Journal of Energy Research and Environmental Technology (JERET)
Print ISSN: 2394-1561; Online ISSN: 2394-157X; Volume 2, Number 4; April-June, 2015; pp. 324-327

http://www.krishisanskriti.org/jeret.html

Extraction and Characterization of Novel Dyes from Plant Sources for Dye Sensitized Solar Cells

Vipinraj Sugathan[1], Elsa John[2] and K. Sudhakar[3]

[1,2,3]Energy Centre, MANIT
E-mail: [1]vipinraj11889@gmail.com, [2]john.elsa91@gmail.com, [3]nittsudhakar@gmail.com

Abstract—*The Dye-sensitized Solar Cell (DSSC) is a cell that involves photo-electrochemical process of conversion of incident photon energy to electrical energy. It functions similar to a plant cell, involved in photosynthesis. The role of conversion of incident photon energy to electron flow is played by the Dyes used in the fabrication process of the DSSC. The light harvesting efficiency of the Dye should be improved, for an ideal cell with maximum efficiency. This paper concentrates on synthesis of novel dyes from natural plant sources, their characterization and study to decide on the most compatible dye for a typical DSSC. Four new dyes were extracted from plant sources- flowers of Thevetia Peruviana, Acalypha Hispida, and Celasia Cristata, and leaves of Acalypha Wilkesiana. The extracted dyes were studied using visible spectro-photometer. The absorbance, transmittance and concentration were observed. The paper consists of the comparative analysis of the characteristics obtained for the different dyes. The degradation of the dye properties, over time was also studied.*

Keywords*: Dye Sensitized Solar Cell, Absorbance, Concentration, Transmittance, Organic dyes, visible spectro-photometer, Degradation Study.*

1. INTRODUCTION

1.1 Dye Sensitized Solar Cell

The Dye Sensitized Solar Cell (DSSC) came into light from the work done by O'Regan and Gra¨tzel as applications of nano-sized TiO2 porous film electrodes in Dye Sensitized Solar Cells (DSSCs) [1]. The basic components of DSSC are photoanode, sensitizer, electrolyte, and counter electrode. Nano structured semiconductors are employed in fabrication of the DSSC. A number of developments have been seen in the DSSCs over the years. New sensitizers have been developed using various compounds. Experiments have been carried out with a number of metal-free organic photosensitizes for DSSCs [2]. Few dyes used for fabrication are, Coumarin [3], indoline [4], merocyanine [5] and hemicyanine [6], showing sizeable photovoltaic performance. Organic Dyes seize several advantages over the ruthenium-based sensitizers. They are lower cost, can be produced on a large-scale, environment friendly and less toxic and have high molar extinction coefficients [7], [8], [9], [10] and [11].In this paper we present novel dyes extracted from commonly found flowers and leaves. The characterization and graphical comparisons of the performances of different dyes has been included. The peak values obtained for absorbance have been highlighted and the degradation in properties of the Dyes with time has also been analyzed. Some basic terms are to be familiarized before getting into the details of the work.

1.2 Absorbance and Transmittance

As light passes through, atoms or molecules take up a fraction of the energy from the photon, this event is called absorption. The amount of energy absorbed is denoted by the term absorbance (A). This reduces the transmission of light as it is passed through a sample. Light looses energy exponentially as it passes through clear materials or solutions [12].Transmission is the term used to describe the process by which, incident radiant flux leaves a surface or medium from a side other than the incident side, more often than not the opposite side [12].In a measurement system, the transmittance is simply the fraction of light in the original beam that passes through the sample and reaches the detector. This fraction can be termed as 'T'. The remnants of the light, i.e. 1 - T, are the fraction of the light that gets absorbed by atoms or molecules in the sample.

1.3 Beer's Law

In many applications the concentration of the light absorbing molecule is required. The absorbance varies linearly with both the cell path length (l) and the analyte concentration (c). These two relationships can be pooled to get a general equation called Beer's Law [13].

$$A = \varepsilon l c$$

'ε' here denotes the molar absorptivity; also called the extinction coefficient. The molar absorptivity varies with the wavelength of light used in the measurement. This forms the basis of all Spectral Analysis [14] [15].

1.4 Spectrophotometer

An absorbance spectrophotometer measures, the fraction of the incident light transmitted through a solution. In principle it measures the difference between the amount of light falling on a sample and the amount of light leaving from the sample [12].

The procedure for the measurement is as follows.

- First, the light intensity (I_0) passing through a blank is measured. The intensity is the number of photons per second. The blank is a reference solution, usually distilled water that does not contain the solute that absorbs light. This measurement helps in neutralizing the effect of the instrumental environment and other factors that affect the absorbance.
- The intensity of light (I) passing through the sample solution is measured.
- Then the experimental data is used to calculate the transmittance (T) and the absorbance (A).

$$T = \frac{I}{I_0}$$

$$A = \log_{10} T$$

If no light is absorbed, the absorbance is zero (100% transmittance). Each unit in absorbance corresponds with an order of magnitude in the fraction of light transmitted. For A = 1, 10% of the light is transmitted (T = 0.10) and 90% is absorbed by the sample. For A = 2, 1% of the light is transmitted and 99% is absorbed. For A = 3, 0.1% of the light is transmitted and 99.9% is absorbed.

Here we measure the different parameters- Absorbance, transmittance and concentration, using the visible spectro-photometer.

1.5 Sources of Dye

The experimental procedure begins with, extraction of dyes from various natural sources. It is necessary to know the potential sources of dyes before starting with the extraction process. Dye can be extracted from any part of the plant. To check the capability of a plant portion to yield dyes, a simple check by crushing it can be conducted. If on crushing, colors are obtained then it can be a good dye source.

2. METHODOLOGY

2.1 Experimental Procedure

The experimental procedure involved Dye extraction, Synthesis and characterization. The natural sources of dyes like Thevetia Peruviana, Acalypha Hispida, and Celasia Cristata, and leaves of Acalypha Wilkesiana were used as raw materials. The choice of these flowers was made based on abundance and easy availability. The dye extracted from these sources was mixed to obtain different combinations and the characteristics were studied.

2.2 Dye Extraction

The dye extraction was done using simple alkaline method of extraction. The method involved Boiling of Dye-stuff in 1% alkaline solution with addition of 1g sodium carbonate in 100 ml of soft water, at 10000 C and Filtering the obtained dye. A magnetic stirrer was used for this purpose. The extracted dyes were filled in glass jars and kept for inspection, and were coded as TP, AH, CC and AW respectively.

2.3 Dye Characterization

Once the synthesis of dyes and coding was done, the characteristics could be easily studied and so the dyes were inserted into the cuvettes of the visible spectrophotometer. The absorbance and transmittance values were noted down for a range of wavelengths from 320nm to 720nm basically concentrating in the visible range.

3. RESULTS AND DISCUSSIONS

The spectrophotometer gave the absorbance, transmittance and concentration values for the dyes. The values were tabulated as shown below. The absorbance is considered to be the most important parameter here as the transmittance and concentrations are dependent on it.

3.1 Spectro-photometric analysis of dyes

Data was collected using the visible spectro-photo meter. The data was obtained in November 2014. The absorbance and transmittance value obtained have been summarized in the following tables. Table 1 shows the absorbance, transmittance and concentration values of the dye obtained from TP. It can be observed that the absorbance of TP is fairly good over certain range of wavelengths in the visible region, but not consistent in the visible region.

Insert Table 1

Insert Table 2

Table 2 shows the characteristics of the dye obtained from AH and table 3 showed the characteristic of the dye obtained from CC. AH shows very good magnitude of absorbance in the visible region and also has consistent performance over the entire range of visible region. CC shows good absorbance initially but its absorbance falls as the wavelength decreases.

Insert Table 3

Table 4 shows the absorbance, transmittance and concentration of AW Dye. AW shows good amplitude of absorbance in the mid visible region, but not very good in the high wavelength region.

Insert Table 4

3.2 Comparative analysis of dyes characteristics

To study the variations in absorbance and transmittance properties of the different dyes and their combinations, a comparative plot was made for the absorbance as well as the transmittance parameters. Figure 1 shows the comparative plot of the absorbance of the different dyes, while Figure 2 shows the transmittance of the different dyes. It can be seen from figure 1, that the AH has a consistent absorbance in the visible range as compared to the other three dyes. CC and TP show a similar trend in absorbance variations, and are potentially less useful in the DSSC as they show good absorbance only in the low wavelength region. AW is seen to show good absorbance in the mid visible wavelength range, which is a good sign as per applications in DSSC. The magnitude of absorbance of the dyes and the wavelength range for which they give substantial absorbance is very important. Based on the parameters the feasibility of a dye for use as sensitizers in DSSC can be predicted.

Insert Figure 1

As seen from figure 2, the percentage transmittance of TP and CC is high in the high wavelength region. AH is found to have low transmittance in almost all the wavelengths in the visible region. AW shows high transmittance as the wavelength of light is near the high end of the visible region.

Insert Figure 2

Insert Figure 3

Figure 3 shows the comparative concentration values of the dyes. It can be seen that the graph follows a similar trend as that of the absorption graph. It is followed by the fact that concentration is directly proportional to the absorbance of the dyes.

3.3 Absorbance Peak

For practical applications of the dye in DSSC it is necessary to know the peak values of absorbance and the corresponding wavelengths. The values have been summarized in the following tables 5 shows the peak values for TP, table 6 shows the peak values for AH, the peak values CC, and AW is shown in table 7 and 8 respectively.

Insert Table 5

Insert Table 6

Insert Table 7

Insert Table 8

The peak absorbance for AH is 2.11 obtained around 620nm wavelength of light. Though the magnitude of absorbance is fairly good the peak being near to the higher end of visible region can be a hindrance for its use in the DSSC. AW has a peak absorbance of 2.024 at 500nm wavelength which makes it more potentially feasible for DSSC. TP has a peak value of 1.916 at 400nm wavelength and Celasia Cristata, 1.92 at 320 nm wavelength. The latter two do not show much promise as compared to AH and AW as not only their magnitude of absorbance is less but also the wavelength range is a matter of worry.

3.4 Absorbance property Degradation Analysis

The Dyes extracted from these natural sources may face the demerit of property degradation over the time. In order to comment on the feasibility of these dyes for application in DSSC, study of the degradation in the absorbance property was done by taking another set of readings in February 2015. The data obtained is shown in the following tables.

Table 9 shows the characteristics obtained for TP, the data shows slight improvement in the absorbance at the smaller wavelengths of light.

Insert Table 9

Table 10 shows the characteristics obtained for AH, the data shows improvement in the absorbance with time, which is a positive sign and can make AH potentially suitable for DSSCs.

Insert Table 10

Table 11 shows the characteristics obtained for CC; the data shows that there is significant degradation in the dye absorbance properties.

Insert Table 11

Table 12 shows the characteristics obtained for AW, the data shows degradation in the high wavelength region, but does not show any significant change in the absorbance at the mid wavelength region.

Insert Table 12

Figure 5 shows the absorbance variations in the dyes with respect to wavelength as in February 2015. The graph shows almost the same trend as shown by the dyes in November 2014, except some changes in the magnitudes. The magnitude of absorbance for CC shows significant degradation in the mid wavelength region. AH shows improvement in the absorbance in almost the entire visible range. AW shows significant degradation in the high wavelength region. TP does not show much change in its absorbance parameters, except for slight improvements in the small wavelengths of light.

Insert Figure 4

Figure 5 shows the transmittance variations with wavelength. The variations in the absorbance are reflected here too. The transmittance seems to vary for the dyes inversely as to the variations in absorbance.

Insert Figure 5

Figure 6 shows the concentration variations which follow a similar trend of that of the absorbance, further validating the linear relationship between absorbance and concentration.

Insert Figure 6

3.5 Degradation Analysis

The Area Graph shown in figure 7 depicts the variation in the degradation of dye absorbance properties at different wavelengths of light. Here negative degradation indicates an improvement in the absorbance properties exhibited by the dyes.

Insert Figure 7

Insert Figure 8

Figure 8 shows the bar chart of the degradation values, for better understanding the variations with respect to different wavelengths of light.

It can be seen that AH shows degradation in absorbance only for a few wavelengths of light, while AW shows significant degradation for large wavelengths. AH has shown improvement for most of the wavelengths. CC shows significantly high degradation in mid wavelength only while TP shows very less variations.

The dyes obtained can be used as the sensitizer in DSSC fabrication. From the results it can be inferred that Acalypha Wilkesiana and Acalypha Hispida can be used to extract dyes that can give better results as compared to the other plant materials. This also opens scope for a research on the Acalypha family of plants for better dyes to enhance the efficiency of DSSCs.

4. CONCLUSION

The Acalypha Hispida produced a dye that had the maximum range of good absorbance in the visible region. The magnitude of absorbance was 2.11. Acalypha Wilkesiana has less absorbance range and magnitude of about 2.05. But has the peak absorbance in the range of 500nm wavelength which is desirable for solar cell applications. The Thevetia Peruviana showed lesser range and magnitude of absorbance. Celasia Cristata though better than Thevetia Peruviana has a lesser potential application in DSSCs.

As far as the degradation in the absorbance properties are concerned, AH shows improvement in absorbance over time. CC shows high degradation in the mid range of visible wavelengths. TP hardly shows any change in its absorbance properties. AW shows some significant degradation for large wavelengths, though its properties are unchanged in the mid range of visible wavelengths. Numerous natural sources are available for dye extraction. Many such sources can be experimented upon and novel dyes can be extracted and the efficiency of the DSSC can be enhanced for making if feasible for practical applications. Acalypha family can be a potential research segment for dye extraction with respect to application in DSSCs.

5. ACKNOWLEDGEMENTS

The authors are very much thankful to Dr. Appukuttan K K, the Director, Maulana Azad National Institute of Technology Bhopal, for the financial support and providing the facilities for the research work.

REFERENCES

[1] O'Regan, B., Gra¨tzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films. Nature 1991; 353: 737–739.

[2] Bing, Z., Bai, X., Haijun, N. Organic dye-sensitized nanocrystalline solar cells. Prog. Chem. 2008; 20: 828–840.

[3] Kandavelu, V., Hung, H.S., Jian, J.L., Wang, K.L., Hung, S.T. Novel iminocoumarin dyes as photosensitizes for dye-sensitized solar cell. Sol. Energy 2009; 83: 574–581.

[4] Horiuchi, T., Miura, H., Uchida, S. Highly-efficient metal-free organic dyes for dye-sensitized solar cells. Chem. Commun. 2003; 164: 3036–3037.

[5] Sayama, K., Tsukagoshi, S., Hara, K., Ohga, Y., Shinpou, A., Abe, Y., Suga, S., Arakawa, H. Modeling of dye-sensitized solar cells based on TiO2 electrode structure model. J. Phys. Chem. B 2002; 106: 1363–1371.

[6] Yao, Q.H., Shan, L., Li, F.Y., Yin, D.D., Huang, C.H. Porphyrin sensitizers with p-extended pull units for dye-sensitized solar cells. New J. Chem. 2003; 27: 1277–1283.

[7] A. Mishra, M.K.R. Fischer, P. Bäuerle Metal-free organic dyes for dye-sensitized solar cells: from structure: property relationships to design rules Angew Chem Int Ed, 48 (2009), pp. 2474–2499

[8] Y. Ooyama, Y. Harima Photophysical and electrochemical properties, and molecular structures of organic dyes for dye-sensitized solar cells ChemPhysChem, 13 (2012), pp. 4032–4080

[9] R.K. Kanaparthi, J. Kandhadi, L. Giribabu Metal-free organic dyes for dye-sensitized solar cells Tetrahedron, 68 (2012), pp. 8383–8393

[10] Y. Wu, W. Zhu Organic sensitizers from D–π–A to D–A–Pπ–A: effect of the internal electron-withdrawing units on molecular absorption, energy levels and photovoltaic performances Chem Soc Rev, 42 (2013), pp. 2039–2058

[11] B.-G. Kim, K. Chung, J. Kim Molecular design principle of all-organic dyes for dye-sensitized solar cells Chem Eur J, 19 (2013), pp. 5220–5230

[12] James M Palmer, The Measurement Of Transmission, Absorption, Emission , And Reflection.2003; 25

[13] Alexia Gobrecht, Ryad Bendoula, Jean-Michel Roger, Véronique Bellon-Maurel, Combining linear polarization spectroscopy and the Representative Layer Theory to measure the Beer–Lambert law absorbance of highly scattering materials Analytica Chimica Acta, Volume 853, 1 January 2015, Pages 486-494

[14] W. Brügel Quantitative analysis An Introduction to Infrared Spectroscopy. Translated from the German Original by A.R. Katritzky and A.J.D Katritzky, John Wiley & Sons, Inc, New York (1962) pp. 279-286

[15] A.A. Lamola, N.J. Turro Spectroscopy K.C. Smith (Ed.), The Science of Photobiology, Plenum Press, New York (1977), pp. 27–61

[16] Philippe Steemans, Kevin Lepot, Craig P. Marshall , Alain Le Hérissé, Emmanuelle J. Javaux, FTIR characterization of the chemical composition of Silurian miospores (cryptospores and trilete spores) from Gotland, Sweden, 2010, 162:4: 577-590.