

THE ABSORPTION SPECTRA OF NATURAL DYES AND THEIR SUITABILITY AS A SENSITISER IN ORGANIC SOLAR CELL APPLICATION

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Abstract

This paper analyzes the suitability of organic dyes (hibiscus, *Solanum nigrum*, beetroot and eggplant) that are locally available in East Africa for low-budget dye sensitized solar cells (DSSC). The natural dyes were extracted in different ways, where the nightshade berries and eggplant were simply crushed and sieved to obtain their juices, while for hibiscus and beetroot, the fruits was boiled in water and then ethanol. The most promising results are found from hibiscus extracted in water at 50°C, which exhibit a significantly better performance in U_{mpp} (311.35mV), I_{mpp} (236.43μA) and efficiency (0.43%). The results also show that *Solanum nigrum* is strong in terms of voltage but poor in terms of current, while Eggplant fails due to a difficult extraction process. Beetroot turns out to be a poor candidate since it contains betanin which does not chelate to the TiO₂ surface of the cell. The analysis of *Solanum nigrum* and hibiscus mixture shows that these mixtures do not lead to a better performance. It is also observed that the process of chelating to the TiO₂ shifts the absorption spectra of the dyes slightly towards lower wavelengths. The analysis of the molecular structures of betanin and certain anthocyanins shows the number of =O and -OH groups relative to the total number of atoms per molecule is higher for most anthocyanins, so that they can connect better to TiO₂ than betanin.

Key words: Dye-sensitised solar cells, hibiscus, *Solanum nigrum*, beetroot, egg-plant, complex dye- molecules

1.0 Introduction

The dye-sensitized solar cell (DSSC) is one of the photochemical electric cells which consists of the photoelectrode, the dye, the electrolyte, and the counter electrode. The most speciality of the DSSC relative to the other types of solar cells is the use of the dye. The DSSC is used in the conversion of visible light into electricity, based on the sensitization of wide bandgap semiconductors (Grätzel, 2003). The performance of the cell mainly depends on a dye used as sensitizer. The cell's efficiency is determined by the absorption spectrum of the dye and the anchorage of the dye to the surface of TiO₂.

The DSSC (also referred to as Grätzel Cell), was invented by Grätzel and O'Regan (1991) but was not explored sufficiently for a long time. Recently, most of the researchers in this field have used ruthenium complex as dye in the dye-sensitized solar cells. For example, Nobuko *et al.*, (2011) have investigated the near-IR dye-sensitized solar cells using a new type of ruthenium complexes having 2,6-bis(quinolin-2-yl)pyridine derivatives, while Takashi *et al.*, (2009) analyzed ruthenium (II) complexes with π expanded ligand having phenylene-ethynylene moiety as sensitizers for dye-sensitized solar cells. Generally, transition metal coordination compounds (ruthenium polypyridyl complexes) are used as the effective sensitizers, due to their intense charge-transfer absorption in the whole visible range and highly efficient metal-to-ligand charge transfer (Hao *et al.*, 2006). However, ruthenium polypyridyl complexes contain a heavy metal, which is not environmentally benign (Amao and Komori, 2004), and the process to synthesize the complexes is complicated. Also, Ruthenium is a rare metal, so the cost of the ruthenium complex is very high.

Therefore, investigation of low cost, readily available dyes as efficient sensitizers for DSCs still remains a scientific challenge. In this context, application of naturally occurring dyes for DSCs has several advantages such as being readily available, easy extraction into cheap organic solvents, can be applied without further purification, is environment-friendly and considerably reduces the cost of the devices. Numerous efforts have been done by several research groups all over the world to utilize these natural dyes as sensitizers in these devices (Hao *et al.*, 2006; Amao and Komori, 2004; Polo and Iha, 2006; Garcia *et al.*, 2003; Kumara *et al.*, 2006). For example, Shoji *et al.* (2009) have reported on the characteristics of dye-sensitized solar cells using various natural dyes such as the dye of red-cabbage, curcumin, and red-perilla, with an efficiency of about 0.6%. Chang and Lo, (2010) have investigated pomegranate leaves and mulberry fruit as natural sensitizers for dye-sensitized solar cells and found conversion efficiency of the anthocyanin dye from mulberry to be 0.548%, and 0.722% for chlorophyll and anthocyanin as the dye mixture.

The anthocyanins belong to the group of natural dyes responsible for several colors in the red–blue range, found in fruits, flowers and leaves of plants.

Carbonyl and hydroxyl groups present in the anthocyanin molecule can be bound to the surface of a porous TiO₂ film. This makes electron transfer from the anthocyanin molecule to the conduction band of TiO₂ possible (Hao *et al.*, 2006). It has been reported that although several fruits and leaves contain anthocyanins, their extracts may not chelate to the TiO₂ surface (Smestad and Gratzel, 1998). These pigments are not suitable for the dye-sensitized cell. Also, anthocyanins from various plants gave different sensitizing performances (Takashi *et al.*, 2009; Hao *et al.*, 2006; Amao and Komori, 2004; Polo and Iha, 2006; Garcia *et al.*, 2003; Kumara *et al.*, 2006). A requirement for the dye structure is that it possess several =O or -OH groups capable of chelating on the Ti sites on the TiO₂ surface.

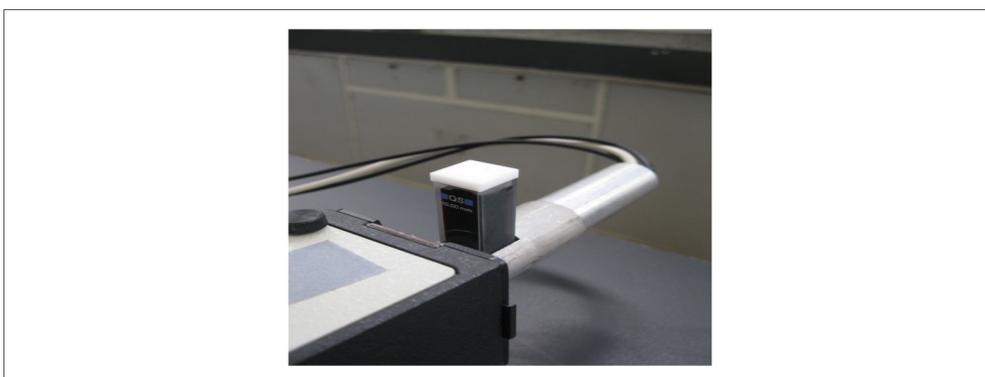
Since some natural dyes are readily available, it is imperative the more research is done in this area with the view of not only improving efficiency but also reducing the production cost. In this work, the absorption spectra of some natural dyes that are locally available in East Africa (hibiscus, *Solanum nigrum*, beetroot and eggplant) and their mixtures are analyzed for the use in a dye-sensitized solar cell. Suitable dyes are assembled into dye-sensitized solar cell and electrical properties characterized.

2.0 Experimental Details

The juices from the considered natural dyes were extracted in different ways (methods). The nightshade berries and eggplant were simply crushed and sieved to obtain their juices. For hibiscus and beetroot, the dried (hibiscus) or fresh (beetroot) fruit was boiled in water and then ethanol. Hibiscus was also extracted at temperature of 50°C. The dye was placed inside a cuvette and plugged into the cuvette holder in front of the photo diode (see Figure 1). A halogen lamp was used as a light source. The diode and cuvette holder were set up behind the monochromator to register the intensity of the light transmitted. To capture the signal of the diode, a voltmeter was used. The Qti-plot1 software was used for plotting the diagrams. Object of interest was the spectral range within wavelengths between 300 nm and 820 nm. After analyzing the single components, hibiscus and *Solanum nigrum* were mixed and analysed as well to test if the different dyes can complement one another. Also the difference in absorption between the pure dye and the dye absorbed by TiO₂ was analysed. Afterwards, the two best candidates (hibiscus and *Solanum nigrum*) were used as sensitizers in the cell.



The monochromator



Cuvette in cuvette holder

Figure 1: Experimental setting for measuring the dye's transmission spectrum

The instructions for preparing the cell are close to those given by Smestad and Gratzel (1998). The TiO_2 is covered by the counter electrode and a 4 mm strip of glass not coated by TiO_2 is exposed. The two exposed sides of the device are the contact points for the negative and positive electrodes, so that electricity can be extracted to test the cell. Two binder clips are used to hold the plates together loosely at the other edges as shown in Figure 2. One or two drops of the electrolyte solution have to be placed at the edges of the plates and the two binder clips are alternately opened and closed while in place. The liquid is drawn into the space between the electrodes by capillary action, and can be seen to wet the stained TiO_2 film. For a better long-life performance, a plastic UV-filter can be placed over the cell, since too much UV light will damage the organic dyes. But since the focus of this work was the analysis of the dyes, experiments with an additional UV-filter were not considered.

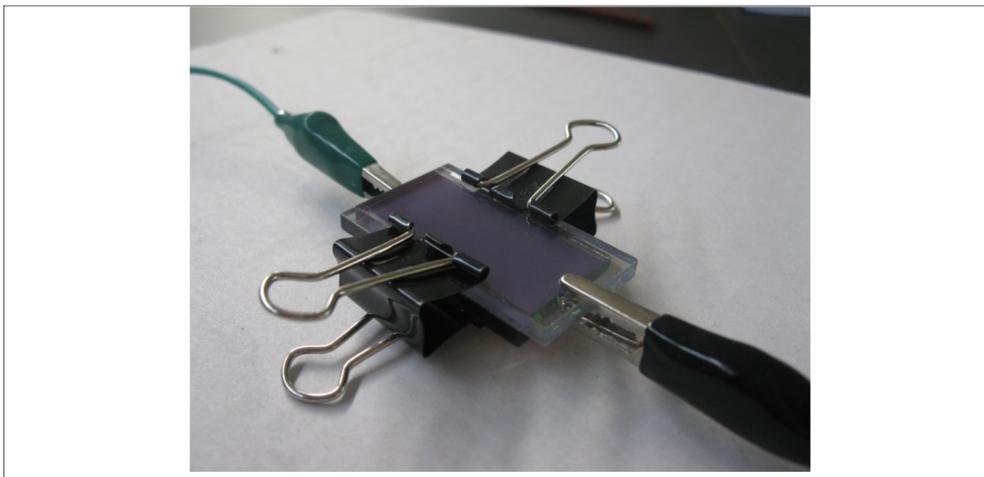


Figure 2: Assembled dye sensitised solar cell

3.0 Results and Discussions

3.1 Absorption Properties

The intensity of the transmitted light (I_t) was measured in terms of the wavelength (λ). Without the dye from the setting, the intensity of the light without absorption (I_i) can be obtained from the equation;

$$T(\lambda) = I_t(\lambda) / I_i(\lambda) \dots\dots\dots(1)$$

which describes the transmission. The Beer-Lambert-Law relates the intensity of the transmitted light with the concentration and the length of the light path through the solution:

$$I_t = I_i \times e^{-\epsilon_n k d} = I_i \times 10^{-\epsilon k d} \dots\dots\dots(2)$$

where ϵ_n is the absorption coefficient, ϵ is the extinction coefficient, k is the concentration and d is the length of the light path through the solution. At a closer look, equation (2) can be written as;

$$-\ln\left(\frac{I_t}{I_i}\right) \propto \epsilon_n k \dots\dots\dots(3)$$

Since the path length d is the same for all dyes, it is therefore considered as a constant. Therefore, the absorption can be obtained from;

$$\alpha(\lambda) = -\ln\left(\frac{I_T(\lambda)}{I_i(\lambda)}\right) \dots\dots\dots(4)$$

which describes the absorption in terms of the wavelength.

From the Fresnel equation, the reflection R at each interface is given by the equation;

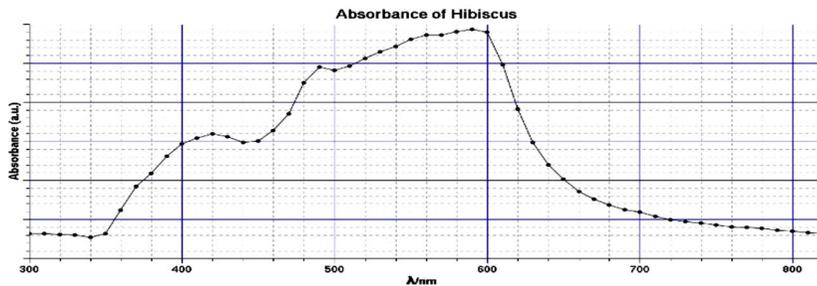
$$R = \left(\frac{n-1}{n+1} \right) \dots \dots \dots (5)$$

where $n = n_2/n_1$ is the ratio of the refractive indices of the two media, provided that the light beam is perpendicular to the interface. In our case, four such interfaces: air-cuvette, cuvette-dye, dye-cuvette and cuvette-air are seen. The air-cuvette and cuvette-air interfaces do not present a problem, since it is the same interface having light coming in from opposite directions. But the cuvette-dye and dye-cuvette could influence the values, especially if the refractive indices of the dyes were very different. In this case, the differences were very small and therefore the reflection was considered negligible too, so that $\alpha(\lambda)$ gives a good curve of absorption.

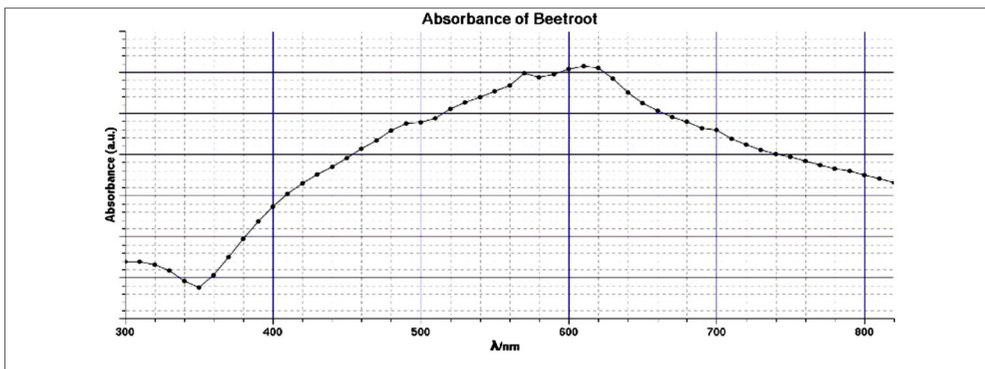
Figure 3 shows the absorbance of different natural dyes investigated. The absorption spectrum of hibiscus dye extracted at 100°C can be seen with peaks in the blue-violet range between 400 nm and 600 nm (Figure 3a). This explains the red colour of the extract. Hibiscus is seen to chelate extremely well to the TiO₂ surface. After a short time in the dye bath (just a few minutes) the TiO₂ surface was strongly coloured. Beetroot was chosen because of its strong colour. Its absorption spectrum (Figure 3b) compares well with that of hibiscus but problems occurred when building the cell. After exposing the TiO₂-coated glass slide to the dye, it was noticed that the dye could not be absorbed by the TiO₂. Smestad and Gratzel (1998), have reported that although several fruits and leaves may contain anthocyanins, their extracts may not chelate to the TiO₂ surface due to the dye structure not possessing several =O or -OH groups capable of chelating on the Ti sites on the TiO₂ surface. Indeed, this might explain the disappearance peaks observed in Figure 3a.

The absorption spectrum of *Solanum nigrum* can be seen in figure 3c. Just like in Hibiscus, it peaks in the blue-violet range between 400 nm and about 700 nm. It was also seen to chelates well to TiO₂ surface. For Eggplant, the spectrum is extremely close to that of beetroot. The main absorption is around 540 nm and 640 nm. This is close to what was reported by Lin *et al.*, (2007). The main problem with eggplant was the difficulty in the extraction of the dye.

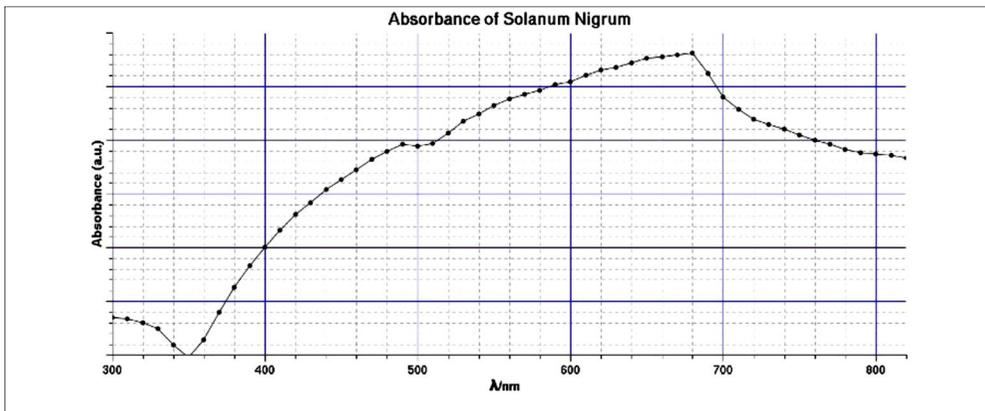




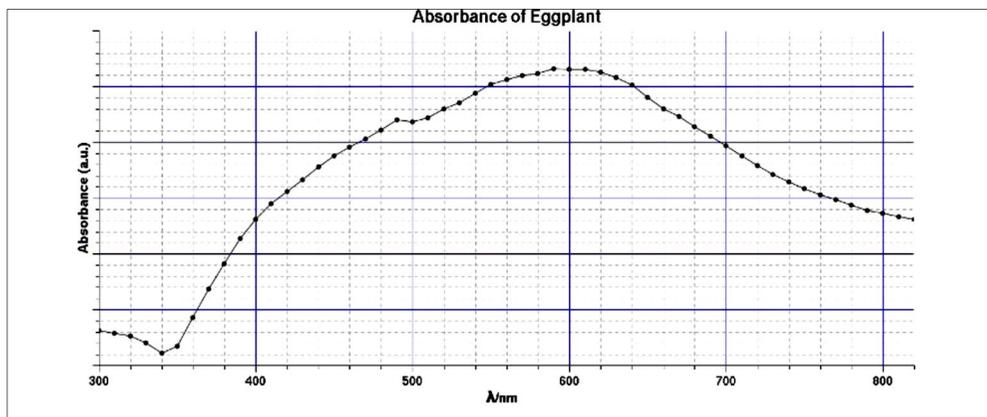
(a)



(b)



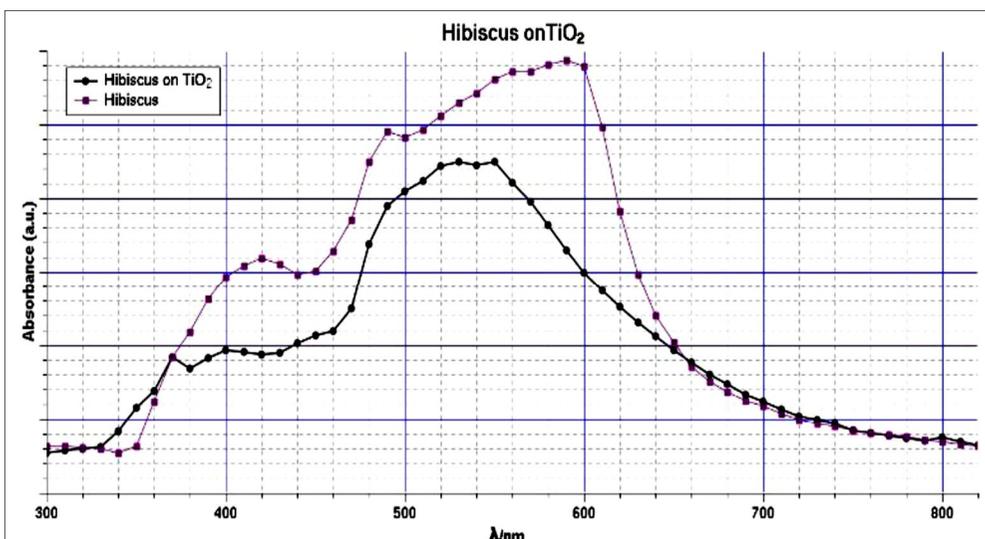
(c)



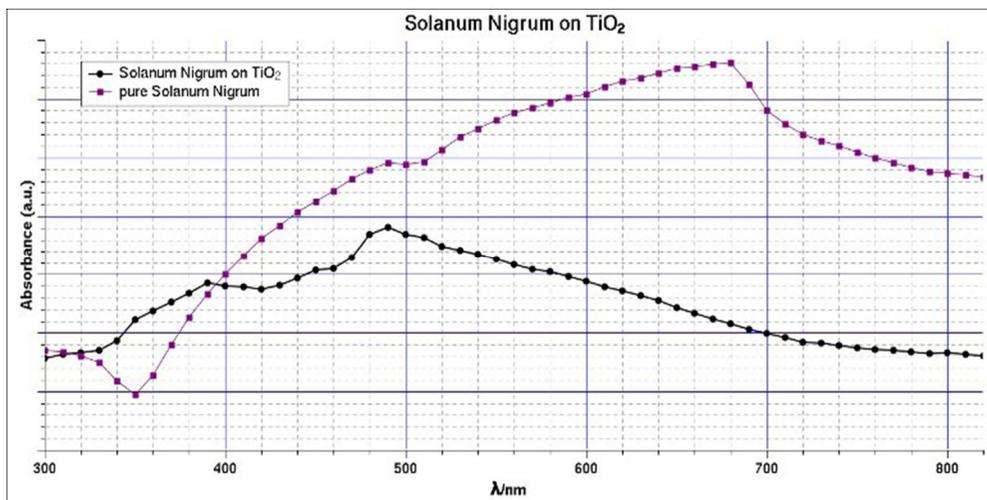
(d)

Figure 3: Absorption spectrum of dyes extracted from (a) hibiscus, (b) beetroot, (c) *Solanum nigrum*, (d) eggplant peeling.

Due to the difficulties seen with beetroot and eggplant peeling, they were not considered for further analysis. Figure 4 shows the absorption spectrum for hibiscus and *Solanum nigrum* chelated to the TiO_2 surface.



(a)



(b)

Figure 4: Absorption spectrum of hibiscus and *Solanum nigrum* chelated to the TiO_2 surface.

By comparing the absorption spectra of hibiscus and *Solanum nigrum* after chelating to the TiO_2 , some similarities are observed. In both cases the peaks of the spectra are shifted slightly towards shorter wavelengths. While the strongest peak for pure hibiscus lies between 540 nm and 600 nm, the chelated hibiscus has its strong peak between 490 nm and 560 nm. For *Solanum nigrum* the difference is even stronger. The peak shifts from around 680 nm for pure *Solanum nigrum* to around 490 nm after chelating to TiO_2 . The shift to lower wavelengths observed here can be attributed to the change in energy levels. Generally, the chemical attachment affects the energy levels of the highest occupied molecular level and the lowest unoccupied molecular level of these pigments, which eventually affects the band gap of the materials and a shift in the absorption peak of the absorption spectra. It is noted that the TiO_2 seems to have a structural influence on the absorption behaviour. This is noted when analyzing a pure dye's spectrum with regard to suitability for DSSC application.

In experiments with beetroot, it was found that the dye is not able to chelate to TiO_2 . Although the beetroot juice gave a nice absorption spectrum it did not turn out to be a good sensitizer. This was established as due to the fact that Beetroot contains betanin which does not chelate to the TiO_2 -surface of the cell (Siegel and Daly, 1966). Even though betanin also shows =O and -OH groups, they seem to be too few for its complex molecule structure. This might give an answer to the question, why certain anthocyanins chelate so well to TiO_2 , while betanin does not. The absorption spectrum of hibiscus dye extracted in water at 50°C, and in ethanol was analyzed too. The extraction temperature in ethanol had to be changed to 78°C, due to the different boiling point of ethanol. The results are shown in Figure

5. It can be seen that the spectrum is almost similar, but the values for hibiscus at 50°C are generally lower than the one for 100°C. This can be explained by the fact that at 100°C a higher dye concentration was obtained as compared to 50°C. Dye extracts using ethanol gave the lowest absorbance. This is contrary to other reports where its shown that anthocyanin is more soluble in ethanol than water (Lapornik *et al.*, 2005). This poor absorbance observed here might be due to photocatalytic decomposition of anthocyanin by TiO₂. Similar photocatalytic decomposition of anthocyanin have been reported for rosella ethanol extract (Wongcharee *et al.*, 2007). Therefore, ethanol was found to unsuitable as an anthocyanin extracting solvent for DSSC application.

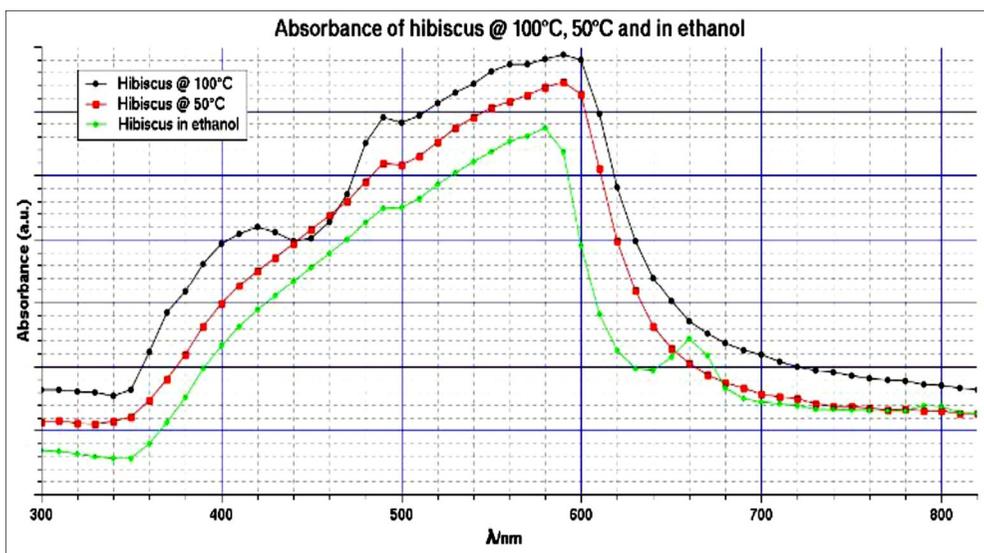
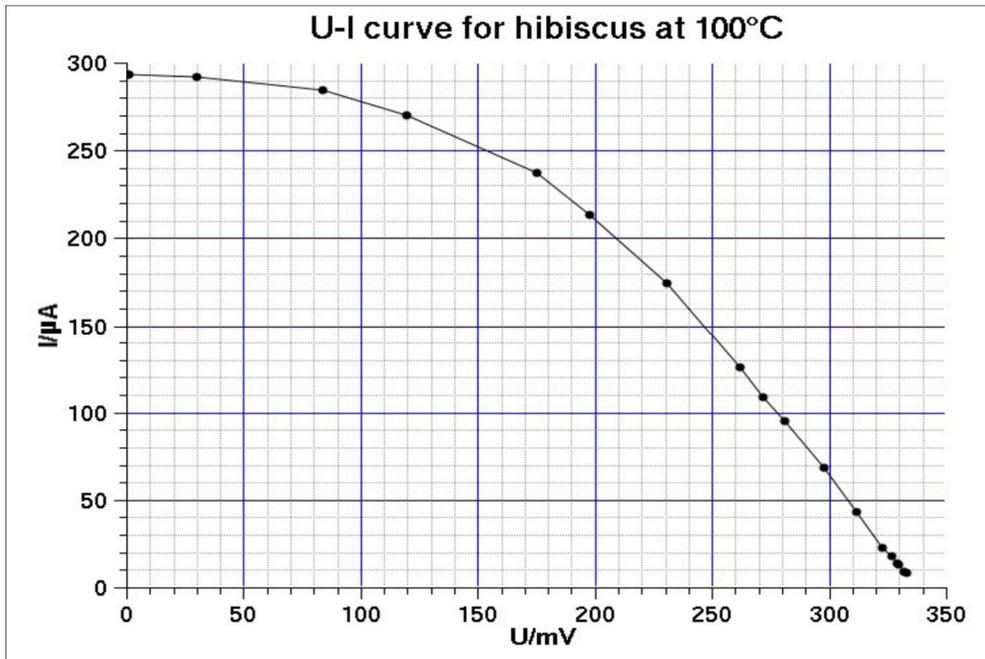


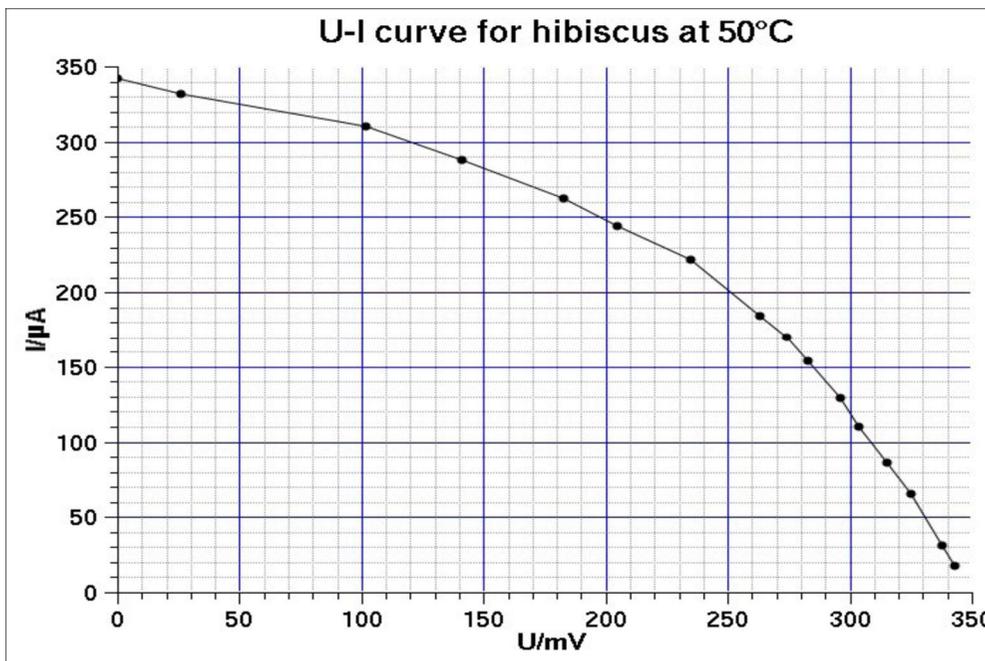
Figure 5: Absorption spectrum of hibiscus, extracted at different temperatures in water and in ethanol.

3.2 Electrical Properties

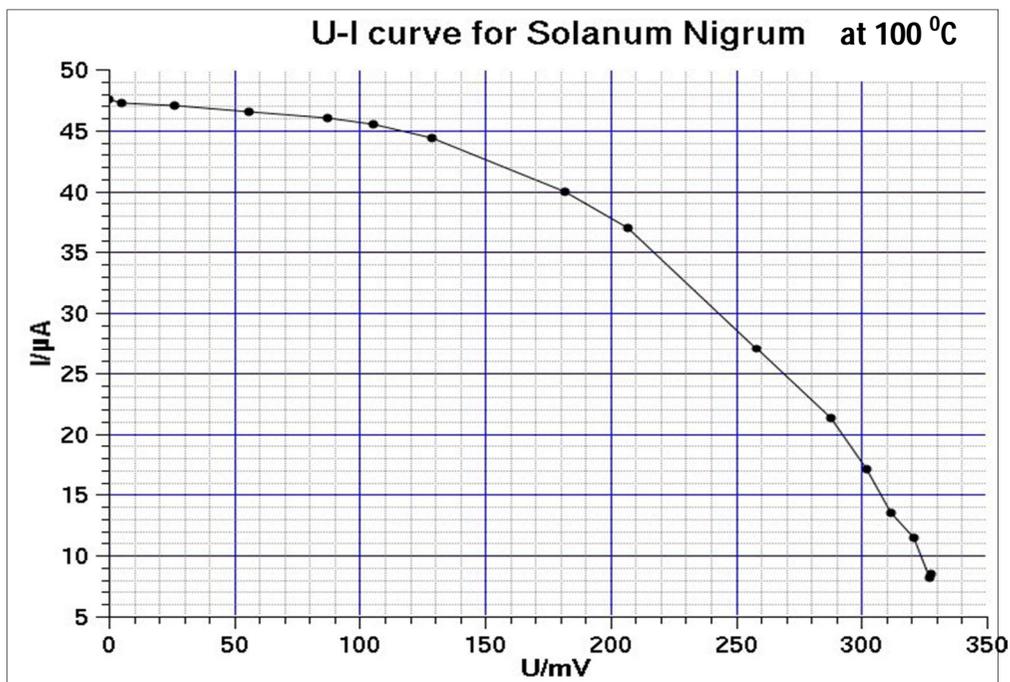
The DSSC of Hibiscus, *Solanum nigrum* and their mixtures were built and electrical properties analyzed. The resulting voltage-current (U-I) curves for the obtained DSSC are shown in Figure 6 and these results are summarized in Table 1.



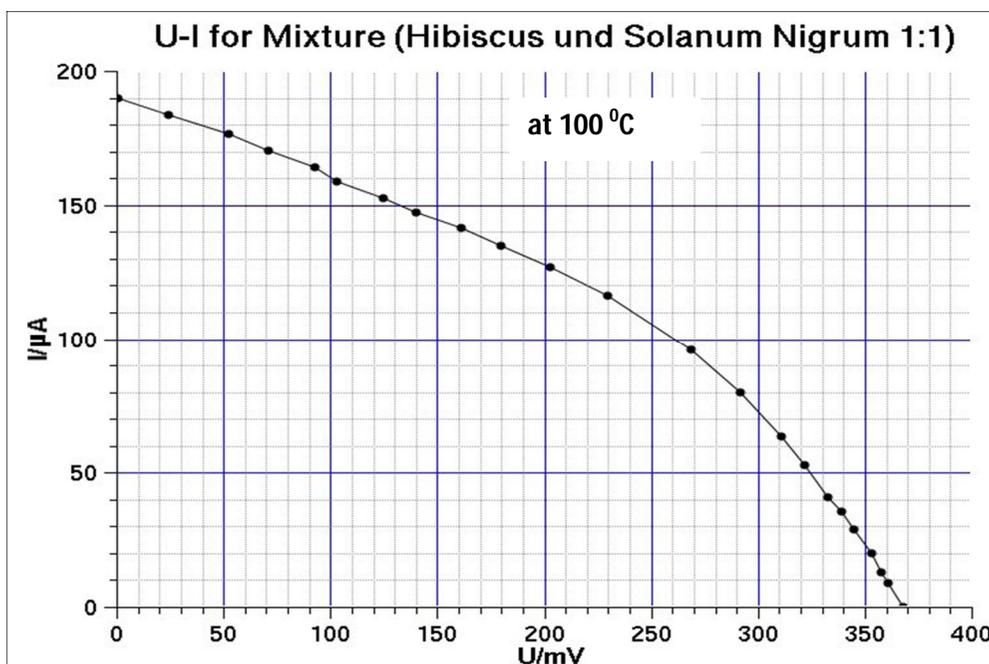
(a)



(b)



(c)



(d)

Figure 6: U-I-curve of a DSSC with hibiscus, solanum nigrum and hibiscus-solanum nigrum mixture.

Table 1: Electrical properties of Hibiscus, Solanum Nigrum and Hibiscus-Solanum nigrum mixture

Dye	U_{oc} (mV)	I_{sc} (μ A)	U_{mpp} (mV)	I_{mpp} (μ A)	η (%)
Hibiscus at 50°C	349.03	343.10	311.35	236.43	0.43
Hibiscus at 100°C	339.02	294.01	208.05	210.41	0.26
Solanum Nigrum	331.02	47.80	216.61	34.70	0.04
Hibiscus/Solanum Nigrum mixture	368.03	190.10	214.05	118.31	0.15

From these results, it can be seen that the Hibiscus extracted at 50°C has the highest conversion efficiency. The absorption spectrum shifted a little bit towards shorter wavelengths after chelating to TiO₂ (Figure 5). The most probable explanation for this behaviour is that high temperatures destroy the complex molecule structure of the organic dye and therefore lead to lower efficiency. Indeed, this shows how sensitive organic materials are and underlines the importance of dye protection (heat control, UV-filtering, etc). Wongcharee *et al.*, (2007), have reported similar results where an extraction of anthocyanin from rosella above 50°C results in decreasing in the DSSC efficiency. They also attributed this to a decrease in the stability of anthocyanin at elevated temperature. At high temperature, the thermal degradation of anthocyanin could be caused by a loss of glycosyl moieties and α -diketone formation (Rubinskiene *et al.*, 2005; Adams, 1973). At lower temperatures below 50°C, anthocyanin extracted gave even lower DSSC efficiency than that extracted at 100°C (Wongcharee *et al.*, 2007). The optimum extracting temperature was found at 50°C which is in between room temperature and boiling point of water which was performed in the literature (Hao *et al.*, 2006; Polo and Iha, 2006; Garcia *et al.*, 2003).

Generally, although the efficiency for the obtained DSSC is much lower than that for silicon based cells, it compares well with other reports in the field. For example, Wongcharee *et al.*, (2007) obtained efficiencies between 0.05% and 0.37% for DSSC using natural dyes extracted from rosella and blue pea flowers as sensitizers, while Baxter *et al.*, (2005) have reported an efficiency of 0.5% on ZnO nanowire-based dye-sensitized solar cell. One reason why the efficiencies obtain in this paper are slightly lower might be due to the use of a halogen lamp light instead of a sun simulator. Even though it might not be very obvious, there is a huge difference. In fact, the cells assembled in this paper might give much higher values when they are tested with a sun simulator instead of the halogen lamp. That can be understood more easily after analyzing the differences in the spectra of the lamp and the sun. The reddish colour of hibiscus as well as the absorption spectrum in figure 3(a) suggests that the hibiscus-DSSC is most efficient in the blue and green spectrum (400 nm to 600 nm). For the sunlight that is pretty good

because it has a peak at around 600 nm. Therefore, the efficiency is expected to be comparatively high. For the halogen lamp the situation is a little bit different. Figure 7 shows the spectrum of the lamp used in this study. It can be seen that the peak is at around 800 nm and the intensity between 400 nm and 600 nm is very low. That is why the lamp emits most of its power as light in the red spectrum, where the conversion of the DSSC is lower. So the total conversion efficiency is much lower than the one for sun light.

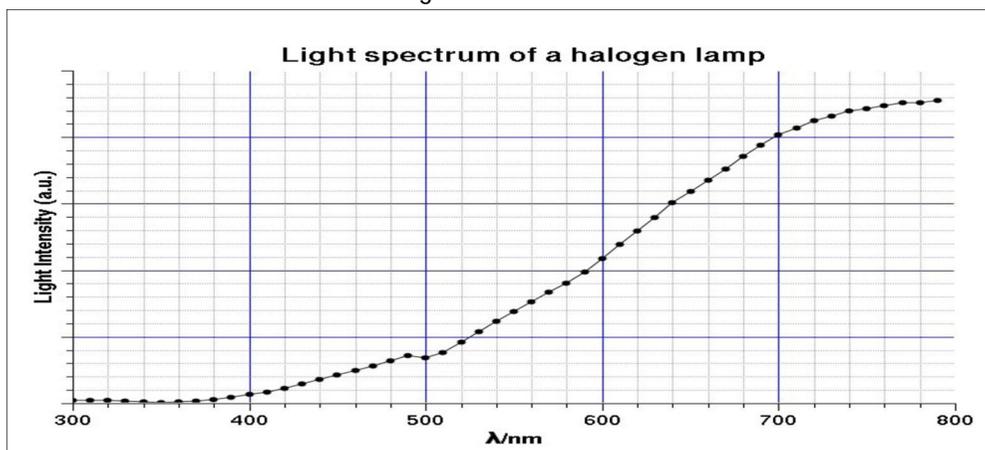


Figure 7: Light spectrum of the halogen lamp

4.0 Conclusions

The measurements and analysis of the absorption spectra for locally available natural dyes extracted from hibiscus, *Solanum nigrum*, beetroot and eggplant are carried out. The results show that the dye extracted from the Hibiscus shows good performance, while *Solanum nigrum* is strong in terms of voltage but poor in terms of current. The DSSC using the hibiscus extracted at 50°C has the best photoelectric conversion efficiency of 0.43%. This result was associated with the sensitivity of the complex organic dye molecules used and how easily they can be destroyed. It is also found that the process of chelating to the TiO₂ shifts the absorption spectra of the dyes slightly towards lower wavelengths. This is attributed to the chemical attachment affecting the energy levels of the highest occupied molecular level and the lowest unoccupied molecular level of these pigments, eventually affecting the band gap of the material and shifting the absorption peak of the absorption spectra. The mixing of *Solanum nigrum* and hibiscus did not lead to a better performance of the obtained DSSC, while the extracts from the Egg-plant fails due to a difficult extraction process, and beetroot turns out to be a poor candidate since it contains betanin which does not chelate to the TiO₂-surface of the cell. From above results, it is imperative that further research work is needed not only on these dyes but many more locally available natural dyes to evaluate their performance for DSSC.

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