RASĀYAN *J. Chem.*
Vol. 14 | No. 2 |1175-1182| April - June | 2021
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

PHOTOVOLTAIC ANALYSIS OF FABRICATED DSSCs BASED ON NATURAL COLORANTS

M. Devi[1], R. K. Saini[2,✉] and S. Shrivastava[1]
[1]Department of Chemistry, Kalinga University, Naya Raipur-492101 (Chhattisgarh), India
[2]Department of Chemistry, Goswami Ganesh Dutt Sanatan Dharma College, Palwal-121102 (Haryana), India
✉Corresponding Author: ramansaini07@gmail.com

ABSTRACT

The dye-sensitized solar cells (DSSCs) had been made using naturally extracted colorant from flowers of red Bougainvillea, Nerium Oleander, and Tecoma stans as sensitizers. The fabrication of the device with a thin film of TiO_2 nanoparticles as photoanode was applied on fluorine-doped tin oxide (FTO) glass plate. The redox electrolytes containing iodine with iodide ions were used e.g., NaI/KI with iodine. The UV-Vis absorption spectrum of natural colorant showed peaks due to the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions in the visible range. The optical band gap also calculated using Tauc's relation to natural dyes. The solar cell properties of the sensitization activity of dye were determined in terms of the current-voltage curve (I-V curve), V_{oc} (open-circuit voltage), I_{sc} (short circuit current), FF (fill factor), and η (efficiency). The V_{oc} was obtained in range 0.132 to 0.554 V while short circuit current density (J_{sc}) was found in range 3.22 to 15.22 mA/cm^2. The efficiency of fabricated solar cells was obtained in the range of 0.300 to 0.685. The easy fabrication, economical cost, and extensive accessibility of natural colorants exhibited promising alternatives to synthetic dyes in DSSCs.

Keywords: DSSCs, Natural Dyes, Optical Band Gap, Redox Electrolytes.

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INTRODUCTION

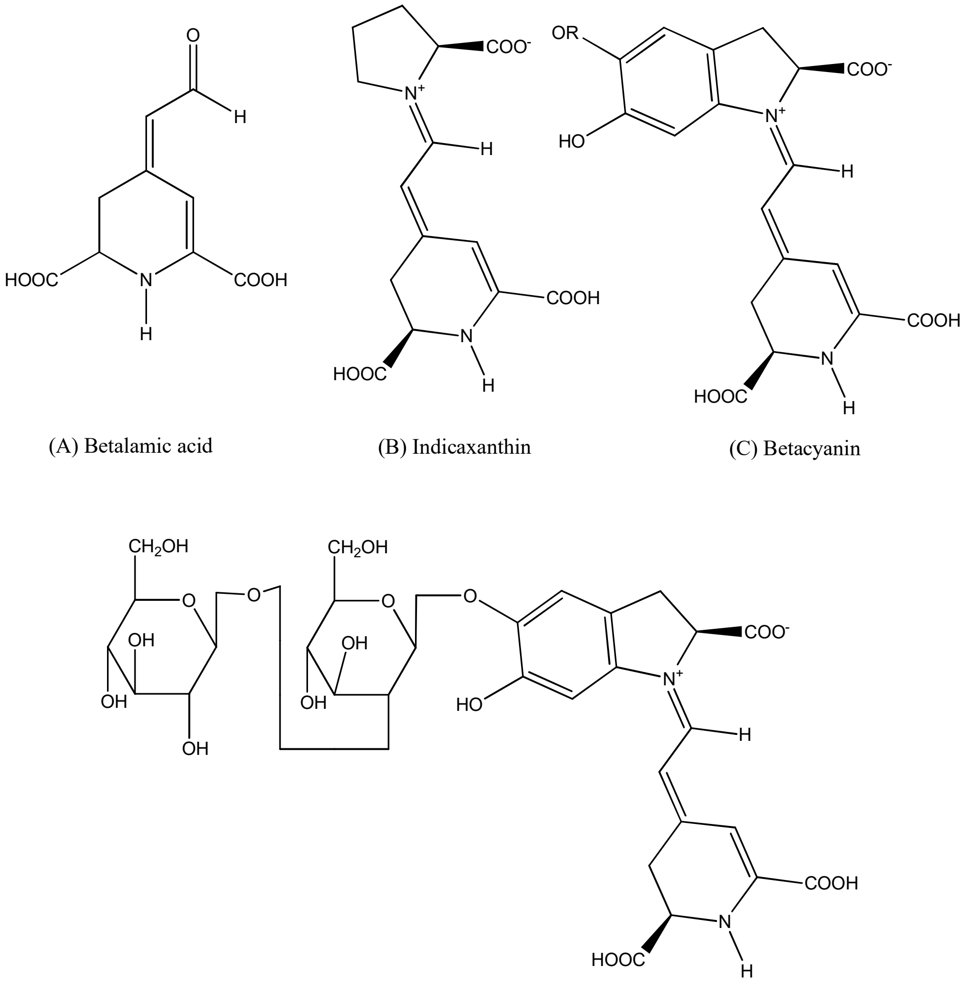
DSSCs (Dye-sensitized solar cells) are photovoltaic cells that generate electric energy from solar radiations derived from sensitization of extensive bandgap semiconductors.[1] These cells have the following components i.e. photoanode made of a nano-porous semiconductor oxide, dye absorbed on photoanode, redox electrolyte, and counter electrode.[2-5] The performance of DSSCs mainly depends on the nano-particle semiconductor layer on which sensitizer molecules are absorbed and solar radiations are absorbed by the sensitizers.[6-7] Various organic, inorganic, and hybrid sensitizer have been used in the fabrication of DSSCs.[8-9] The ruthenium metal complexes (N719 and N3) based dye are toxic in nature and expensive. Various dyes (organic dyes without metal) have been used as sensitizers exhibited good prospects in dye-sensitized solar cells.[10-11] Various natural Colorants i.e. carotene, tannin, anthocyanins, and chlorophyll, obtained from several parts of the plant such as flower, fruit, leaves, and roots have been effectively used as sensitizers in DSSCs.[12–19] Researchers are focused on natural dye which can easily be extracted and has good efficiency i.e. chlorophyll, red yeast rice, etc. Monascus yellow dye as sensitizer reported by Ito et al. exhibited 2.3% efficiency.[20] Wang et al. reported Chlorophyll as a sensitizer has shown 4.6% effieiency.[21] These natural dyes have various advantages over synthetic dyes such as easy preparation, color variety, and economical cost but have very low efficiency.[22]

Bougainvillea flower contains betacyanins which are the prospective resource of natural dyes and soluble in water. Betacyanin pigments have a high molar absorbency index equivalent to synthetic dyes. The pigment betalain that occurs from betalamic acid is alienated into two sub-groups: the yellow betaxanthins and the red betacyanins. The chemical structures of (A) betalamic acid, (B) indicaxanthin (C) betacyanin (Betanidin R = H: Betanin R = β-D-glucose)[23] and (D) bougainvillein-r-I (betanidin 5-*O*-β-sophorosides)[24] shown in Fig.-1.

Nerium flowers as dye have excellent fastness properties. The dyes obtained from Nerium flowers have a good perspective as a commercial dye in the carpet industry for wool yarn. Nerium oleander flower has Flavonoid Compound i.e., Myricetin responsible for Yellowish-brown in Fig.-2(A). Tecoma stan flower

http://dx.doi.org/10.31788/ RJC.2021.1426149

contains various important chemicals i.e., flavonoids, quines, saponins, tannins, phenols, glycosides, triterpenes, monoterpenes, phytosterols, amino acids, and alkaloids.[25]



(A) Betalamic acid (B) Indicaxanthin (C) Betacyanin

(D) Bougainvillein-r-I (betanidin 5-O-2-sophorosides)

Fig.-1: Structures of Betacyanin (A) BetalamicAcid, (b) Indicaxanthin, (C) Betacynin, and (D) bougainvillein-r-I (betanidin 5-O-2-sophorosides)

Tecoma stan flowers have been studied as a yellow dye to coloring cotton objects. Tecoma stan flowers as dye have excellent fastness properties. The natural pigment present in the Tecoma stans were zeaxanthin, rutin with flavonoids as represented in Fig.-2 (B and C). In this present work, the study of optical and photovoltaic performance of fabricated DSSCs. The experimental studies of natural colorants obtained from flowers of red Bougainvillea, Nerium Oleander, and Tecoma stans colorants have been broadly analyzed. The photovoltaic properties of fabricated solar devices have been represented with redox electrolytes i.e. sodium iodide (NaI), potassium iodide (KI) with iodine (I_2) in acetonitrile solvent.

EXPERIMENTAL

Material and Methods

The FTO (fluorine-doped tin oxide) conducting substrate of fused silica having resistance 6-8 Ω/square purchased from Sigma-Aldrich was used in the fabrication of DSSCs. The conventionally available P25 (nano-titania) was used as photoanodic material. The nano-titania P25 (purchased from Sigma-Aldrich) having rutile (20%) and anatase (80%) ~21 nm size was utilized for the fabrication of DSSCs. The fresh flowers of Bougainvillea, Nerium Oleander, and Tecoma stans were collected from the university

campus, India. The acetonitrile (AN) as a solvent in redox electrolyte, NaI (sodium iodide), KI (potassium iodide), and I_2 (iodine) of analytical reagents grade were taken from Sigma–Aldrich.
The UV-Vis absorption spectra of the naturally extracted colorants were taken using UV–Vis spectrophotometer with a range 180–1100 nm (model: Shimadzu 2450). The digital source meter (Keithley 2450) having computer-controlled kickstartsoftware was used to obtain the I-V (current-voltage) plots. The fabricated DSSCs were simulated by irradiation used 200W tungsten (W) arc lamp.

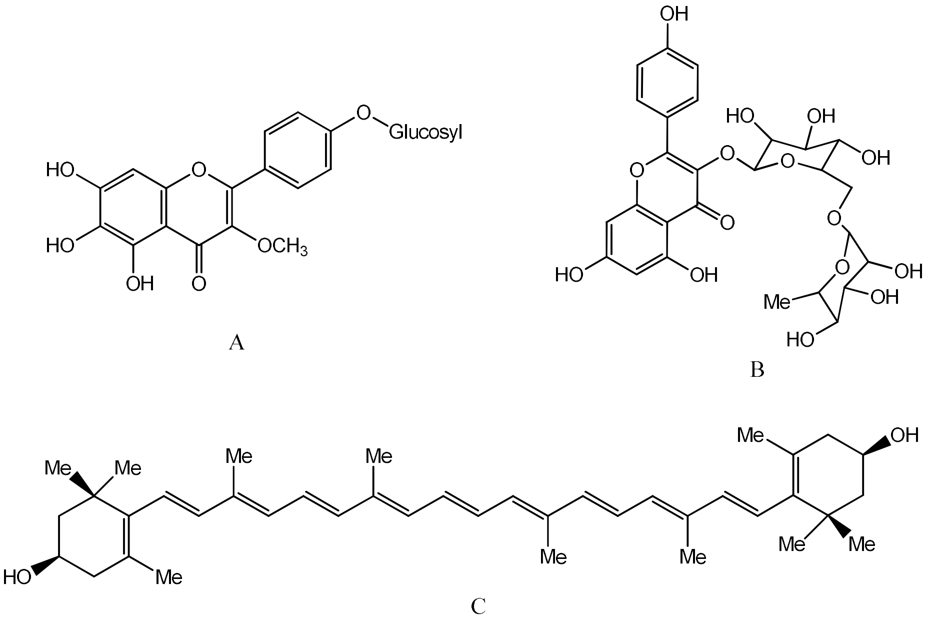


Fig-2: Structure of Myricetin (A), Rutin (B), and Zeaxanthin (C)

FTO coated fused silica substrate was cleaned using distilled water then neutral soap and washed various times with distilled water for the complete removal of soap then rinsed with acetone solvent. The clean substrate was dried under the oven at 40 ^{0}C. The cleaned substrate was boiled in propan-2-al to remove all organic impurities. The performance of DSSCs depends on the cleaning of FTO substarte.[26] The 1 gm of nano-TiO_2 particles (P25 Degussa) mixed in 1 ml of glacial acetic acid and sonicated for 15 min. Further, 0.1 ml of glacial CH_3COOH was added, and then sonicated in hot water for 15 min. to avoid the reaggregation of nanoparticles. The portion of the transparent conducting substrate was cover with adhesive plastic tape. The layer of TiO_2 was applied to the uncovered portion on the substrate. The paste of TiO_2 with glacial acetic acid was applied on the uncovered surface of the substrate using the doctor blade technique. The prepared TiO_2 layer on the substrate was dried under the oven at room temperature. The plastic tapes were removed after dried, the TiO_2 layer on the substrate was sintered in an oven at 300°C for 2h. After sintered the all-organic binder burnout and electronic contacts were improved.
The petals of Bougainvillea flowers separated and washed with distilled water. The petals were transferred in a round bottom flask with distilled water and methanol (1:1 ratio) as a solvent. The contents were boiled with a water condenser to avoid the removal of the solvent. The petals of Nerium Oleander were transferred in a round bottom flask with ethanol (95%) for 24 hours at room temperature. The Tecoma stans flower petals were finely chopped into small pieces and boiled with distilled water. The extraction was stored properly to protect from direct sunlight and utilize for fabrication and characterization. The sintered TiO_2 film on the substrate was immersed in a natural extracted colorant solution at room temperature for 24 h. The absorption of naturally extracted colorant on TiO_2 film was obtained superior as represented in Fig.-3. The redox electrolytic solutions were made by mixing sodium iodide (NaI)/ potassium iodide (KI) (0.1M) with iodine (I_2) (0.01M) in CH_3CN solvent. The counter electrode was formed by preparing a thin layer of graphite on conducting substrate and dried in an oven at 80°C for 30 minutes. The fabrication of DSSCs was done by clamping photoanode (substrate with TiO_2

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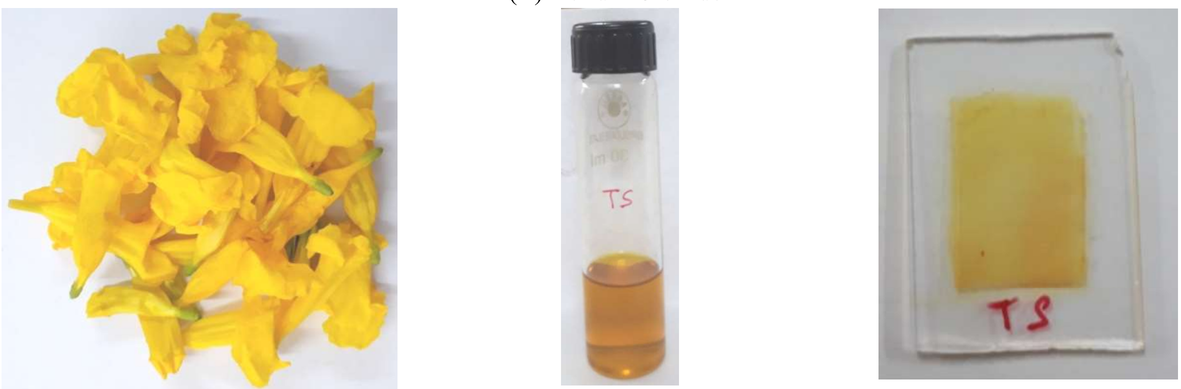
layer) with a natural colorant and counter electrode. The redox electrolyte was put in between the sandwich of electrodes.

(A) Red Bougainvillea

(B) Nerium Oleander



(C) Tecoma stan

Fig.-3: Natural extracted Colorant with the Absorption of Dye on TiO_2 film (A) Red Bougainvillea (B) Nerium Oleander (C) Tecoma stan

The configurations of fabricated dye-sensitized solar cells were as follows:

Substrate	Photoanode	Sensitizer	Electrolyte	Counter Electrode
FTO	Nano-TiO_2	Red Bougainvillea/Nerium Oleander/Tecoma stans flowers Extract Colorant	NaI With I_2	Graphite
FTO	Nano-TiO_2	Red Bougainvillea/Nerium Oleander/Tecoma stans flowers Extract Colorant	KI With I_2	Graphite

RESULTS AND DISCUSSION

Optical Properties of Natural Colorant

The absorption spectra of colorant extracted from the flower of Bougainvillea (distilled water and methanol 1:1 ratio), Nerium Oleander (ethanol), and Tecoma stans (aqueous) are represented in Fig.-4. The absorption spectrums of red Bougainvillea flower have two broad absorption peaks at 478 and 530 nm due to indicaxanthin, betanin, etc. The absorption spectrum of the flower of Nerium Oleander colorant has absorption peaks at 266 and 538 nm. The absorption peaks were due to the various kinds of flavonoids. These compounds have an aromatic structure and heterocyclic aromatic ring. So, the absorption peaks appeared due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The peaks observed in the absorption spectrum of the flower of Nerium Oleander colorant, absorption of the electromagnetic spectrum in the range of 200 to 700 nm that was in the visible region. The UV-Vis absorption spectrum of the flower of Tecoma stans colorant has shown two maximum peaks at 270 and 330 nm wavelength. The peaks were due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The intensity and wavelength of absorption peaks frequently tell about the dipole moment in the transition from the ground state molecule to the excited singlet state and the energy involved in the transition. The energy of the excited state of the sensitizer is supposed to be compatible with the nano-TiO_2 layer. The Tauc's equation was used to calculate the optical band gap of red flower Bougainvillea extract.[27-29]

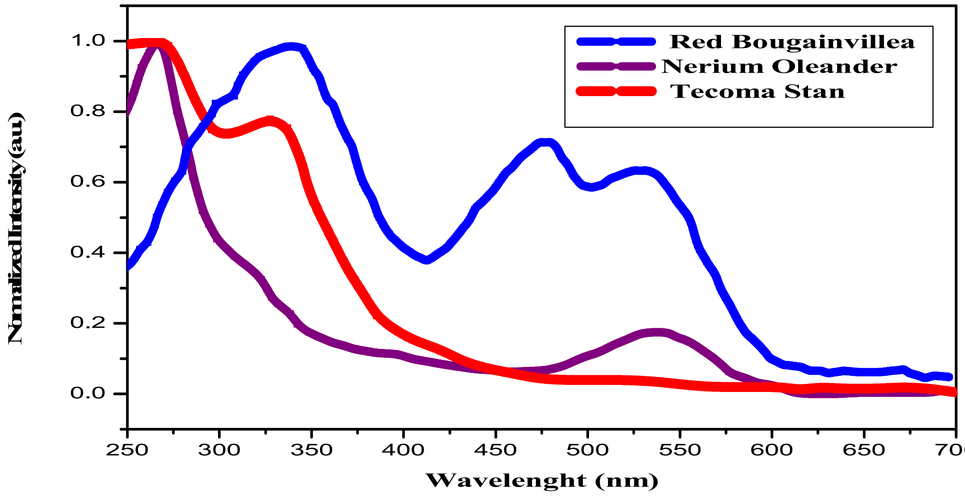


Fig.-4: UV-Vis Spectrum of Natural Colorants extracted from Flowers of Bougainvillea, Nerium Oleander, and Tecoma stans

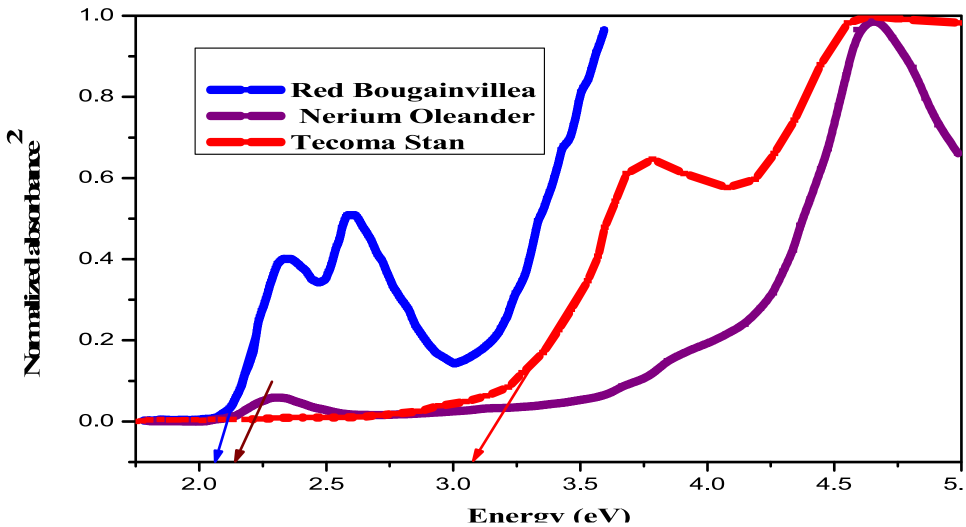


Fig.-5: Optical Bandgap of Natural Colorants extracted from Flowers of Bougainvillea, Nerium Oleander, and Tecoma stans

The Tauc's equation used to obtain the optical band gap as:

$$\mu h\nu = A(h\nu\text{-}E\ )^n \qquad \text{(i)}$$

Where A=Constant varies with transitions,
E_g= Optical bandgap of colorant,
h = Plank's constant
n= index may have values ½, 3/2, 2, and 3(dependent on electronic transition nature)
μ = Absorption coefficient,
ν = Frequency

Tauc's equation was used to calculate the optical band gap of flower extract. The plot of $(\alpha h\nu)^2$ Vs energy is represented in Fig.-5. The optical band gap of red Bougainvillea, Nerium Oleander, and Tecoma stans flowers extract were found 2.37, 2.10, and 3.20 eV, respectively.

Photovoltaic Properties of Fabricated DSSCs

The DSSCs were fabricated with FTO (fluorine-doped tin oxide) coated glass substrate, nanoparticles of TiO_2 (P25), colorant extracted from red Bougainvillea, Nerium Oleander, and Tecoma stans flower as sensitizers, NaI and KI with I_2 as redox electrolyte in Acetonitrile solvent. The current–potential (J–V) curve of fabricated solar cells was determined under the illumination of the 200W tungsten arc. From this $J-V$ curve J_{sc}, V_{oc}, *FF*, and η were evaluated as described below. The FF and light photon to electron conversion efficiency (η) of the fabricated DSSCs were found using the relations given below in equations:

$$FF = (I_{max} \times V_{max}) / (I_{sc} \times V_{oc}) \qquad \text{(ii)}$$

Where, V_{oc}= open circuit voltage,
I_{sc}= short circuit current,
V_{max} = maximum voltage
I_{max}= maximum current

$$\eta = (I_{sc} \times V_{oc} \times FF) / P_{in} \qquad \text{(iii)}$$

Table-1: Photovoltaic Properties of Fabricated DSSCs

S.No.	Electrolytes	V_{oc} (V)	J_{sc} (mA/cm^2)	Fill factor (FF)	Efficiency
Photovoltaic properties of Red Bougainvillea Colorant extraction as a Sensitizer					
1	NaI-I_2	0.132	15.22	0.197	0.397
2	KI-I_2	0.405	3.91	0.268	0.425
Photovoltaic properties of Nerium Oleander Flower Colorant extraction as a Sensitizer					
3	NaI-I_2	0.358	7.41	0.204	0.542
4	KI-I_2	0.544	3.22	0.390	0.685
Photovoltaic properties of Tecoma stans Flower Colorant as a Sensitizer					
5	NaI-I_2	0.413	3.56	0.204	0.300
6	KI-I_2	0.439	3.69	0.232	0.377

Figure-6 represented the current density (J)-voltage (V) plot of fabricated DSSCs with flower extract as a sensitizer. Table 1 exhibited the photovoltaic properties of fabricated DSSCs. The fabricated DSSC Red Bougainvillea flower extract with NaI/I_2 redox electrolyte exhibits the photovoltaic parameters i.e. V_{oc}= 0.132 V, J_{sc} = 15.22 mA/cm^2, FF = 0.197 and efficiency (η) = 0.397. The V_{oc}= 0.405 V, J_{sc}= 3.91 mA/cm^2, FF = 0.268 and η = 0.425 were found in fabricated device with redox electrolyte KI/I_2 in acetonitrile solvent. In the case of Nerium Oleander flower extract as a sensitizer, the V_{oc} of fabricated DSSC with NaI/I_2 was found 0.358 V while 0.544 V with KI/I_2. The J_{sc} was found 7.41 and 3.22 (mA/cm^2) with NaI/I_2 and KI/I_2 respectively. The efficiency of fabrication with NaI/I_2 and KI/I_2 was found as 0.542 and 0.685. Meanwhile, the fill factors of fabricated DSSCs were NaI/I_2 <KI/I_2.

Tecoma stans flower extraction as sensitized cell had V_{oc} of 0.395 V and J_{sc} of 3.97 mA/cm^2 with redox electrolyte NaI/I_2 as compared to 0.418 V and 7.39 mA/cm^2 with redox electrolyte KI/I_2 inacetonitrile solvent. The fill factor was found 0.240 and 0.258 with redox electrolytes NaI/I_2 and KI/I_2 respectively. The efficiency of fabricated devices was found with redox electrolyte KI/I_2 (0.798)>NaI/I_2 (0.376). The efficiency of the device fabricated with redox electrolyte KI/I_2 was found more as compared to redox electrolyte NaI/I_2. The change occurred due to the size of potassium and sodium ions. As the size of cation increase the bond length increase which decreases the bond energy and enhances the kinetics of electron transfer.

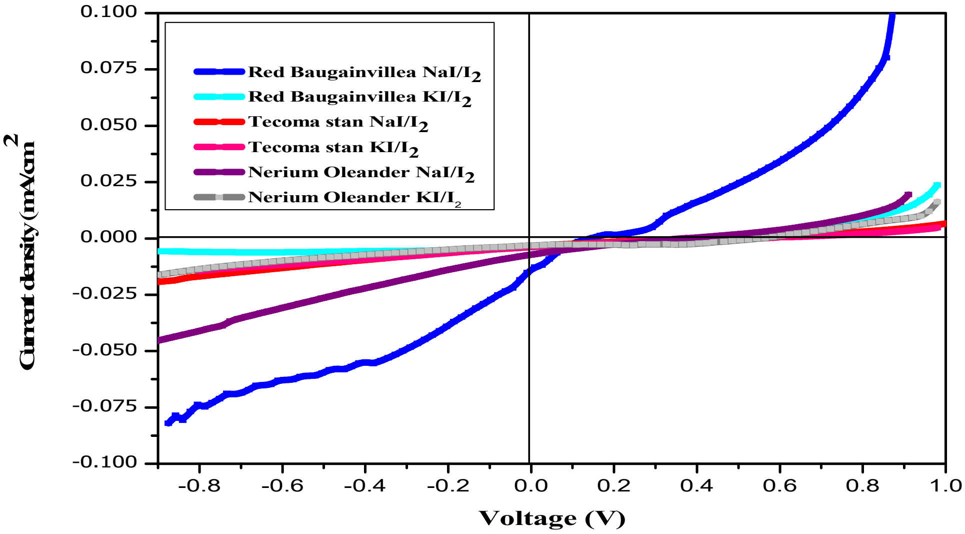


Fig.-6: Current-voltage Plot of Fabricated DSSCs with NaI/I_2 and KI/I_2 electrolytes using Natural Colorants as Sensitizers

CONCLUSION

The natural colorant based DSSCs had been fabricated and studied successfully. The red Bougainvillea, Nerium Oleander, and Tecoma stan flowers naturally extracted colorants were used as sensitizers. The flower chosen for fabrication have different colors. The natural colorants were used as sensitizers with FTO coated glass substrate, Nano-TiO_2 as a semiconductor, and the graphite-based counter electrode. The redox electrolytes i.e., NaI and KI with I_2 in acetonitrile solvent were used for fabrication. The J–V plots of NaI and KI with I_2 in acetonitrile solvent were studied for DSSCs. The solar cell conversion efficiency of KI/I_2 was higher than NaI/I_2 based DSSCs with the same condition.

ACKNOWLEDGEMENT

The authors are gratefully thankful to Head, Department of Chemistry, Kalinga University, Naya Raipur–492101 (Chhattisgarh), India, for providing necessary facility for carrying out research work.

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