EXTRACTION OF DYE FROM BARK OF SYZYGIUM GUINEENSE FOR TITANIUM DIOXIDE BASED DYE SENSITIZED SOLAR CELL AS PHOTO SENSITIZER

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ABSTRACT

This work was aimed to extract, prepare and use dyes from bark of Syzygium guineense as photosensitizer for dye sensitized solar cell. The extraction processes were takes place in presence of acetone, ethanol and water as solvent. The photoelectron-chemical performance of the DSSCs based on the acetone extract showed V_{oc} of 0.36 V, FF of 0.546, J_{sc} of 1.57 mA cm^{-2} and a power conversion efficiency of 0.319% under the sunlight illumination of 100 mW cm^{-2} and active area of 1 cm². The J-V curves were plotted according to collected data of DSSCs by using Extech Multimeter, and electrical circuit with resisters made from wood board. The acetone extract of day from bark of Syzygium guineense offered the highest conversion efficiency than ethanol and water extracts. Generally, the dye extracted from bark of Syzygium guineense as natural photosensitizer could be a possible alternative for the production of low cost and environment friendly DSSCs. [African Journal of Chemical Education—AJCE 10(1), January 2020]
INTRODUCTION

The world’s energy consumption is continuously increasing and this creates a heavy demand for renewable energy sources to be developed [1]. The burning of the fossil fuels emits tons of carbon dioxide that pollute the environment and also change the climatic condition [1, 2]. The development of renewable sources of energy may lead towards clean green technology for a healthy environment. Renewable energy sources, such as photovoltaic (PV), hydropower, wind, solar thermal and biomass, have the potential to meet the rising energy demand, and are expected to play an essential role in moving the world to a more safe, reliable and sustainable energy system [3].

Currently, the solar cells available commercially are based on inorganic silicon semiconductors, made of p-n junctions, which are relatively expensive to manufacture and also the manufacturing process releases, harmful emissions to the environment that cause pollution [4]. Hence, dye sensitized solar cell appear to be highly promising and cost-effective alternatives for photovoltaic energy sectors due to its relatively cheapness to produce, environment friendly and promising efficiency. In this regard, researchers have been given considerable attention for natural DSSCs. In DSSC, the dye plays an important role in harvesting solar energy and converting it to electrical energy with the aid of a semiconducting photo anode [5]. Therefore, the cell performance is mainly dependent on the type of dye used as a sensitizer in which the absorption spectrum and the anchorage of the dye to the surface of TiO₂ are important parameters in determining the efficiency of the DSSC. The natural dyes that we use for sensitization are mainly found in flowers, leaves, barks, roots and fruits of plants can be extracted by simple procedures [3].
In this work natural dye extracted from bark of *Syzygium guineense* were used as photosensitizer in DSSC fabrication.

**Working principles of DSSC**

Generally, the key processes in the operating mechanism of a DSSC can be divided into four basic steps [6].

Light absorption $\rightarrow$ Charge separation $\rightarrow$ Charge collection $\rightarrow$ Dye regeneration

The efficiency of the DSSC depends on the optimization of each of the interfacial electron transfer processes.

The crucial idea is to separate the light absorption process from the charge collection process, mimicking natural light harvesting procedures in photosynthesis, by sensitizers with in semiconductors [7]. The principle of operation of a DSSC is quite simple, shown by the scheme in Figure.1

![Figure 1: Basic working mechanism of Dye sensitized solar cell (DSSC)](image)
The operating cycle of DSSC can be summarized in the following chemical reactions

**Anode:** $S + h\nu \rightarrow S^*$  
Photo-excitation of the dye

$S^* \rightarrow S^+ + e^- (TiO_2)$  
Electron injection in TiO$_2$

$2S^+ + 3I^- \rightarrow 2S + I_3^-$  
Regeneration of the dye

**Cathode:** $I_3^- + 2e^- (Pt) \rightarrow 3I^-$  
Reduction of the redox

Where: $S$ - Dye sensitizer; $S^*$- excitation upon irradiation; $S^+$ - Oxidized dye

**EXPERIMENTAL**

**Chemicals**

Potassium iodide (INDENTA, chemical, INDIA, Pvt, analytical reagent), Iodine,(INDENTA, chemical, INDIA, Pvt, analytical reagent), TiO$_2$ (powder, Sisco Research Lab. Pvt. Ltd, Maharashtra; INDIA), ethanol(96%, HAYMAN Ltd), n-hexane(99%, LOBA ), ethylene glycol(99%, India), Acetone(99.8%, Blulux® Laboratory(P), Ltd, analytical reagent), 0.1 M HNO$_3$ (69-72%, Blulux® Laboratory(P), Ltd, analytical reagent), Triton-100(bought from SiscoResearch Laboratories Pvt. Ltd, India), was used to conduct this work.

**Extraction of natural Dyes**

The bark of *Syzygium guineense* sample was washed with pure water and air dried at 40°C in a vacuum drying Oven and then the raw material was crushed and changed in to powder by using Pestle and mortar. 2.5g of the powder was put in to 50 mL 95% Ethanol solution and the glass containers were covered with aluminum foils to prevent damage from light exposure and was stay for 24 h in dark conditions. After that, by using filter funnel and conical flask, the solutions were filtered in order to remove solid fragments. And finally, evaporate the liquid at
50% to get the dye only and repeat the procedure using 50 mL distilled water, and 50 mL acetone. And then the extracted dye was characterized with spectroscopic techniques [7].

**Preparation of working electrode**

The FTO conductive glass substrate was cleaned in a detergent solution using an ultrasonic bath for 21 min, rinsed with water and ethanol, and then dried in an oven at 60°C for 30 min [8]. The sheet resistance of the FTO conductive glass was measured and expected to be 15-20 Ω/cm².

The TiO₂ film was prepared by mixing 2 g of commercial TiO₂ powder, 0.4 mL of nitric acid (0.1 M), 0.08 mL of polyethylene glycol and one drop of a Triton x-100. The mixture was homogenized by using magnetic stirrer for 1 h and the resulting paste was carefully spread over an FTO conductive glass plate having 15 Ω/cm², as shown in Figure:2.

![Figure 2: Preparation procedure of working electrode](image)

Successively the TiO₂ paste was spread uniformly on the substrate by sliding a metallic rod along the tape spacer by doctor-blade technique. The active area of DSSC was made to be 1 cm² (1.0 cm × 1.0 cm). The TiO₂ thin film was sintered at 450°C for 30 min to increase the film compactness and crystallites. The TiO₂ film was confirmed by heat treatment, in order to increase the internal void of film organization and enhance its absorption performance. After cooling down, the electrode was immersed in the natural extracts for 24 h [9]. Finally, the electrode was withdrawn from the solution and rinsed with anhydrous alcohol to remove the
residues left on the TiO$_2$ film and dried in air which was used as photoelectrode (photoanode) as shown Figure:2.

**Preparation of counter electrode**

Because of its high exchange current density, good catalytic activity, and transparency platinum (Pt) counter electrode is considered a preferred catalyst but its cost is a major challenge. Therefore, Carbon counter electrode have also been used as alternative materials for counter electrode [10]. Because their electrical efficiency is similar to that of Pt counter electrode. To make the, the FTO glass is managed to be wiped with ethanol and the graphite-coated slide, the conductive side of the glass plate was coated gently by sweeping the surface with a graphite stick (2B pencil). The surface was checked to ensure that no space that the carbon is not cover.

![Pencil graphite coating](image1) ![Counter electrode](image2)

**Figure 3: Preparation of counter electrode**

**Preparation of Electrolyte**

The iodide/triiodide electrolyte liquid electrolyte were prepared as follow. A 0.83 g of 0.5 M KI and a 0.1269 g of 0.05 M I$_2$ were mixed in a mixture of solvent of 10 mL of ethylene glycol. The mixture were stirred by using glass rod so as to be homogenized until they have no grain of iodine and potassium iodide remained [11]. And it was placed between a TiO$_2$ porous film electrode (anode electrode) and a conductive glass sheet plated with graphite (cathode electrode).
DSSC Assembling

To assemble the cell device the graphite-coated slide was made to face down on top of the stained titanium dioxide coated side. The two electrodes were placed one on top of other with a slight offset to guarantee that all of the stained titanium dioxide covered by the counter electrode and a space for connecting the crocodile clips. Next two binder clips were used on opposite edges to gently hold the slides together.

Figure 4: (a) Prepared working electrode (b) prepared counter electrode (c) using binder clips to sandwich anode (top) and cathode (bottom) slides (d) measuring performance parameters of assembled DSSC by using multi-meter.

The iodide/iodine electrolyte solution were placed at the edges of the plates to percolate into the cell. Afterward, the two binder clips were alternately opened and closed so as to promote the uniform dispersion of the iodide/iodine electrolyte between the slides. Finally, the alligator clips were attached to the overhanging edges to be connected to the multi-meter. The negative and positive terminals were attached to the stained titanium dioxide (working electrode) and graphite stained (counter electrode) slides, respectively [12].

Characterization of dye

Optical properties of extracted day

The optical absorption of the as prepared dye solution was determined by UV-visible absorption spectrophotometer in the wave length of 400-800 nm. The energy band gap of the
extracted dye where also calculated by taking maximum wave length of extracted dye [13, 14]. The band gap energy, near the absorption edge determined by using (equation 9)[15].

**Characterization of prepared DSSC**

The performance of each prepared DSSC was characterized based on the parameters such as short circuit current ($I_{sc}$), open circuit voltage ($V_{oc}$), maximum voltage, maximum current, fill factor (FF) and efficiency ($\eta$) by using ExtechMultimeter.

Sun light at noon was used as a light source to measure photoelectrical performance of prepared DSSC. ExtechMultimeter was used to characterized prepared DSSC from bark of *Syzygium guineense* plant. The voltage and current readings were taken at mid-day assuming that the sun would give 100 mW/cm$^2$ as incident power at the global air mass of the data were taken by designing electrical circuit on the wood board with various electronic resistors in series connection as shown in the Figure:5.

The voltage readings were taken by connecting multimeter in series with DSSC and circuit board. The maximum resistance for $V_{oc}$ where current reading became zero and minimum resistance for $I_{sc}$ where voltage reading became zero were determined.

![Figure 5: Measuring of performance parameter at various resistor by using multimeter](image)
Beyond this voltage readings with each resistor were recorded and the currents were calculated from the measured voltage with respective resistance based on Ohm’s law.

\[ I = \frac{V}{R} \] \hspace{1cm} (11)

\[ P = \frac{V^2}{R} \] \hspace{1cm} (12)

RESULT AND DISCUSSION

Results of Extracted Sample

The bark of Syzygium guineense sample were washed with pure water and air dried at 40°C in a vacuum drying Oven and then the raw material was crushed and changed in to powder by using Pestle and mortar as shown in Figure:6.

Figure 1: (a) Syzygium guineense sample (b) bark of Syzygium guineense sample (c) samples was being ground by using Pestle and mortar (d) powdered sample.

The prepared powdered dry samples were soaked in acetone, ethanol and water after 24 hrs. They were filtered as shown Figure 7.

Figure 7: Ethanol, acetone and water extract of Syzygium guineense plant
The filtrates of natural dye have red color for acetone, ethanol and water extract. Finally extracted dye was characterized with spectroscopic techniques the result shown in Figure:7. This extracted dye was taken to rotary evaporator to remove the solvent. The resulted dyes were used as sensitizer and the left extra dyes were kept in amber bottle in the dark place for another next demonstration of DSSC preparation.

The UV-Visible absorption spectra for the dye extracted from bark of *Syzygium guineense* plant using acetone, ethanol and water as solvents in the wave length range of 400-800 nm shown in Figure:12. The peak apppears at the wave length of 573 nm, 580 nm and 587 nm of water, ethanol and acetone extract respectively [5]. All the extracted dye solutions have shown an absorption peak in between 500-600 nm range as shown below Figure 8.

![UV-vis absorption spectra](image)

Figure 8: UV-vis absorption spectra of (a) acetone (c), ethanol and (b) water extract of dye from bark of *Syzygium guineense* plant.

The absorption peak of extracted dyes shows the pigments almost closely related to betalains and anthocyanin [16]. Because betalains absorbs strongly in between 400-600 nm range and Anthocyanin shows absorption peaks in between 500-600 nm range [8]. The same
Anthocyanin and betalains pigments may have different possible colors at different wave length depending on solvents polarity and pH variations in the solution [16].

Anthocyanin is the core component of some natural dyes and is often found in the fruits, flowers, root, barks and leaves of plant. Also, it is efficient sensitizer for wide band gap semiconductors of ethanol, water and acetone extract of dye [17]. The dye extracted by acetone have relatively high wave length and results the best cell efficiency than the dye extracted by ethanol and distilled water. This is due to variation of solvent polarity for anthocyanin and betalains pigments at different wave length.

**Energy Gap Determination of the Dye**

The optical band gaps of the dyes were determined from the $\lambda_{\text{max}}$ UV-Vis absorption spectra using the relation in equation (9) ($E_g = h \nu = \frac{hc}{\lambda}$) where $h$ is the Planck’s constant, $\nu$ is the frequency, $\lambda$ is the maximum wavelength and $c$ is the speed of light, where, $h = 6.63 \times 10^{-34}$ Js, $c = 3.0 \times 10^8$ m/s, 1eV = $1.60 \times 10^{-19}$J. Energy band gap is the energy difference between the conduction band and valence band. It is used for analysing the performance of dye sensitized solar cell. The values of band gape of dyes of *Syzygium guineense* at different solvent are given in Table:1. From the Table:1 it is possible to understand that the dyes extracted from *Syzygium guineense* plant by using acetone solvent showed low band gap. A lowest band gap of dye helps the electron move fast from the valence band to the conduction band and only need less energy to the recombination of electrons and resulted high efficiency. Therefore, acetone extract has showed higher efficiency among extracted solvent due to low band gap.
Table 1: The band gap of the extracts of *Syzygium guineense* in ethanol, water and acetone.

<table>
<thead>
<tr>
<th>Source of dye</th>
<th>Extracting solvent</th>
<th>Maximum wave length</th>
<th>Energy band gap</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Syzygium guineense</em></td>
<td>Ethanol</td>
<td>580</td>
<td>2.14</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>573</td>
<td>2.17</td>
</tr>
<tr>
<td></td>
<td>Acetone</td>
<td>587</td>
<td>2.11</td>
</tr>
</tbody>
</table>

**Photoelectrochemical Measurement**

The J-V curves of prepared DSSC from *Syzygium guineense* plant was evaluated by short circuit current density (Jsc), open circuit voltage (Voc), fill factor (FF) and power conversion efficiency (η).

\[
FF = \frac{P_{\text{max}}}{I_{\text{sc}}V_{\text{oc}}} = \frac{I_{\text{MP}}V_{\text{MP}}}{I_{\text{sc}}V_{\text{oc}}} \ldots \ldots (13)
\]

\[
\eta = FF \times \frac{J_{\text{sc}}V_{\text{oc}}}{P_{\text{in}}} \times 100 \ldots \ldots (14)
\]

The results of each parameter that have been obtained was 1.57 mA cm\(^{-2}\) of short circuit current density, 0.36 V of open circuit voltage, 0.564 of fill factor for acetone extract, 1.48 mA cm\(^{-2}\) of short circuit current density, 0.345 V of open circuit voltage, 0.351 of fill factor for ethanol extract and 1.42 mA cm\(^{-2}\) of short circuit current density, 0.24 V of open circuit voltage and 0.509 of fill factor for water extract. Among this extracting solvent acetone have showed the highest short circuit current density, fill factors and power conversion efficiency. As shown in Table 2.
As we have seen from the figure above the higher Jsc, Voc and $\eta$ was obtained for the DSSC sensitized from acetone extract of bark of *Syzygium guineense* and the lowest Jsc, Voc and $\eta$ was obtained for water extract of dye where recorded as shown in Table:2.

This is due to the good interaction of TiO$_2$ with anthocyanin pigment extracted from bark of *Syzygium guineense* by acetone solvent which resulted good charge transfer and higher solubility of the pigment in acetone solvent. This anthocyanin instantly adsorbed to the surface of TiO$_2$ by displacing an OH$^-$ counter ion from the Ti (IV) site that combines with a proton which is donated by the anthocyanin.

Power conversion efficiency of DSSC obtained from this work where compared with other natural dye sensitized so far by other groups as showed in Table:2. DSSC fabricated from dye of *Syzygium guineense* extract by using acetone as a solvent shows the highest power conversion efficiency than using water and ethanol. This might owe to the fact that anthocyanin

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Figure 9: J-V characteristic curves of *Syzygium guineense* day using acetone, ethanol and water as extracting solvent.
is more soluble in acetone, and hence, the aggregation of dye molecules is less as expected. Therefore, the extracting solvent has an effect on the efficiency of DSSCs as shown in Table 2.

Table 2: The photoelectrochemical parameters of the as prepared DSSCs sensitized with dyes extracted from bark of *Syzygium guineense* at acetone, ethanol and water solvents compared with other work.

<table>
<thead>
<tr>
<th>Plant name</th>
<th>Extracting Solvent</th>
<th>J&lt;sub&gt;SC&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>Voc (V)</th>
<th>P&lt;sub&gt;max&lt;/sub&gt; (mW/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>FF</th>
<th>η%</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bougainvillea spectrois</td>
<td>Water</td>
<td>0.545</td>
<td>0.541</td>
<td>0.164</td>
<td>0.552</td>
<td>0.164</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>0.549</td>
<td>0.574</td>
<td>0.175</td>
<td>0.555</td>
<td>0.175</td>
<td></td>
</tr>
<tr>
<td>Olive grain</td>
<td>Ethanol</td>
<td>0.58</td>
<td>0.55</td>
<td>0.12</td>
<td>0.38</td>
<td>0.12</td>
<td>[18]</td>
</tr>
<tr>
<td>Rosella</td>
<td>Water</td>
<td>0.37</td>
<td>0.372</td>
<td>0.05</td>
<td>0.33</td>
<td>0.05</td>
<td>[19]</td>
</tr>
<tr>
<td>Blue pea</td>
<td>Water</td>
<td>0.82</td>
<td>0.382</td>
<td>0.15</td>
<td>0.47</td>
<td>0.15</td>
<td>[19]</td>
</tr>
<tr>
<td>Lemon leaf</td>
<td>Acetone</td>
<td>0.225</td>
<td>0.017</td>
<td>0.04</td>
<td>0.514</td>
<td>0.04</td>
<td>[20]</td>
</tr>
<tr>
<td></td>
<td>Acetone</td>
<td>1.57</td>
<td>0.36</td>
<td>0.319</td>
<td>0.564</td>
<td>0.319</td>
<td></td>
</tr>
<tr>
<td>Syzygium guineense</td>
<td>Ethanol</td>
<td>1.48</td>
<td>0.345</td>
<td>0.179</td>
<td>0.351</td>
<td>0.179</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>1.42</td>
<td>0.24</td>
<td>0.174</td>
<td>0.509</td>
<td>0.174</td>
<td></td>
</tr>
</tbody>
</table>

Three different solvents: water, acetone and ethanol were showed various result of photoconversion efficiencies as observed at Table 2. The conversion efficiencies of the as prepared DSSC in this study were better as compared to some DSSC values reported in other study as shown in Table 2.
CONCLUSION

Dye extracted from bark of *Syzygium guineense* plant by using acetone, ethanol and water as solvent were used as photosensitizer in DSSCs. The dye extracted from this plant contained anthocyanins and betalains pigments. The acetone extract bark of *Syzygium guineense* dye shows lower band gap.

The Photoelectrochemical performance of acetone extracts showed open circuit voltage of 0.36 V, short circuit current density of 1.57 mA cm\(^{-2}\) and fill factor of 0.564, ethanol extract were showed open circuit voltage of 0.345 V, short circuit current density of 1.48 mA cm\(^{-2}\) and fill factor of 0.351 and water extract showed open circuit voltage of 0.24 V, short circuit current density of 1.42 mA cm\(^{-2}\) and fill factor of 0.509 under the sunlight illumination of 100 mW cm\(^{-2}\) and active area of 1 cm\(^2\). Acetone extract of DSSC sensitized by bark of *Syzygium guineense* plant were offered 0.319 conversion efficiency which is the highest efficiency among the extracts. This work also shows that the effect of extracting solvent on efficiency of fabricated DSSC performance.

The overall results of the study suggest that bark of *Syzygium guineense* could be a possible alternative for the production of DSSCs.

IMPLICATIONS FOR CHEMISTRY EDUCATION

Solar energy is renewable energy resources that pick up their energy from sun and supply this endless energy for human beings. It is one of the most hopeful energy resources due to its abundant, purity, safety and higher economic values that cause energy creation in distant rural areas. A solar cell is an electric device that directly convert incident light into electricity by photovoltaic effect.
Natural Dye-sensitized solar cells (DSSCs) are photovoltaic devices that convert visible light into electricity based on natural dye pigments. It is environmentally friendly, low cost, easy preparation, and high conversion efficiency. But at this time, it has efficiency and durability problem. That is why; at this time chemical educators and researchers at different levels devote their time on searching new natural dye to get efficient DSSCs.

Based on this assumption, we conducted this research on the title “Extraction of Dye from Bark of *Syzygium guineense* for Titanium Dioxide Based Dye Sensitized Solar Cell as Photo Sensitizer”.

So, the result of this work is significant for students at post-graduate level & chemistry educators and researchers as starting material and/or documented reference for their teaching learning process as well as for their research work.

**REFERENCES**

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