



Environmental Friendly Photosensitizing Materials for Harvesting Solar Energy

N.T. Mary Rosana^{1*}, D. Joshua Amarnath¹, S. Anandan², G. Saritha²

¹Department of Chemical Engineering, Sathyabama University, Chennai, India.

²Nanomaterials and Solar Energy Conversion Lab, Department of Chemistry, National Institute of Technology, Thirucharapalli, India.

Received: 19 Jan 2015, Revised 15 May 2015, Accepted 15 May 2015

*Corresponding author: Email: maryrosanachemical@gmail.com

Abstract

Dye sensitized solar cells (DSCs) are designed for the conversion of solar radiation into electric energy. In this present work, chlorophyll dye from fresh leaves of *azadirachta indica* and anthocyanin dye from fresh flowers of *ixora coccinea* were extracted. The absorption spectra and Fourier transform infrared spectra of both the dyes were recorded. The cells were fabricated with the extracted dyes and the *J-V* curves were recorded under solar simulation of 85 mW/cm². The chlorophyll dye from *azadirachta indica* leaf exhibited a short circuit current density (J_{SC}) of 0.23 mA/cm², open circuit voltage (V_{OC}) of 467 mV, a fill factor (FF) of 0.392 and a conversion efficiency (η) of 0.05%. Comparatively, the anthocyanin dye from *ixora coccinea* flower exhibited a short circuit current density (J_{SC}) of 0.36 mA/cm², open circuit voltage (V_{OC}) of 476 mV, a fill factor (FF) of 0.519 and a reasonable conversion efficiency (η) of 0.10%

Keywords—Dye sensitized solar cells, anthocyanin, chlorophyll, energy conversion efficiency.

1. Introduction

The most challenging issue in the present world is to produce clean energy to the society. Energy generated through various technologies has been explored by the different research groups throughout the world. Among the available renewable energy technologies, solar energy is considered as the most challenging candidate to the research community. The energy supplied by the sun is enormous: 3×10^{24} J per year or about 10,000 times greater than what the global population presently consumes [1]. It is also reported that receiving sunlight for one hour is more than enough to satisfy the global energy consumption for the whole year [2]. In order to combat environmental pollution and the severe energy crisis, innovative efforts have been constantly showcased by various researchers with the aim of harnessing the abundantly and naturally available solar power which might be a solution to many of the pressing energy and environmental related problems [3].

The traditional silicon based solar cells are replaced by other innovative technologies owing to their high production cost, and skilled manufacturing techniques. Dye sensitized solar cells (DSCs) have gained considerable attraction due to their environmental friendly nature, attractive appearance, low cost fabrication and ease of manufacture. It is a booming research area with lot of potential applications in the framework of non-conventional energy technologies [4,5]. DSCs are the third generation solar cells and the function of light absorption and charge carrier transport is separated thus making it different from the conventional semiconductor devices. It employs a sensitizer to absorb light in association with a wide band gap semiconductor of nanocrystalline nature. It was first developed by Grätzel and his coworkers in 1991 at Swiss federal institute of technology, Lausanne, Switzerland [6,7]. Since the inception of this novel technology, various research groups have focused on improving the efficiencies by adopting various strategies.

Dye sensitized solar cell work on the principle of photosynthesis which is the naturally occurring cycle in plants that maintains the life on earth. Compared to the traditional silicon based solar cells, the nanocrystalline based dye sensitized solar cell is a photo electrochemical cell. The photo sensitizer plays the role of absorbing sunlight and the electrons from the dye molecule are injected into the conduction band of the titanium dioxide layer

which travel through its porous network to reach the counter electrode. The oxidized dye molecule in turn accepts the electrons from the iodine/iodide electrolyte to regain its original state. A photo sensitizer plays a very important role in the practical implementation of this novel technology.

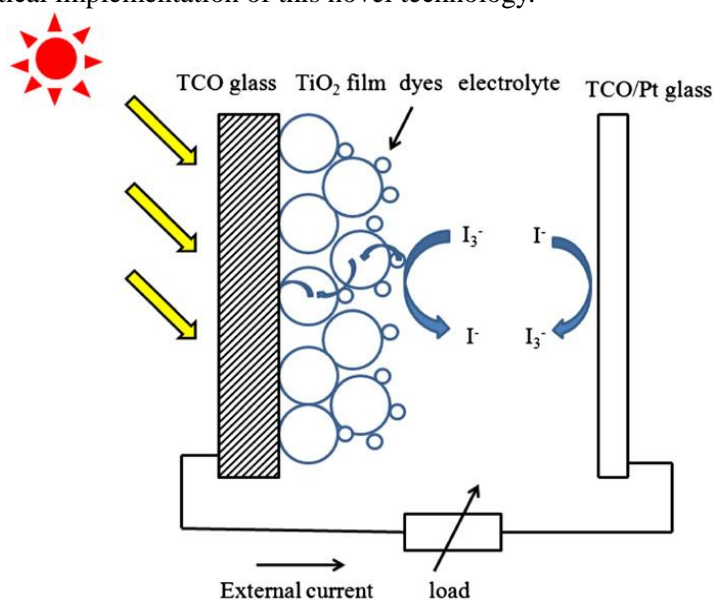


Figure1: Operating principle of a DSC [Data taken from ref 5].

The essential requirements of an efficient photo sensitizer are that it should exhibit intense absorption in the visible and near infra-red regions of the solar spectrum, it has to contain carboxylate and phosphonate anchoring groups for firm attachment onto the semiconductor surface, should be able to inject the electrons in its excited state, it should be stable enough to withstand numerous oxidation and reduction cycles without any decomposition, should be cost effective and environmental friendly in nature[4,5,7,11].Figure1 shows the operating principle of a typical dye sensitized solar cell.

Various synthetic and natural dyes were reported as photo sensitizers in DSCs. Ruthenium sensitizers were reported with their highest conversion efficiency exceeding 11%, and the high conversion efficiency is attributed to their wide absorption range in the near infrared region [8,9].

Due to the drawbacks associated with the ruthenium based dyes, natural dyes extracted from fruits, vegetables, seeds, flowers and plants have gained utmost importance in recent days. Natural dyes are reported to be inexpensive, easily attainable, nontoxic and ecofriendly when compared to the synthetic photo sensitizers. The natural pigments such as chlorophyll, flavonoids, β -carotene, betalains etc. have been explored as photo sensitizers in DSC research [4, 10,11].

In this paper, we have focused on chlorophyll and anthocyanin pigments. Chlorophyll is a green pigment available in the leaves and other parts of the plant. It is a derivative of porphyrin with a magnesium ion in the center [12]. Chlorophylls are not effective sensitizers in their crude form; instead in association with other natural dyes and by purification procedures, they are reported to possess better conversion efficiencies [13-15]. Anthocyanins are naturally available compounds and responsible for colors from red to blue range found in the flowers, leaves, fruits, roots, bulbs and stems of the plant. Different types of anthocyanin's have been identified from plant sources and all are reported as the derivatives of 2-phenyl benzopyrylium (flavylium) ion [13].The alcoholic groups in the anthocyanins are capable of binding on to the semiconductor film [16].

In this present work, we have extracted the chlorophyll dye from fresh leaves of *azadirachta indica* (Common name:neem) and anthocyanin dye from *ixora coccinea* flower (common name: vedchi,colour chosen: pinkish red). Figure2a shows the image of the leaves chosen for extracting the chlorophyll dye. Neem is a popular and an abundantly available medicinal tree of India and all parts of the tree are explored for their biological activities. It is reported for its anti-inflammatory, antifungal, antibacterial, antioxidant and other therapeutic

effects [17-19]. Figure 2b shows the image of the flower chosen for extracting the anthocyanin dye. *Ixora coccinea* is a year round flowering plant species, multiple branched and appears in variety of attractive colors [20]. It is widely used in conventional Indian medicine due to its remarkable health benefits. It is reported for its antioxidant activity, anti-inflammatory effect and also used as an acid base indicator in titrations [21].



Figure 2a: *Azadirachta indica* leaves.



Figure 2b: *Ixora coccinea* flower.

2. Materials and Methods

2.1 Extraction of Dye Sensitizers and Characterization Studies

The fresh leaves and flowers were collected from the Sathyabama University campus, Chennai, India. In the preparation of chlorophyll dye, neem leaves were separated from their midribs and gently washed with distilled water and shade dried for a day to remove the moisture content present. The moisture free material was then transferred to the mortar and pestle and crushed into bits for few min. To the crushed material, 95% ethanol was added and kept in dark for 45 h to ensure maximum extraction and filtered twice to remove the solids. Anthocyanin dye was prepared by boiling the cleaned petals with 95% ethanol at 45° C for 40 min and filtered. Both the dyes were stored in dark and used in its crude form without further purification procedures [22, 23, 27]. The absorption spectra of the freshly extracted dyes were recorded in a 10 mm length quartz cell by using UV-Visible spectrophotometer. The Fourier transform infrared spectra (FTIR) of the extracts were recorded with PerkinElmer model.

2.2 Fabrication of the DSCs

The components for the fabrication of a DSC such as nanocrystalline titanium dioxide (TiO_2 , Degussa P25), conductive transparent coated glass slides (fluorine doped tin oxide; FTO), iodide electrolyte was purchased from the institute of chemical education, Wisconsin, USA, and was used as received. TiO_2 was made into a lump free smooth suspension in a mortar and pestle with few drops of dilute acetic acid and a drop of detergent solution. The suspension was allowed to equilibrate for few min. The square glass slide was cleaned with ethanol and the conducting side of the glass slide was identified with a multimeter. The glass slide was neatly taped on all the four sides and a single smooth nanocrystalline TiO_2 layer was made on to the conducting side of the glass slide with a clean glass rod. The smooth film formed was air dried for a min and sintered in a furnace for 30 min at 450°C and cooled down to room temperature. Now the electrode is ready to be soaked. The chlorophyll dye was taken in a clean Petridish and the TiO_2 semiconductor coated glass slide was immersed in it for 24 h at room temperature. The entire soaked setup was kept without direct exposure to sunlight [22,24]. The same procedure was followed for the anthocyanin dye. The platinum catalyst counter electrode was prepared by the deposition of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution (0.005 mol/dm³ in isopropanol) on FTO glass and then sintered at 400 °C for 20 min [25, 26]. The dye coated glass slide was washed gently with ethanol and dried. A drop of iodide electrolyte solution was sandwiched between the positively and negatively charged electrodes and clipped together to form a complete cell.

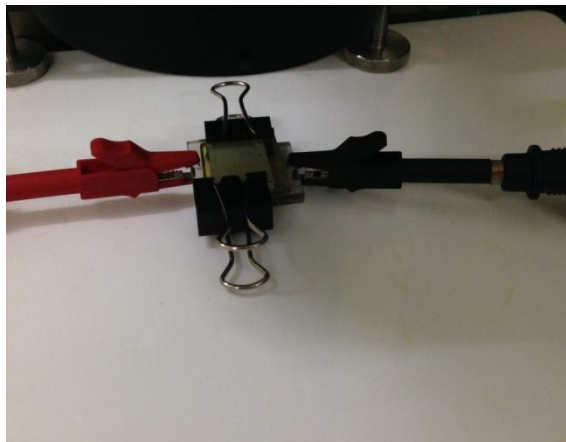


Figure3a: Fabricated cell

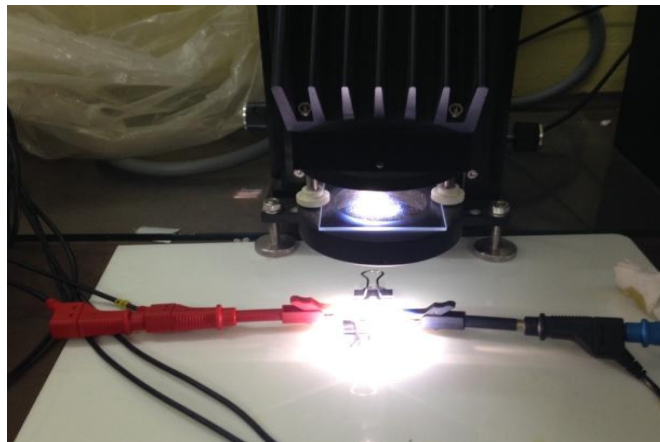


Figure3b: Efficiency measurement

The photovoltaic response of the assembled cell was recorded with a solar simulator at $85\text{mW}/\text{cm}^2$. The current density and voltage (J - V) characteristics were recorded with potentiostat/galvanostat (Autolab-84610) set up. Figure 3 a and Figure 3b shows the fabricated cell with anthocyanin dye and its efficiency measurement with a solar simulator.

3. Results and Discussion

3.1 Absorption spectra of the extracted dyes

The absorption spectra of the chlorophyll and anthocyanin dyes are shown in Figure 4a and 4b. The spectra obtained from the chlorophyll was different from that of the anthocyanin dye. The chlorophyll dye extracted from azadirachta indica leaves shows a broad absorption peak between 300–500 nm and exhibits a sharp absorption peak between 600–700nm with an absorption maxima at 665nm. The peak matches with the reported absorption peaks for the chlorophyll dye. However, the anthocyanin dye extracted from ixora coccinea flower has the absorption range from 400–600nm [15, 27-28]. Though, there are no sharp peaks observed, the dye is observed to exhibit absorption in the visible region. Hence both the dyes have the potential of getting explored as photo sensitizers in DSC technology..

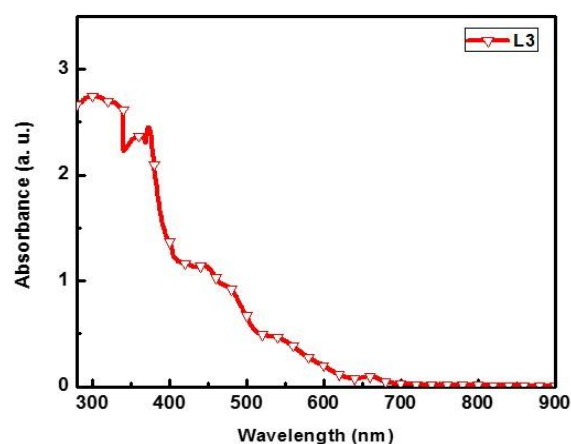
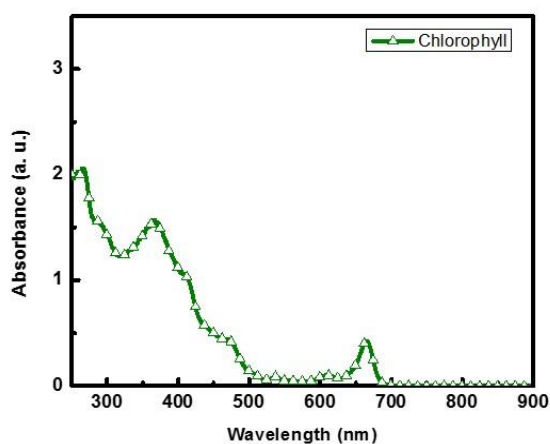


Figure4a: Absorption spectrum of the chlorophyll dye Figure4b: Absorption spectrum of the anthocyanin dye

3.2 Fourier Transform Infra-Red spectroscopic studies

The FTIR was recorded for the dye extracts in the spectral range from $400\text{--}4000\text{cm}^{-1}$ as shown in Figure 5a and 5b. The FTIR of chlorophyll dye and anthocyanin dyes closely matches with the peaks reported [15]. As

observed in the spectrum of chlorophyll dye, peaks observed at 2928 cm^{-1} and 2902 cm^{-1} indicate CH_3 and CH_2 vibration, peak at 1049 cm^{-1} indicates C-O vibration and 1640 cm^{-1} for C-N vibration for porphyrins

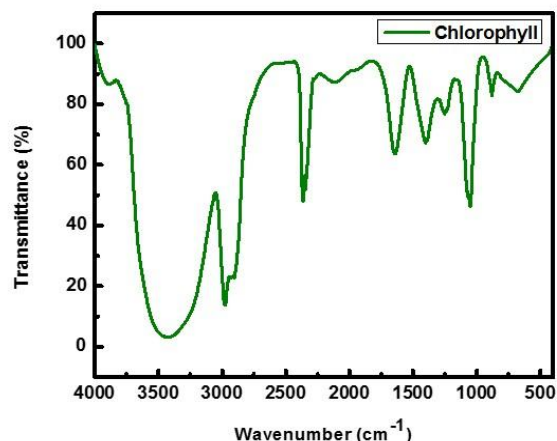


Figure 5a: FTIR of the chlorophyll dye.

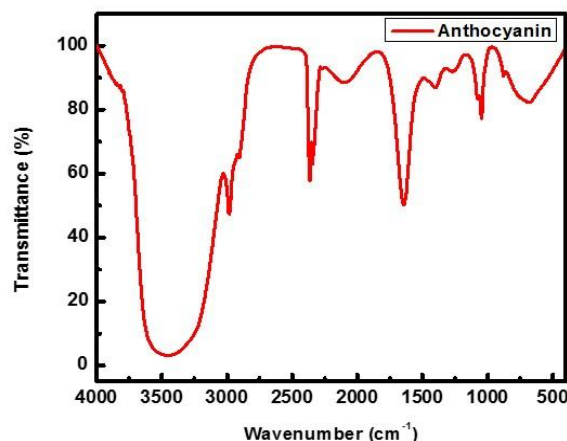


Figure 5b: FTIR of the anthocyanin dye.

As observed in the spectrum of anthocyanin dye, the characteristic peak at 3446 cm^{-1} indicates the presence of H-bond among molecules, peak observed at 1637 cm^{-1} shows C=O stretching vibration and peak at 1046 cm^{-1} shows the stretching vibration of C-O-C esters.

3.3 Photovoltaic performance of the fabricated DSCs

The photovoltaic performance of the assembled cell was obtained with 85 mW/cm^2 solar illumination. Figure 6a and 6b shows the recorded $J-V$ curves for the cells fabricated with chlorophyll and anthocyanin dyes. From the $J-V$ curves, the parameters such as short circuit current density, open circuit voltage, fill factor and conversion efficiency are determined. Compared to the chlorophyll dye, anthocyanin dye is observed to exhibit reasonable conversion efficiency when compared to the chlorophyll based dye. This is due to the better binding of the alcoholic groups present in the anthocyanin extract with the nanocrystalline titanium dioxide layer [16]. Table 1 shows the comparison of natural based DSCs performance.

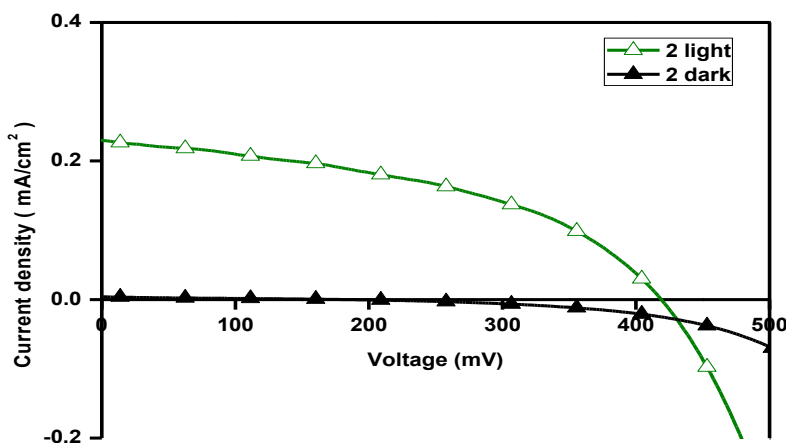


Figure 6a 2 light and 2 dark : Recorded $J-V$ Curve of the cell sensitized with chlorophyll dye

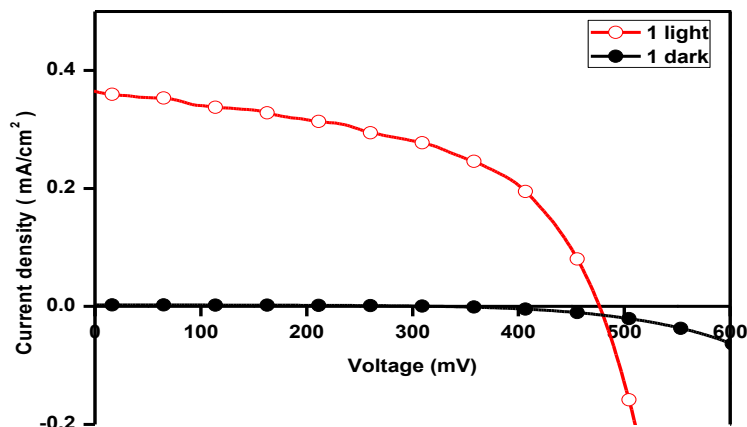


Figure 6b 1 light and 1 dark : Recorded J - V Curve of the cell sensitized with anthocyanin dye

Table 1: Comparison of performance with the natural dye based DSCs.

Dye Source	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	$\eta\%$	Ref.
Ixora coccinea flowers	0.36	476	0.519	0.10	Present
Azadirachta indica leaves	0.23	467	0.392	0.05	Present
Ivy gourd fruits	0.24	0.644	0.49	0.076	16
Red frangipani flowers	0.94	0.495	0.65	0.301	16
Rosella flowers	1.63	0.404	0.57	0.37	29
Blue pea flowers	0.37	0.372	0.33	0.305	29
Wormwood	1.96	0.585	0.47	0.538	15
Purple cabbage	2.08	0.66	0.53	0.75	15
Hiero-chloe Odorata grass	2.199	593.5	0.3554	0.46	30
Torulium Odaratum grass	1.004	654.2	0.4832	0.32	30
Dactyloctenium Aegyptium grass	0.698	718.91	0.4807	0.24	30

Conclusions

The chlorophyll and anthocyanin dyes extracted from the abundantly available natural sources such as azadirachta indica and ixora coccinea were used as photo sensitizer's in DSCs. Compared to the chlorophyll dye, anthocyanin dye extracted from ixora coccinea flower exhibited a reasonable conversion efficiency of 0.10%. The conversion efficiencies obtained cannot be compared with the efficiencies exhibited by most of the synthesized inorganic ruthenium metal based and organic dyes, but the results are encouraging and gives a hope to explore different natural dyes as photo sensitizers in the future. Reasonable efficiencies could be achieved by using sophisticated fabrication procedures. Therefore, research and its efforts on novel renewable energy technologies lead us in marching towards sustainable development and an eco-friendly environment.

References

1. Aduloju K. A., Fatigun A. T., Ewumi T. O., *Eur. J. Appl. Eng. & Sci. Res.* 2 (2013) 44-47.
2. Goncalves L. M., Veronica de Zea Bermudez, Ribeiro H. A, Mendes A. M, *Energ. Environ. Sci.* 1 (2008) 655.
3. Anandan. S., *Sol. Energ. Mat. Sol. C.* 91 (2007) 843-846.

4. Narayan M. R., *Renew. Sust. Energ. Rev.* 16 (2012) 208-215.
5. Gong J., Liang J., Sumathy K., *Renew. Sust. Energ. Rev.* 16 (2012) 5848-5860.
6. Brian O Regan, Grätzel M., *Nature.* 353 (1991) 737-740.
7. Grätzel M., *J. Photoch. Photobiol. C.* 4 (2003) 145-153.
8. Chiba Y., Islam A., Watanabe Y., Komiya R., Koide N., Han L., *Jpn. J. Appl. Phys.* 45 (2006) 638-640.
9. Qin Y., Peng Q., *Int. J. Photoenergy.* (2012) 1-21.
10. Mary Rosana N. T., Joshua Amarnath D., *Ind. J. Appl. Res.* 4 (2014) 169-170.
11. Mary Rosana N.T., *Res. J.Pharm.Boil.Chem.Sci.* 6 (2015)691-698.
12. Ewa Mlodzinska, *Acta Biol. Cracov.* 51 (2009) 7-16.
13. Calogero G., Yum J.H., Sinopoli A., Di Marco G., Grätzel M., Nazeeruddin M. K., *Sol. Energy.* 86 (2012) 1563-1575.
14. Chang H., Lo Y. J., *Sol. Energy.* 84 (2010) 1833-1837.
15. Chang H., Kao M. J., Chen T. L., Chen C. H., Cho K. C., Lai X. R., *Int. J. Photoenergy.* (2013) 1-8.
16. Shanmugam V., Manoharan S., Anandan S., Murugan R., *Spectrochim. Acta A.* 104 (2013) 35-40.
17. Bhowmik D., Chiranjy B., Yadav J., Tripathi K. K., Sampath Kumar K. P., *J. Chem. Pharm. Res.* 2 (2010) 62-72.
18. Girish K., Shankara Bhat S., *Electr. J. Biol.* 4 (2008) 102-111.
19. Biswas K., Chattopadhyay I., Banerjee R. K., Bandyopadhyay U., *Curr. Sci. India.* 82 (2002) 1336-1345.
20. Edward F. Gilman, Fact sheet, FPS 291, Institute of Food and Agricultural Sciences, University of Florida, (1999).
21. Arsia Tarnam Y., Sahitha Nizwan Z., *Int. J. Apl. Med. Sci. & Clin. Res.* 2 (2014) 169-176.
22. Mary Rosana N.T., Joshua Amarnath D., Vincent Joseph K. L., Anandan S., Saritha G., *Int. J. Sci. Eng. Res.* 5 (2014) 340-344.
23. Lin T. W., Lin J. R., Tsai S. Y., Lee J. N., Ting C. C., The 31st national conference on theoretical and applied mechanics, Taiwan (2007) 1-5.
24. Manual supplied by the Institute of chemical education, Wisconsin, USA.
25. Xu W., Peng B., Chen J., Liang M., Cai F., *J. Phys. Chem. C.* 112 (2008) 874-880.
26. He J., Wu W., Hua J., Jiang Y., Qu S., Li J., Long Y., Tian H., *J. Mater. Chem.* 21 (2011) 6054-6062.
27. Kushwaha R., Srivastava P., Bahadur L., *J. Energy.* (2013) 1-8.
28. Noor M. M., Buraidah M. H., Yusuf S. N. F., Careem M. A., Majid S. R., Arof A. K., *Int. J. Photoenergy.* (2011) 1- 5.
29. Wongcharee K., Meeyoo V., Chavadej S., *Sol. Energ. Mat. Sol. C.* 91 (2007) 566-571.
30. Shanmugam V., Manoharan S., Sharafali A., Anandan S., Murugan R., *Spectrochim. Acta A.* 135 (2015) 947-952.

(2015) ; <http://www.jmaterenvirosci.com>