The optical properties of the dye Roselle anthocyanins shows high absorption to visible spectrum because of concentration of anthocyanin in Roselle calyces. Its absorption to sun light is almost constant which an indication of chemical stability. The absorption spectrum of the anthocyanin dye dissolved in methanol shows $\lambda_{\text{max}}$ (283 nm) in the UV region, while $\lambda_{\text{max}}$ (545 nm) in the VIS range. The corresponding energy levels are 4.36 eV and 2.25 respectively. The absorption spectrum of fresh Roselle crude shows in the visible region. The energy gap of Roselle is 2.06, while that of titanium dioxide is 4.125. These values agree with the standard values. The response of optical absorption to temperature shows stability at ambient temperature, while absorption decreases as temperature increases above ambient temperature.

Keywords: Roselle, Anthocyanin, Concentration, Spectrum, Energy gap

INTRODUCTION

Solar Energy is a clean safe energy. Other renewable energies such as water fallow, biomass, etc., encourages scientists to make intensive researches in these fields to avoid pollution (Neaman, 2001, Green, 2010, Hearps, 2011).

As electrical energy is the most popular energy source, solar cells pay more attention (Klaus, 2001). It is well known that the production of solar cell from silicon is pretty expensive and limited in efficiency. One of the very important alternatives was dye solar cells and Dye-Sensitized nano Solar Cell (DSSC) which is one of the photoelectric chemical solar cells, that got an efficiency of about 38% as maximal theoretical value as well as the reasonable cost (Rauschenbach, 2010). The fact of absorbing light and converted to electrons by PV (photo-voltaic cells) can be accomplished by anthocyanin which has a molecular structure that acts lake a photon antenna (Gratzel, 2012). As light is collected, the molecule enters an excited
state whereby it dumps an electron wherever it can to relieve this “excitement”. Titanium dioxide (TiO₂) is one of the most common oxide compounds on Earth beside silica (sand and glass). Titanium is the compound that gives many things their bright white appearance (Gowthaman, 2013). The use of natural dyes in solar cells offers promising prospects for the advancement of this technology. Several natural dyes have been utilized as sensitizers in photovoltaic cells due to their capability of injecting electron from excited pigments to the conduction band of the semiconductor material. Most natural dyes that can be utilized in dye sensitized solar cells undergo rapid photo degradation. Dye Sensitized solar Cells (DSCs) based on nano-particles, are sensitization due to the dye absorption of part of the visible light spectrum were first developed by Grätzel in 1991 (Gratzel, 2012). This work consists of four sections. Section one is the introduction, and section two is concerned with the theoretical back ground, the materials and methods are exhibited in section three, while section four is devoted for results and discussion.

THEORETICAL BACKGROUND

The operation of the dye-sensitized solar cell resembles that of battery (Figure 1), rather than diode. This is since the separation of electrons and holes are done by an electrolyte solution not by an internal electric field. The structure of dye solar cells consists of a glass film at the upper coated at the bottom of the glass by transparent fluorine doped by SnO. This conduction layer is followed by is mixed at its bottom by dyes. Below the dye is an electrolyte which is an iodide electrolyte. Below electrolyte is a platen conductor layer coated at its upper end by catalyst which activates electrolyte reaction (Grätzel, 2012; Regan, 2014).

When light is incident on the dyes, electrons are excited and jump to TiO₂ conduction band. This is because dye level is near to TiO₂ conduction band, one can also assume that dye make covalent bond with to make energy gap of narawer (Cahen, 2014). The free electrons in TiO₂ semiconductor move to the upper conducting transparent level by diffusion since they have high concentration of TiO₂. The dye positive ions take electrons from iodide electrolytes which becomes positive ions, the positive electrolyte ions moves mechanically down to take electrons from plative layer which become positive (Katoh, 2010). The accumulation of free electrons on upper of SnO plate make it act as a negative electrode (anode) while the accumulation of positive ions in platen plate at the lower part of the cell make it act as a positive electrode (cathode). There are two main problems facing attempts made to construct dye cells, the first one is the toxic chemical expensive dyes. The second one is the use of row natural dyes without extracting the pure dye. This work is devoted to contribute to the solution of these two problems. This is done by extracting a pure natural anthocyanin dye from Roselle. Such natural dye is cheap, commercially available, non-toxicity, and pure (Calogero, 2014).

The optical properties of anthocyanin and depends on many factors. If the atom or molecule...
is isolated as in the case of gases or compounds dissolved in water the absorption spectrum shows a characteristic peak corresponding to the absorbed wavelength $\lambda$, which causes electrons to move from to according to the relation.

$$\frac{hc}{\lambda} = E_2 - E_1 \quad \ldots(1)$$

The relation between wavelength $\lambda$ and the absorbed light intensity $I$ is given by Figure (2). In the case of bulk solid mater the pattern of the spectrum shows energy gap and bands in the form of plateau as shown in Figures 3 and 4. Where the photon which is transmitted have energy less than the energy gap $E_g$. Thus (Hearps, 2011).

$$\frac{hc}{\lambda} \leq E_g \quad \ldots(2)$$

$$\lambda \geq \frac{hc}{E_g} \quad \ldots(3)$$
Thus the minimum transmitted light wavelength is given by
\[ \lambda_{\text{min}} = \frac{hc}{E_g} \] ...(4)

In contrary the absorption takes place when
\[ \frac{hc}{\lambda} \geq E_g \] ...(5)
\[ \lambda \geq \frac{hc}{E_g} \] ...(6)

Thus the maximum absorbed wavelength satisfies
\[ \lambda_{\text{max}} = \frac{hc}{E_g} \] ...(7)

The absorption of light by any solvent in a certain solution is strongly dependent on temperature. When temperature is increased the interatomic spacing of the solvent increases thus the concentration of the solvent decreases. The decrease of concentration decreases the absorption of light by the solution.

MATERIALS AND METHODS

Extraction of Natural Dye

The anthocyanin was extracted from Roselle according to the following sketched procedures:

[Plant Material] → Extraction Meth/Hcl → [Crude Product] → TCL → [Anthocyanin]

Experimental Procedures

1. Anthocyanin pure dye dissolved in distilled water with concentration 0.2 g/ 10 mLH₂O was scanned by spectrophotometer to determine its absorption spectrum and to identify maximum wavelength absorption edge or beak \( \lambda_{\text{max}} \).

2. A sample of fresh Roselle immersed in distilled water was scanned by spectrophotometer to display its absorption spectrum and to determine for comparison with anthocyanins.

3. The same anthocyanin sample in (1) was exposed to heat in oven to be heated in the temperature range (40 – 120 ), for different exposure times in the ranges 20, 40, 60 min. The absorption spectrum was recorded for constant maximum wavelength.

4. The same anthocyanin sample in (1) was exposed to direct sun light daily for 1 – 16 days. The absorption spectrum was recorded daily for maximum wavelength.
5. Anthocyanin pure dye was dispersed in distilled water with concentration 0.2 g/10 mL was scanned by spectrophotometer determines the optical transmission.

6. Titanium dioxide was dispersed in methanol and scanned to be found transparent.

RESULTS AND DISCUSSION

Determination of Maximum Wavelength

The absorption spectrum of Roselle anthocyanin dyes is shown in Figure 5. Data indicated that absorption maximum of methanol extract of Roselle anthocyanin was found at wavelength of 283 nm in the UV, and 545 nm in the VIS, in the UV/VIS wavelength range (300-800 nm). Data also showed that absorption maximum did not change over the pH values between 1 to 5. This result indicates that anthocyanins show that the Roselle flowers contain high content of anthocyanin dye. The absorption peaks in Figure 5 correspond to energy levels $= 4.36$ and $= 2.25$, respectively.

Effect of Heat Temperature

Roselle anthocyanin heating effect is studied by heating at 40, 60, 80, 100, and 120°C for holding times of 20, 40, and 60 min. The absorption of 0.2 g/10 mL solution of anthocyanin at different temperature at the maximum wavelength $\lambda_{\text{max}}$ 545 nm, or strictly speaking the wavelength of the absorption edge is recorded in Table 1 below.

Table 1: Relation Between Light Absorption and Temperature Heating Time 20, 40, and 60 Mins at $\lambda_{\text{max}}$ 545 nm

<table>
<thead>
<tr>
<th>Dyeing Temperature °C</th>
<th>Absorption wave length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dyeing time 20 min</td>
</tr>
<tr>
<td>40</td>
<td>1.644</td>
</tr>
<tr>
<td>60</td>
<td>1.210</td>
</tr>
<tr>
<td>80</td>
<td>1.048</td>
</tr>
<tr>
<td>100</td>
<td>0.977</td>
</tr>
<tr>
<td>120</td>
<td>1.530</td>
</tr>
</tbody>
</table>
Data showed that Roselle anthocyanins dye heated for 20 min at temperature of 40, 60, 80, 100, and 120 °C, retained 1.644, 1.210, 1.048, 0.977, and 0.530 a.u of their absorption respectively. As heating time was extended to 40 min, the retention of absorption retained to 1.448, 1.182, 0.776, 0.536, and 0.308 a.u, also heating time was extended to 60 min, the absorption retained to 1.362, 1.00, 0.313, 0.188, and 0.083 a.u, are presented in Table 1.

### Table 2: Relation Between Direct Light Absorption and Temperature 1 to 14 days at $\lambda_{\text{max}}$ 545 nm

<table>
<thead>
<tr>
<th>Days</th>
<th>Absorption (nm)</th>
<th>Days</th>
<th>Absorption (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.849</td>
<td>9</td>
<td>1.846</td>
</tr>
<tr>
<td>2</td>
<td>1.849</td>
<td>10</td>
<td>1.845</td>
</tr>
<tr>
<td>3</td>
<td>1.849</td>
<td>11</td>
<td>1.845</td>
</tr>
<tr>
<td>4</td>
<td>1.849</td>
<td>12</td>
<td>1.844</td>
</tr>
<tr>
<td>5</td>
<td>1.847</td>
<td>13</td>
<td>1.844</td>
</tr>
<tr>
<td>6</td>
<td>1.847</td>
<td>14</td>
<td>1.842</td>
</tr>
<tr>
<td>7</td>
<td>1.847</td>
<td>15</td>
<td>1.842</td>
</tr>
<tr>
<td>8</td>
<td>1.846</td>
<td>16</td>
<td>1.841</td>
</tr>
</tbody>
</table>

**Effect of Direct Sunlight**

Expose the sample to the direct sunlight for one, to 16 days. Dissolve 0.2 g / 10 mL and read the absorption of dye anthocyanins.

**The Optical Transmission**

The optical transmission of Roselle anthocyanins are presented in Figure 6. Were found to be transparent (nearly 100%) in the range after 600 nm. Also the optical transmission of the $\text{TiO}_2$ in
the UV/VIS wavelength range (300-1200) are presented in Figure 7, which was dispersed in methanol, in this case the transparent found (nearly 100%).

For roselle anthocyanin the transmission spectrum shows energy gap of $E_g(600)=2.06$ ev, while for TiO$_2$ the $E_g(299)=4.125$ ev.

**DISCUSSION**

The characteristic absorption spectrum of Roselle anthocyanins in Figure 5 has shown two peaks at 283 nm and 545 nm. This indicates that the electrons in this dye exits in energy levels not in energy bands. The effect of temperature on the absorption of anthocyanin as shown in Table 1, indicates that the absorption decreases as temperature increases above ambient temperature. This may be attributed to the fact that the increase of temperature increases in teratomic sapling, which decreases concentration which in turn decreases absorption.

The absorption of anthocyanin by direct sun light for 16 days, as shown in Table 2, shows constant absorption and high chemical stability.

The transmission spectrum of Roselle anthocyanins in Figure 6 indicates that all wavelengths beyond 600 nm are not transmitted, but absorbed completely. Since the visible light is in the range of 380 nm to 780 nm this means that most of the visible light are absorbed by the dye. Thus Roselle anthocyanin is a very suitable for Dye-Sensitized Solar Cells (DSSCs), as for as it is very efficient in absorbing visible sun light. The transmission wave length edge at 600 nm resembles the well known values. However, in contrast, TiO$_2$ solution spectrum in Figure 7 shows a very high transmission and very low absorption rate in the range 340 – 1200 nm, which covers the visible light spectral range. This indicates that is very transparent to light. It also confirms the fact that the energy gap is two wide to absorb light as indicated in the literature. The absorption beak for Roselle anthocyanins at 283 nm and 545 nm also agrees with the experimental value. It is very interesting to note that the energy gap for is which is near the real value. This value
is larger than that of Roselle anthocyanins thus Roselle anthocyanins make energy gap narrower.

**CONCLUSION**

The thermal properties of the Roselle anthocyanin dye indicates that its absorption property, i.e., the ability of atoms to trap visible photons, is stable and does not affected by temperature at ordinary ambient temperature. But at higher temperatures the absorption decreases. It shows also almost temperature absorption to direct sun light thus indicates high chemical stability. The optical property of the Roselle anthocyanin dye shows high efficiency to absorb visible light. This may have a direct impact on increasing the efficiency of the solar cell, as for as the function of the dye is to trap visible light.

**REFERENCES**
