work was prepared as described elsewhere [13]. For a typical electrolyte preparation, it was carried out by dissolving 8.3 g of 0.5 M of KI and 1.27 g of 0.05 M of I_2 in ethylene glycol until it was 100 mL to obtain an (I^-/I_3^-) ions which used as an acceptor and donor for electrons through a redox reaction and counter electrode. The mixture was stirred by using magnetic stirrer the as to be homogenized.

2.5 Assembly and Fabrications of DSSC

A DSSC was assembled by introducing the electrolyte into the space between the TiO_2 electrode (photo anode) and the counter electrode (cathode) by capillary action [4]. The two electrodes were clipped together using binder clips as depicted in Figure 3. The excess electrolyte solution wiped off from the exposed areas of the glass cell; because the survival affects the work of the cell and this may prevent the electrolyte from leakage.

2.6 Optical Characterization and Measurements of the Cell

The optical absorption property of the as prepared dye solution was investigated for dye only and dye with TiO_2 the as dye loading investigation carried out by using UV-Vis spectrophotometer. The sintered TiO_2 paste was immersed with dye solution in a petri dish about 48 hrs. and the absorbance was taken for both (pure TiO_2 and dye with TiO_2) samples at wave length range between 400-800 nm to investigate dye loading effect.

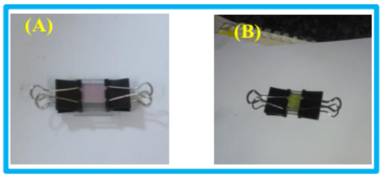

Fig. 3: The as assembled DSSCs of *Discopodim peninervum* (A) fruit and (B) leaf.

The power conversion efficiency was determined using a two digital multimeter keeping the as prepared DSSC in sunlight of approximately 100 mW cm-2. Herein, the light source we used was the sun at mid-day around 10:30 hr. using digital multimeter. The data were taken by designing electrical circuit on the card board with various different electronic resistors in series connection as load to estimate J-V curve. The maximum resistance for Voc where current reading became zero and minimum resistance for Jsc where voltage reading became zero were determined.

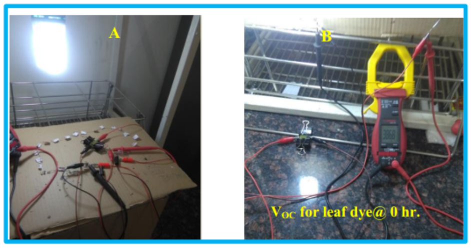

Fig. 4: Using binder clips to sandwich anode (top) and cathode (bottom) slides (A) digital multimeter connected to variable series resistors the as measured V_{OC} and J_{SC} and (B) testing the as prepared DSSC voltage using card board circuit.

2.7 Investigations of the Stability of Natural Dye Sensitizers

To date, DSSCs faces stability problem which is a serious issue in the fabrications of DSSCs. In this work the stability of the as prepared DSSCs for both fruit and leaf were studied at different time intervals with their assembly and consequently the effect of duration of the cell and was tried to compare with their efficiency of the as prepared DSSC at each time intervals as shown in Figure 9 [13, 14].

3 Results and Discussion

3.1 Optical Characterizations of Natural Dyes

The absorption spectra for fruit and leaf of *Discopodium peninervum* dye, fruit and leaf of *Discopodium peninervum* dye with TiO_2, and pure TiO_2 are illustrated in Figure 5. Fruit of *Discopodium peninervum* dye and fruit of *Discopodium peninervum* dye with TiO_2 shows a broad absorption in the visible region with a peak at 576 nm and 578 nm respectively. This intense absorption related with that reported for anthocyanin and is the reason for the efficient harvesting of photons in NDSSC [10]. Plant parts containing anthocyanin have been widely investigated for use as photosensitizers in the fabrication of NDSSC. In addition to their high absorption coefficient in the visible region of the electromagnetic spectrum, the presence of hydroxyl and carbonyl anchoring groups on anthocyanins enable their adsorption on to the surface of the TiO_2. This adsorption facilitates the transfer of the injected electron from dye to the conduction band of TiO_2 which ultimately enhances the efficiency of NDSSC [10].

Consequently, the appearance of absorption peaks spectra for leaf of *Discopodium peninervum* dye solutions at wavelength of 537, 618, 642, and 661 nm and leaf of *Discopodium peninervum* dye with TiO_2 at wavelength of 539, 620, 662, and 670 nm indicates that leaf extracted dyes contain an anthocyanin and chlorophyll pigments and may also be used as anticipating photo-sensitizer of DSSC due to its good absorbance in the visible region [15].

3.1.1 Energy Band Gap Determination

The optical absorption band gap energy for fruit and leaf of *Discopodium peninervum* extracted dye solutions and dye solutions adsorbed on TiO_2 wave length in the range of 400-800 nm were studied. From the recorded fed results the absorption spectrum analysis and absorption coefficient calculation as a function of photon, band gap energy were carried out using equation-1.

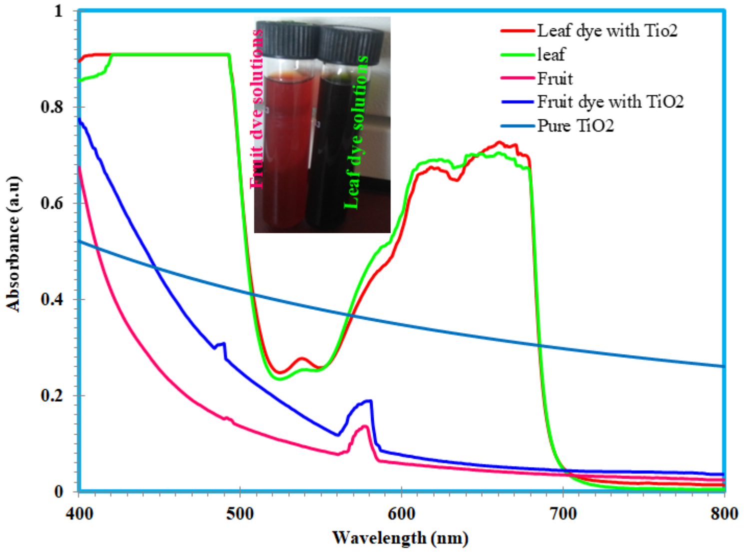

Fig. 5: Absorption spectra of *Discopodium peninervum* fruit dye, fruit dye with TiO_2, leaf dye, leaf dye with TiO_2 and pure TiO_2.

$$E_g = \frac{hc}{\lambda} \qquad (1)$$

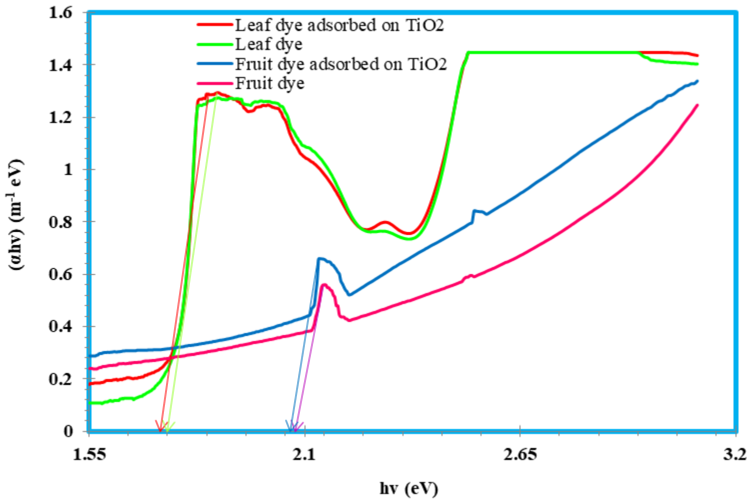

Fig. 6: Optical band gaps energy of *Discopodium peninervum* fruit dye (pink), fruit dye with TiO_2 (blue), leaf dye (red), and leaf dye with TiO_2 (green).

Table 1: Maximum absorption wave length and band gap energy of extracted dye and their adsorption on TiO_2 surface.

Dye	λ_{max} (nm)	λ_{onset} (nm)	$E_{g(\lambda max)}$ (eV)	$E_{g\,(onset)}$ (eV)

Fruit dye	576	584	2.154	2.125
Leaf dye	661	703	1.877	1.765
Fruit dye with TiO_2	578	588	2.147	2.110
Leaf dye with TiO_2	670	709	1.852	1.750

3.2 Photo Electrochemical Measurement

The photovoltaic properties of the DSSCs the as prepared dye were studied using digital multimeter and electrical circuit on wooden board made from several variable resistors as load. At sun irradiance in mid-day were used as light source and the obtained voltages with respective resistor were used to compute current according Ohm's law;

$$I = \frac{V}{R} \tag{1(a)}$$

$$P = I \times V \tag{1(b)}$$

The results were used to characterizing J-V and P-V curves as shown in Figure 19. The corresponding photo-electrochemical parameters have been listed in Table 5.

The DSSC performances were decided by their overall conversion efficiency (ɳ). The solar cells outputs were characterized by the following parameters (J_{sc}, V_{oc}, J_{max}, V_{max}, P_{max}, and FF).

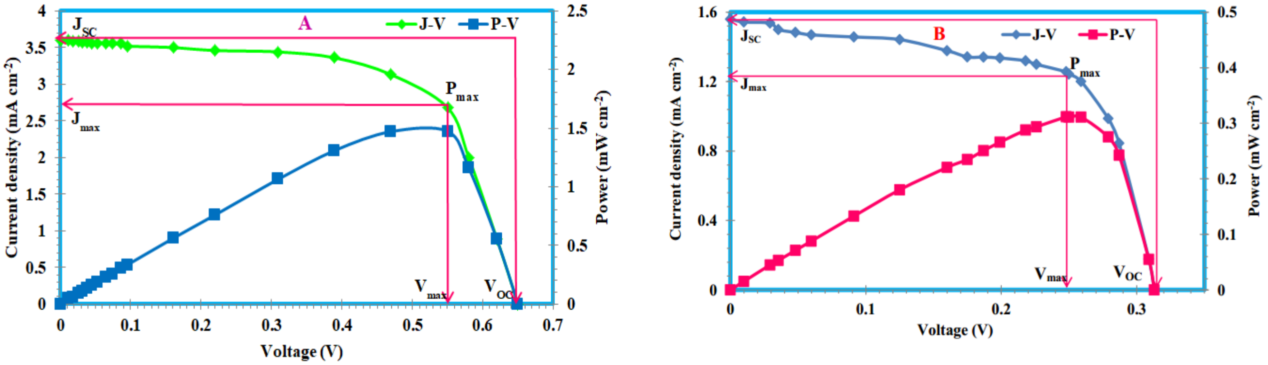

Fig. 7: The J-V and P-V characteristic curves of *Discopodium peninervum* (A) leaf and (B) fruit of the as prepared DSCC under illumination of 100 W cm $^{-2}$ (1.5 AM).

Table 2: The photovoltaic performance of the as fabricated DSSCs from fruit and leaf of *Discopodium peninervum* comparisons with other previous works (fruits and leafs).

Dye	J_{sc} (mA cm^{-2})	V_{oc} (V)	J_{max} (mA cm^{-2})	V_{max} (V)	P_{max} (mW cm^{-2})	FF (%)	ɳ (%)	Remarks
Fruit	1.560	0.313	1.201	0.259	0.311	63.69	0.311	This work
Leaf	3.60	0.650	2.680	0.550	1.474	62.99	1.474	This work

Red amaranth leaf	1.310	0.582				69.70	0.530	[14]
Jabuticaba fruit	0.230	0.350				23.00	0.080	[16]
Pomegranate dye	12.20	0.390	8.500	0.230		41.00	2.00	[10]
Black berry dye	11.16	0.470	6.980	0.200		26.00	1.400	[10]

3.3 *Investigation of the Stability of DSSC*

In this work we have tried to compare the performance of the as prepared DSSC with different time interval of after their assembly (0, 1, and 6 hrs.) as shown in Figure 20. And the overall power conversion efficiency after their assemblies were calculated based on equation 2 and 3 and their efficiencies are summarized in Table 6 consequently their efficiency decreases as the duration of DSSC increase.

$$FF\,(\%) = \frac{P_{max}}{P_{in}} = \frac{V_{max} \times J_{max}}{V_{oc} \times J_{sc}} \times 100 \qquad (2)$$

$$\eta\,(\%) = FF \times \frac{J_{sc} \times V_{oc}}{P_{in}} \times 100 \qquad (3)$$

Where P_{in} is the energy of the incident light falls on the DSSC and is obtained when the light intensities of the whole spectral range are integrated.

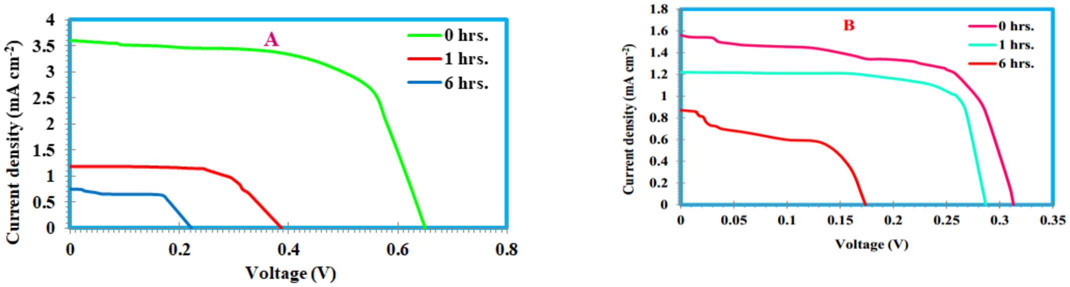

Fig. 8: Comparisons of J-V characteristics curve for (A) leaf and (B) fruit of *Discopodium peninervum* in three different times 0, 1, and 6 hrs. Respectively.

After six hours, the fabricated DSSC using *Discopodium peninervum* fruit and leaf dyes that were extracted from ethanol solvent shows poor stability indicates that in liquid electrolyte as the duration of DSSC increase stability became decrease. This may be due to the fast degradation of a highly volatility of liquid electrolyte. Improving the attachment of the dyes onto TiO_2 by introducing carbonyl groups and the use of quasi-solid state electrolyte may address the stability problem [17].

Table 3: The photovoltaic performance stability results of the as prepared DSSCs at three different time intervals.

Dye	Time (hrs.)	J_{sc} (mA cm^{-2})	V_{oc} (V)	J_{max} (mA cm^{-2})	V_{max} (V)	P_{max} (mW cm^{-2})	FF (%)	η (%)
Leaf	0	3.60	0.650	2.680	0.550	1.474	62.99	1.474
	1	1.18	0.387	0.995	0.287	0.286	62.63	0.286

	6	0.75	0.222	0.635	0.167	0.106	64.24	0.106
Fruit	0	1.560	0.313	1.201	0.259	0.311	63.69	0.311
	1	1.22	0.287	1.021	0.255	0.260	74.26	0.260
	6	0.87	0.174	0.565	0.134	0.076	50.20	0.076

Despite of their numerous advantages, DSSC faces stability problem which is a vital parameter in DSSCs. In this study we have compared the overall efficiency of the as prepared DSSC from fruit and leaf of *Discopodium peninervum* between 0, 1, and 6 hours of their assembly as shown in Figure 9 and Table 3.

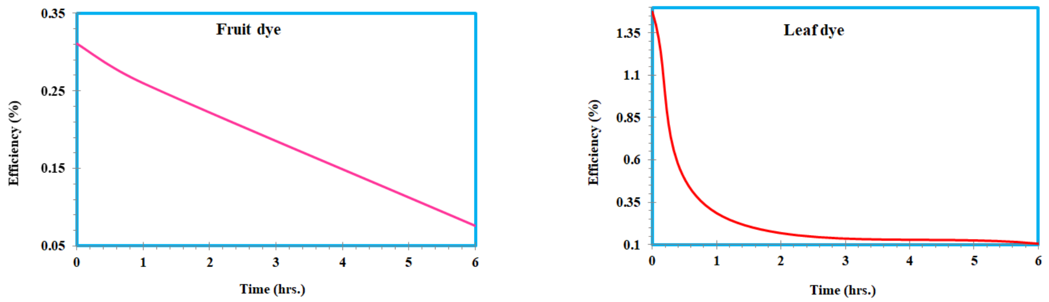

Fig. 9: Stability graph of the as prepared DSSC from fruit and leaf of *Discopodium peninervum* based on their efficiency and durations at different time intervals.

4 Conclusions

The UV-Vis spectrophotometer absorbance measurements of dye only and dye with TiO_2 for both fruit and leaf of *Discopodium peninervum* extracted dyes using ethanol as a solvent were carried out and their absorption peaks were in the visible regions may be due to the presence of chlorophyll and anthocyanin pigments. The extracted dyes from fruit and leaf of *Discopodium peninervum* have shown continuous broader absorption trend in the visible region at wave length ranges 480-585 and 515-705 nm respectively. However, after TiO_2 loading in to dyes the red (bathochromic) and blue (hyper chromic) shift to the pure extracted dye peaks were observed. It depicts that the dye molecules have made chemical bond with oxygen site of TiO_2 surface. The optical absorption band gaps for both fruit and leaf of *Discopodium peninervum* were determined from UV-Vis absorption spectrophotometer and were 2.125 eV for fruit and 1.765 eV for leaf.

The stability and photovoltaic performance of the extracted from fruit and leaf of *Discopodium peninervum* dye sensitizers for the constructed DSSCs were determined between the time intervals of 0 and 6 hrs. And, the resulted efficiency of the as prepared DSSC for fruit and leaf of *Discopodium peninervum* were 0.311 at 0 hr., 0.260 at 3hrs. and 0.076 at 6 hrs. for fruit and 1.474 at 0 hr., 0.286 at 3 hrs., and 0.106 at 6 hrs. for leaf which shows as the duration of the as assembly increase the efficiency of the cell becomes lower. The highest attainable efficiencies from both fruit and leaf of *Discopodium peninervum* dyes were observed at 0 hrs. and decreases rapidly after 6 hrs. This may due to the fast degradation of highly volatility of liquid electrolyte.

The overall of this study suggests that the exploitation of *Discopodium peninervum* fruit and leaf as photosensitizers could be taken as a possible alternative realization for further fabrication of DSSCs from other natural dyes.

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