

## Performance Evaluation of Natural Dye Sensitizers for nano-crystalline TiO<sub>2</sub> based Enhanced solar cells design

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### Abstract

In recent days, the society demands energy resources and its solutions as cheap and best with maximum efficiency. Several recent researchers were concentrated on Dye Sensitized Solar Cells (DSSCs) that extracts the natural models as sensitizer. It attracted worldwide attention because of its low production cost when comparing with traditional photovoltaic devices. Hence, we made a research about to find the effective natural dye as a sensitizer. Some traditional natural dyes are substances that can easily be obtained from vegetable, leaves and flowers through extraction and further it can be employed in dye-sensitized photo electrochemical cells (PECs). Similarly, Tannins is considered here because it contains naturally occurring water soluble polyphenolic compounds with high molecular weight. The comparison starts with Catechu dye, which is isolated from the heartwood of Acacia catechu, Tamarindus indica, Marknut dye and Marknut dye. Finally, the DSSCs were fabricated using natural dye extracted. To measure the effectiveness, a UV-VIS spectrum profile detection process of the catechu, tamarindus, marknut and eclipta dyes of water extracted samples were scanned in the wavelength ranging from 200-800nm under UV spectrophotometer.

Keywords--- Dye Sensitized Solar Cells, Nanocrystalline, Electrolyte, Catechu dye, Tamarindus dye, Marknut dye, Eclipta dye.

### I. INTRODUCTION

In budding world, there is a necessity of decent standard of living with the utilization of resources; it may be natural or artificial. Based on the population growth there is a necessity to increase the conservation. The efficiency and conservation are the two factors that may not predict the demand in terms of energy. Some traditional resources such as fossil fuels results in the risky environmental crisis such as acid rains and global warming. Parry et al., (2007) [3] accompanied the devastating effects with a few various consequences of climate change.

Among various resources solar energy is one of the major sources that may not affect or return any side effects. It is one of the promising techniques used for improving the performance with respect to the limited degradation. Traditional Organic Photovoltaic contains pure organic materials such as small molecules or polymers. But Dye sensitized solar cell is a hybrid technology as it involves organic and inorganic materials in the active layer.

The merits of organic solar cells over conventional solar cells are listed below

- 1) Various synthetic strategies are available for the production of organic materials
- 2) Broad absorption spectra, suitable energy levels and self - organization abilities make organic materials as suitable candidates for photovoltaic applications.
- 3) Solubility of organic compounds is high in common organic solvents. So they can be processed easily by low-cost technologies such as drop-casting, spin coating, dip coating etc.
- 4) Solar cells based on organic materials are structurally flexible and these are applicable on large surfaces.

In 1990, the Dye-Sensitized Solar Cells (DSSCs) was initiated by O'regan and Grätzel. They also extended the research with energy conversion efficiency that exceeding 7% in 1991 [1] and 11.4% in 2001 [2] by combining nano-structured electrodes to efficient charge injection dyes. When comparing the traditional photovoltaic device a DSSC is one of the third generation devices for converting solar energy into electrical energy in low cost. The DSSC is one of the simple fabrication processes that have relatively high conversion efficiency. Power conversion efficiency of a solar cell is determined by the formula given below

$$\text{Power conversion efficiency} = \frac{V_{oc} * I_{sc} * FF}{P_{in}} \quad (1)$$

$$\text{Fill Factor} = \frac{V_{mpp} * I_{mpp}}{V_{oc} * I_{sc}} \quad (2)$$

Where, Voc is the open circuit voltage, Isc is the short circuit current, FF is the fill factor and Pin is the

incident light power density.  $V_{mpp}$  and  $I_{mpp}$  are the voltage and current at the maximum power point. Brief descriptions of the parameters are as follows. Open circuit voltage ( $V_{oc}$ ) is the maximum voltage obtained from a solar cell when no current is flowing. The photo voltage (or open-circuit voltage,  $V_{OC}$ ) is directly related to the energy difference between the LUMO level of the acceptor and the HOMO level of the donor, which provides the primary driving force for charge separation. Short circuit current density ( $J_{sc}$ ) is directly linked to the product of the cell responsively and incident solar spectrum irradiance. Basically a polymer molecule having a lower HOMO level enhances the 'Voc'. Short circuit current ( $I_{sc}$ ) is the maximum current obtained from a solar cell when the voltage across the device is zero. Under an external load, the current will always be less than  $I_{sc}$ . Short circuit current density ( $J_{sc}$ ) is another important parameter determining the performance of a solar cell.

Riyas et al., (2002) stated that the Titanium dioxide ( $TiO_2$ ) is one amongst the top 20 inorganic chemicals of industrial, which is also known as titanium (IV) oxide discovered in 1821. It is mostly used as a pigment in paints, coatings, sunscreens, ointments, and toothpastes because of its brightness and a very high refractive index. Khataee et al., (2012) stated that  $TiO_2$  production is started in the year 1918. However, several semiconductors are being used as photocatalysts. In this work, the Extraction of Tannin is made from four categories such as Catechu dye which is extracted from the heartwood of Acacia catechu, Tamarindus dye that extracted from both leaves and barks of Tamarindus indica, next is Marknut dye it is extracted from Semecarpusanacardium and Eclipta dye leaf which is extract from Ecliptaprostrata. At present, the research on dye-sensitized solar cells is focused on the dye synthesis, electron transport process, photoanode, solid-state electrolyte and counter electrode.

As per the authors Mphande, B. C., & Pogrebnoi (2015) the function of the sensitizer is to absorb the incident light, inject the excited electron into the semiconductor, and become regenerated by the redox couple in the electrolyte. The use of natural dyes have been considered as potential candidates to enhance the light response of semiconductor in active layers of solar cells and have been demonstrated in several solar cell materials. The results from the sensitization performance are promising. The efficiency of a dye-sensitized solar cell depend upon the charge transfer taking place between highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (Cherepyet al., 1997).

The remaining part of this paper is organized as follows: In section 2, the literature review is made under Natural Dye Sensitizers, Preparation of Dye-Sensitized Solar Cells. In section 3, the research materials are discussed with testing process. The experimental results were analyzed in section 4. In section 5 the paper is summarized.

## II. REVIEW OF LITERATURE

In this section an earlier work on the preparation and characterization of semi-conducting metal oxide thin films such as ZnO, Cu<sub>2</sub>O, SnO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> are focused with the scope of the present investigation. Amongst the advanced oxidation processes (AOPs), the semiconductor-mediated heterogeneous photocatalysis has emerged as very attractive methods in many applications. Chatterjee and Mahata (2001) stated that many methods use oxide semiconductor photocatalysts, titanium dioxide ( $TiO_2$ ). Hence, fundamentals of semiconductor photocatalysis along with the structure and properties of  $TiO_2$  have been presented. The mechanism, applications, drawbacks, and the operational parameters affecting  $TiO_2$  photocatalysis have also been described. Few methods for enhancing the efficiency of  $TiO_2$  photocatalysts along with the need of its immobilization have been dealt with. Different types of polymer-supported  $TiO_2$  photocatalysts have also been briefly described. Details of the substrate and the probe molecule chosen for the present study have been furnished.

Generally, materials are classified into conductors, insulators, and semiconductors based on its ability to conduct the electricity. The electrons are free to move from one position to another in a conductor, whereas in case of an insulator no such movement of electrons is permitted. Miadlikowska et al., (2014) Semiconductors are characterized by an intermediate electronic behavior i.e., a semiconductor is a solid whose electrical conductivity is between that of a conductor and an insulator.

Suhaimi et al., (2015) discussed Dye sensitized solar cell (DSSC) as a device that generates electric power from light without undergoing any permanent chemical transformation. DSSCs can be considered as the new technology in the category of solar cells. Schneider et al., (2015) stated some merits while anchoring  $TiO_2$  onto suitable substrates, that are Relatively high quantum utilization efficiency as compared to the powder photocatalyst, it is ease of post-treatment recovery that would reduce the operational cost when used for large-scale practical applications, it is used to minimizing the catalyst loss, and availability of longer contact time of the photocatalyst with pollutants to be degraded.

Singh et al., (2013) discussed some merits of Polyaniline (PANI). They stated it as a Conductive Polymer (CP) that has an extended pconjugated electron system. Combining PANI with inorganic semiconductor metal oxides like TiO<sub>2</sub> has been a topic of great research interest due to high absorption coefficients in the visible part of the spectrum, high mobility of charge carriers, excellent environmental stability, and noticeable electrical, optical and photoelectrical properties. It is suitable for large-scale production and low cost. Merikangas et al., (2011) processed a charge separation process in a DSSCs consists with several steps.

Suhaimi et al., (2015) stated that natural dyes have also been used in DSSCs because of their low cost, easy extraction, nontoxicity, and the environmentally benign nature. There are two classes of plant pigments, namely, carotenoids and flavonoids. In addition, there are three subclasses of flavonoids: anthocyanins, proanthocyanidins, and flavonols. But only anthocyanins of the flavonoid group are responsible for cyanic colors, which range from salmon pink through red and violet to dark blue of most flowers, fruits, and leaves.

Narayan (2012) reviewed Anthocyanins, they stated it as the group most extensively investigated as natural sensitizers and their extracts show maximum absorption in the range of 510 to 548 nm, depending on the fruit or solvent used. The chain length of the substituent R also affects the performance of anthocyanins. The performance of a dye containing an R group with a long chain length will be lower due to steric hindrance, which restricts the transfer of electrons from dye molecules to the conduction band of the semiconductor. The efficiency of natural dyes is very low because of the weak interaction between the semiconductor (TiO<sub>2</sub>) and dyes. Dye aggregation on the nanocrystalline film is another important cause of low efficiency.

Wang et al., (2014) proposed a NiO based Efficient Counter Electrode Catalyst for Dye-Sensitized Solar Cells. Recently, interest in the use of natural dyes has been growing rapidly due to the result of stringent environmental standards imposed by many countries in response to toxic and allergic reactions associated with synthetic dyes. Research has shown that synthetic dyes are suspected to release harmful chemicals that are allergic, carcinogenic and detrimental to human health. On the other hand, natural dyes are environment-friendly; for example, turmeric, the brightest of naturally occurring yellow dyes is a powerful antiseptic which revitalizes the skin, while indigo gives a cooling sensation. Though, dyes have been discovered accidentally, their use has become so

much a part of man's customs that it is difficult to imagine a modern world without dyes.

Ooyama, Y., & Harima, Y. (2009) demonstrated that a cell based on black dye is more efficient than that of cell based on red dye in the near infrared region and attained an efficiency of 10.4%. Further, Mehmood et al. (2014), reviewed that improvement in the dye design to absorb radiation in the NIR region might drastically increase the efficiency and stability of DSSCs. Omar, A., & Abdullah (2014) proposed zinc oxide-based dye-sensitized solar cells. Similarly, Memarian et al., (2011) proposed an assembled ZnO Nanocrystallites for High-Efficiency Dye-Sensitized Solar Cells.

### III. RESEARCH METHODOLOGY

#### 3.1. Materials

##### a) *Acacia catechu*(L.f.) Willd.

*Acacia catechu* (L.f.) Willd. is a moderate sized tree growing up to 15m tall. This plant belongs to the family Mimosaceae, and is called as Black catechu or Cutch in English. Blackish brown cutch dye shows excellent fastness on cotton and silks. It produces brown tones. The geographical distribution of *A. catechu* is listed below: Indian distribution: Andhra Pradesh, Assam, Bihar, Karnataka, Madhya Pradesh, Maharashtra, Punjab, Rajasthan, Sikkim, Tamil Nadu, Uttar Pradesh and West Bengal. Tamil Nadu distribution: Coimbatore, Kanniyakumari, Nilgiri and Theni. The Macroscopic features of *A. catechu* is a small or medium sized tree, up to 15 m tall, deciduous; dark grey or greyish brown bark peeling off in long strips or in narrow rectangular plates, brown and red inside.

##### b) *Tamarindus indica* L.

*Tamarindus indica* L. is a large evergreen tree, growing up to 20m tall. This plant belongs to the family Ceasalpinaceae and is called as tamarind, camalindo, Indian date, Madeira mahogany and sweet tamarind, in English. Leaves yield a red dye, which is used to give a yellow tint to cloths previously dyed with indigo. Its Geographical distribution of *T. indica* is listed. Indian distribution: Throughout India except Jammu & Kashmir, Himachal Pradesh, Sikkim, Arunachal Pradesh. The Macroscopic features of *T. indica* is described as Trees, to 20 m high, bark brown to brownish-black, rough with vertical fissures; branchlets warty, tomentose. Leaves paripinnate, alternate; stipules lateral, minute, cauducous; rachis 8-13 cm long, slender, glabrous, pulvinate; leaflets 20-34, opposite, sessile, estipellate; lamina 1.5-4 x 0.4-1.3 cm, oblong, base unequal, apex obtuse, margin entire,

glabrous, chartaceous; lateral nerves 10-15 pairs, pinnate, slender, obscure, looped at the margin forming intramarginal nerve; intercostae reticulate, obscure. Flowers bisexual, 1 cm across, yellow with reddish-pink dots, in lax terminal racemes; bracts and bracteoles ovate-oblong, coloured, caudaceous; pedicels upto 5 mm; calyx tube narrowly turbinate, lined by disc; lobes 4, subequal, oblong, imbricate; petals 3, outer one, 1 x 0.3 cm, rolled up, pink dotted, lateral 2, 1-1.5 x 0.7-1 cm, clawed, subequal, oblong-lanceolate, lower pair scaly; stamens 9 monadelphous, only 3 fertile, others reduced to bristle, base pubescent; anthers versatile; ovary half inferior, stipitate, adnate to the disc, ovules many; style attenuate, tomentose; stigma globose. Fruit a pod 10-15 x 1-2 cm, oblong, fruit wall crustaceous, mesocarp pulpy, endocarp septate, leathery, indehiscent; seeds 3-8 or more, obovoid-orbicular, compressed, brown.

As shown in the process diagram which is represented in figure 1, the tannin was extracted following the method of Karamacet al. (2007). Shade dried heart wood pieces are milled to coarse (below 5mm.) size. Distilled Water is used to extract tannin. The material is extracted under pressure on autoclaving at 10 PSI for 30 min and the resultant extract was evaporated with vacuum filter. The obtained powder form was dissolved in 20 mL of ethanol was applied on a column (5 x 40 cm) packed with Sephadex LH-20 gel. Ethanol (1L), used as first eluent, allowed removing low molecular weight phenolic compounds. Then 600 mL of 50% acetone (v/v) was used to elute tannins. Solvent from tannin fractions was removed using rotary evaporator, and water was removed during lyophilisation.

The tannins play an important role in cotton dyeing to retain colouring matter permanently. The ultimate aim, the purpose of preparing the vegetable fibres with tannin is not so much to fix the colouring matter, as to fix certain metallic salts such as copper, iron, etc., in the form of insoluble tannates. The metal tannates present on the material forms insoluble lakes with the natural dyes during the dyeing process and results in improved fastness properties (Gulrajani, 1999).

i) Catechu dye

Catechu, which is marketed as a solid extract, is isolated from the heartwood of *Acacia catechu*. The dark catechu or Pegu cutch is used to tan heavy hides into sole leather, often in a mixture of tan stuffs. Catechu extract is also used for dyeing silk, cotton, canvas, paper and leather to a darkbrownish colour (Lemmensand Wulijarni-Spetjijtoed,1991).

ii) Tamarindus dye

Both leaves and bark of *Tamarindus indica* are rich in tannins. Leaves yield a red dye, which is used to give a yellow tint to cloth previously dyed with indigo (ICRAF, 2007). Tamarind leaves are a fair source of

vitamin C and  $\beta$ -carotene and the mineral content is high, particularly potassium, phosphorous, calcium and magnesium (El-Siddiget al., 2006).

iii) Marknut dye

*Semecarpusanacardiumis* used for non-medicinal purpose like marking of cloth, hair dye etc. since ancient time (Jain and Sharma, 2013). In certainparts of India, an aqueous extract of the crushed seeds is used in conjunction with iron salts for producing a jet-black dye on cloth (Satyanarayana Naidu, 1925).

iv) Eclipta dye

Commonly therural peoples of India, use the leaf extract of *Ecliptaprostrata* as a natural dye to colour their hair. The juice of the herb contains an oil-soluble black dye (Tripathi and Mondal, 2015). Leaves of the plant producing black dye which is used to hair blackening and cotton staining (Leeet al., 2008).

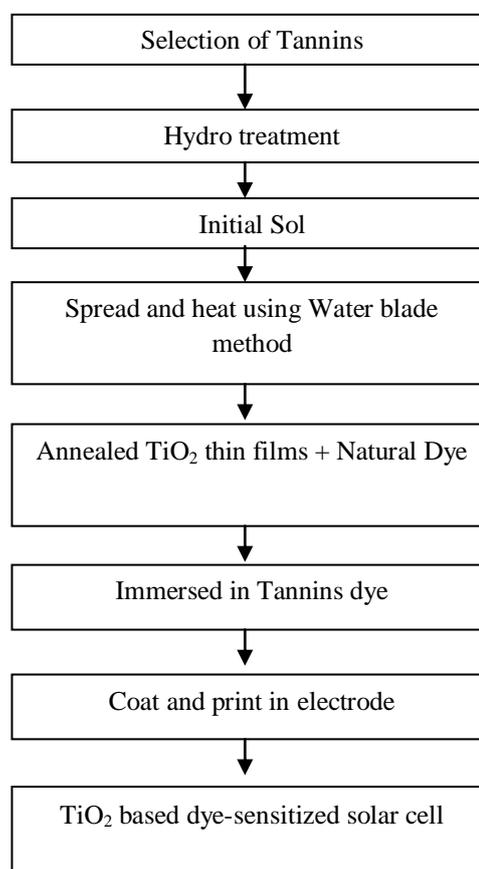


Figure 1 Representation of proposed  $\text{TiO}_2$  based Enhanced solar cells design

The phytochemical screening of water extraction of catechu, tamarindus, marknut and eclipta dye samples tested to conform the presence of tannins in  $\text{FeCl}_3$  and  $\text{FeSO}_4$  tests. All the four dye samples showed dark green or blue black colour in addition of

FeCl<sub>3</sub> and violet colour observed in FeSO<sub>4</sub> test. The obtained positive results conform the presence of tannins all the dye samples.

#### IV. EXPERIMENTAL RESULTS

##### a) Ultraviolet-visible spectrophotometry (UV-Vis)

A beam of visible light and/or UV light source (colored red) is separated into its component wavelengths by a prism. Each monochromatic beam in turn is split into two equal intensity beams by a half-mirrored device. One beam, the sample beam (colored), passes through a small transparent container (cuvette) containing a solution of the compound being studied in a transparent solvent. The other beam, the reference (blank), passes through an identical cuvette containing only the solvent. The intensities of these light beams are then measured by electronic detectors and compared. The intensity of the reference beam,

which should have suffered little or no light absorption, is defined as I<sub>0</sub>. The intensity of the sample beam is defined as I. Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. The ultraviolet (UV) region scanned from 200 to 400 nm, and the visible portion is from 400 to 800 nm.

The absorption of ultraviolet/visible radiation by a molecule leads to transition among the electronic energy levels of the molecule. A typical electronic spectrum consists of a series of absorption bands which corresponds to electronic transition for which the energies are around the bonding energies involved in organic compounds. The optical characterization of four dyes (Tannins) and dye coated TiO<sub>2</sub> films carried out using Shimadzu double beam spectrophotometer in the wavelength range 200-800 nm with wavelength resolution of 0.95 nm and wavelength accuracy of 0.5 nm.

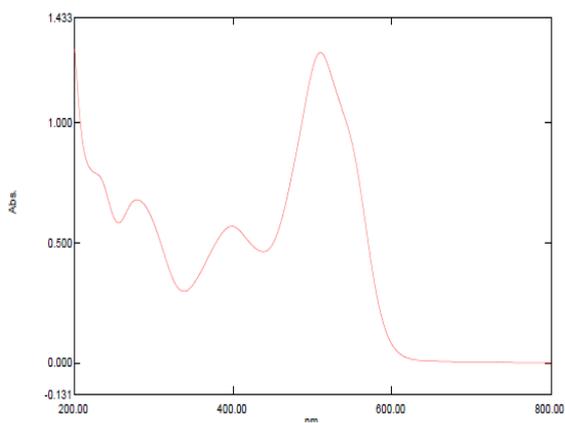


Fig 2 UV-Vis. spectrum of water extract of Catechu dye

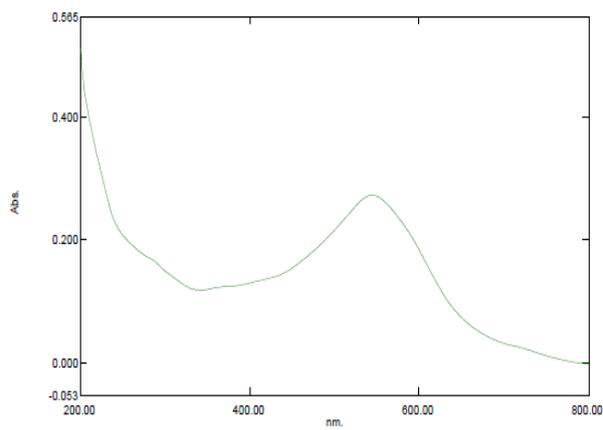


Fig.3:UV-Vis.spectrum of water extract of Tamarindus dye

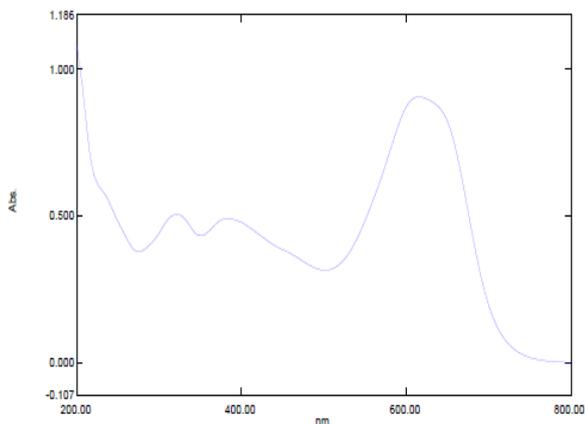


Fig.4:UV-Vis.spectrum of water extract of Marknut dye

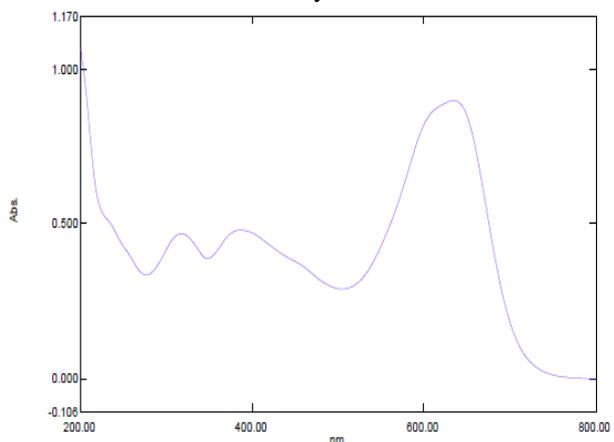


Fig. 5: UV-Vis. spectrum of water extract of Eclipta dye

b) Gas chromatogram Molecular structure Analysis

GCMS is an effective tool used for the direct analysis of components existing in traditional medicinal plants (PurushothPrabhuet al., 2013). It is a hyphenated system which is a very compatible technique and the most commonly used technique for the identification and quantification purpose. The unknown organic compounds in a complex mixture can be determined by interpretation and also by matching the spectra with reference spectra.

The extracted compounds have been injected to FeCl<sub>3</sub> and FeSo<sub>4</sub> teststo conform the presence of components as tannins. GC-MS analysis has been performed for all the four dyes such as catechu dye, tamarindus dye, marknut dye and eclipta dye. The Clarus 500 GC used in the analysis employed a fused silica column packed with Elite-1 [100% dimethyl poly siloxane, 30 nm × 0.25 nm ID × 1µm df] and the components were separated using helium as carrier gas at a constant flow of 1 ml/min.

The 2µl tannin sample injected into the instrument was detected by the Turbo gold mass detector (Perkin Elmer) with the aid of the Turbo mass 5.1 software. During the 36th minute of GC extraction process, the oven was maintained at a temperature of 110°C for 2 minutes. The injector temperature was set at 250°C for mass analysis (MS). The different parameters involved in the operation of the Clarus 500 MS, were also standardized (Inlet line temperature: 200°C; Source temperature: 200°C). Mass spectra were taken at 70 eV; a scan interval of 0.5 s and fragments from 45 to 450 Da. The MS detection was completed in 36 minutes.

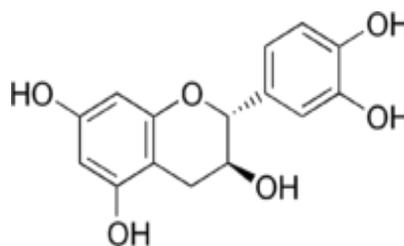
i) GC-MS analysis of Catechu dye

The heart wood of Acacia catechu yielded catechu dye. Catechin, (-)-Epigallocatechingallate (EGCG) and catechol are major constituents of catechu dye, which are tannin based phenolic compounds (Stohs and Bagchi, 2015; Gokhaleet al., 2009).

a) Catechin

Molecular formula: C<sub>15</sub>H<sub>14</sub>O<sub>6</sub>

Molecular weight: 290.26 g/mol

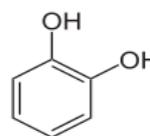


Molecular structure of Catechin

b) Catechol

Molecular formula: C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>

Molecular weight: 110.1 g/mol

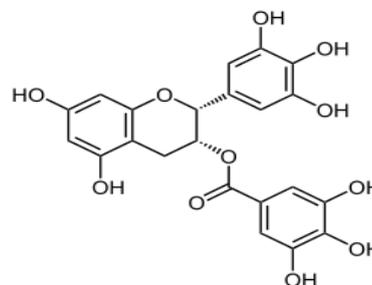


Molecular structure of Catechol

c) (-)-Epigallocatechingallate (EGCG)

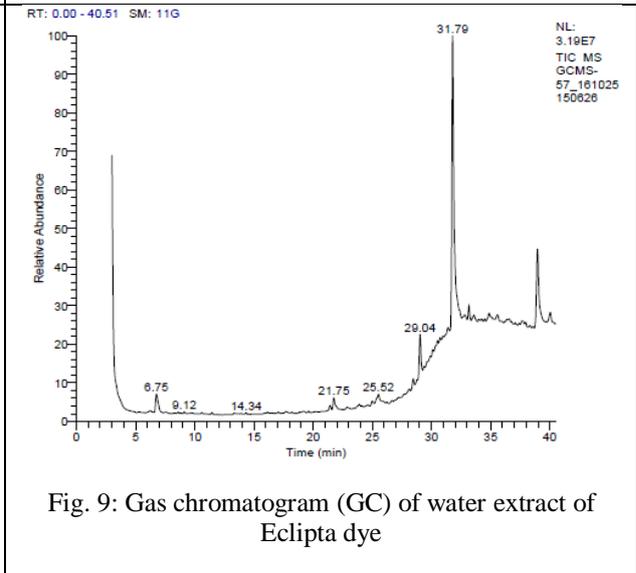
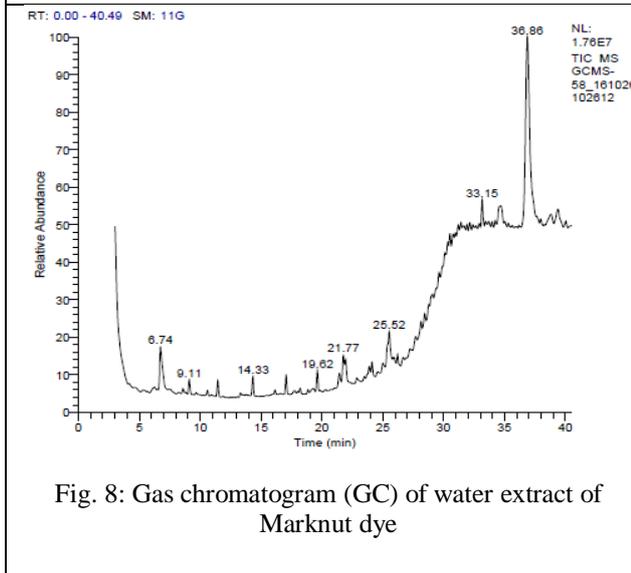
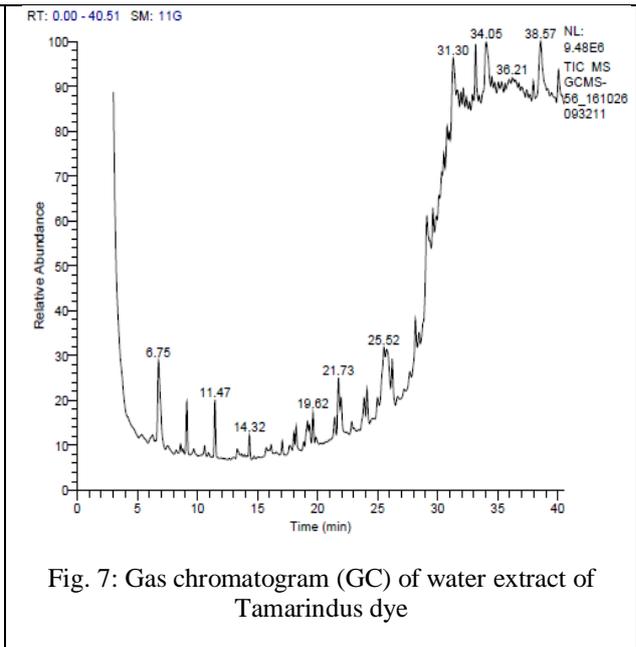
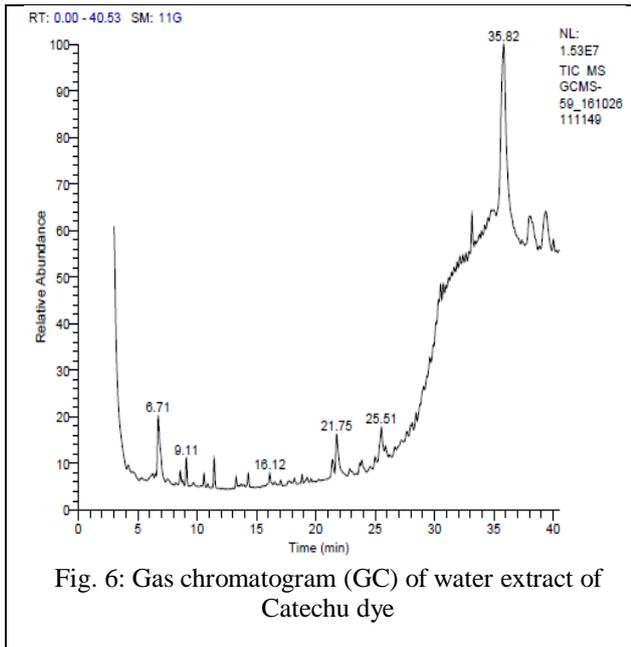
Molecular formula: C<sub>22</sub>H<sub>18</sub>O<sub>11</sub>

Molecular weight: 458.375 g/mol



Molecular structure of(-)-Epigallocatechingallate

The gas chromatogram from Acacia catechu is depicted in figure5. The chromatogram shows a major peak atRT35.82 with relative abundance (RT) 100%, whereas minor peaks with retention time 6.71 (22%), 25.51 (19%) and 21.75 (18%). The major peak represents the compound, catechin whereas the minor peaks with RT 35.82 belongs to (-)-Epigallocatechingallate (EGCG) and catechol. The colour of the compound in solution appears dark red or blackish red.



ii) GC-MS analysis of Tamarindus dye

The leaves of *Tamarindus indica* is a good source for red dye. Tartaric acid, benzyl benzoate and isovitin have isolated from it and are major phytochemicals of it. Isovitin or vitexin derivatives are components of oxidative dyes.

Generally, tartaric acid and benzyl benzoate contains hydroxyl and carboxyl functional groups which may bonded together with tannins of tamarindus (El-Siddiget al., 2006; Tariq et al., 2013; Bhadoriya et al., 2011). The gas chromatogram from *Tamarindus indica* is depicted in figure 6. The chromatogram shows major peaks at RT 38.57 and 34.02 with relative abundance (RT) 100%, whereas minor peaks with

retention time 6.75 (29%), 25.52 (29%) and 21.73 (18%). The major peak represents the compound, isovitexin vitexin derivatives whereas the minor peaks with RT 6.75 and 25.52 belongs totartaric acid and benzyl benzoate or derivatives of tannins. The colour of the compound in solution appears red.

iii) GC-MS analysis of Marknut dye

Marknut is a well-known natural dye obtained from *Semecarpusanacardium*. Bhilawanol Nut Shell Liquid (BNSL) is an indigenous extract from the shell of nuts of *S. anacardium* and form an important raw material of paint industry. BNSL contains Bhilawanol, Semecarpol, catechol and a mixture of hydrocarbons. Bhilawanol as the main constituent (46 %) of BNSL

and it is an O-dihydroxy phenol (Board, 2002). The mixture of BNSL components produces black colour. In addition, anacardic acid, tetrahydrorobustaflavone and semecarpetin also isolated in the nuts of *S. anacardium* (Murthy, 1985; Murthy, 1988; Chattopadhyaya and Khare, 1969).

The gas chromatogram from *Semecarpus anacardium* is depicted in figure 7. The chromatogram shows a major peak at RT 36.86 with relative abundance (RT) 100%, whereas minor peaks with retention time 33.15 (56%), 25.52 (22%), 6.74 (18%) and 21.77 (16%). The major peak represents the compound, Bhilawanol whereas the minor peaks with RT 33.15 represents the compound Semecarpetin and 25.52, 6.74 and 21.77 belongs Anacardic acid, Tetrahydrorobustaflavone and Catechol. The colour of the compound in solution appears black.

iv) GC-MS analysis of Eclipta dye

A black dye obtained from leaf extracts of *Eclipta prostrata* is used for dyeing hair and tattooing. Desmethylwedelolactone and Wedelolactone are major constituents of leaf, desmethylwedelolactone is a dying agent of the plant (Wagner et al., 1986; Meena et al., 2010). The gas chromatogram from *Eclipta prostrata* is depicted in figure 8. The chromatogram shows a major peak at RT 31.79 with relative abundance (RT) 100%, whereas minor peaks with retention time 29.04 (22%), 6.75 (8%), 25.52 (6%) and 21.75 (6%). The major peak represents the compound, Desmethylwedelolactone whereas the minor peaks with RT 29.04 represents the compound Wedelolactone. The colour of the compound in solution appears black.

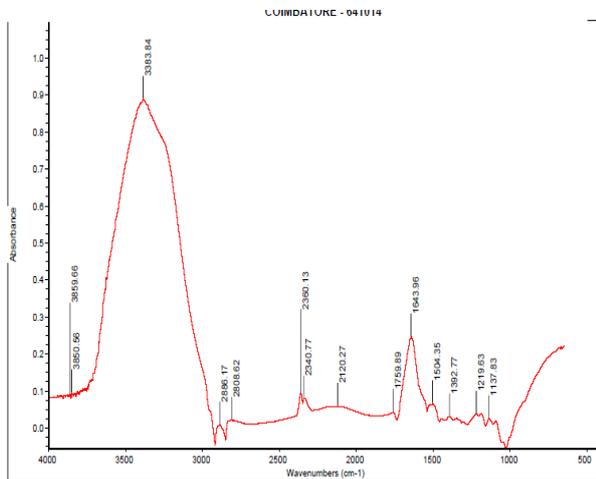


Fig. 10: FTIR spectrum of water extract of Catechu dye

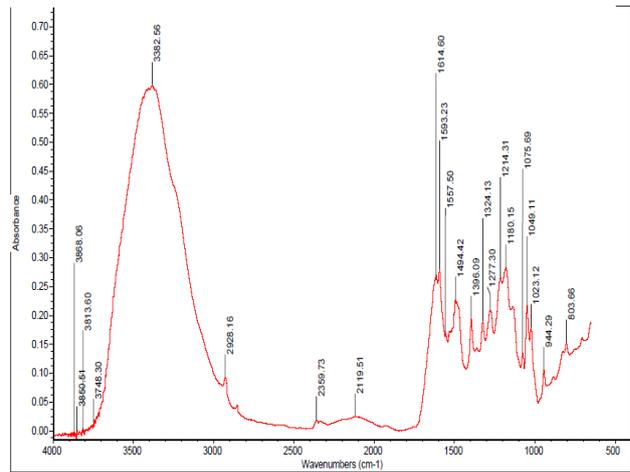


Fig. 11: FTIR spectrum of water extract of Tamarindus dye

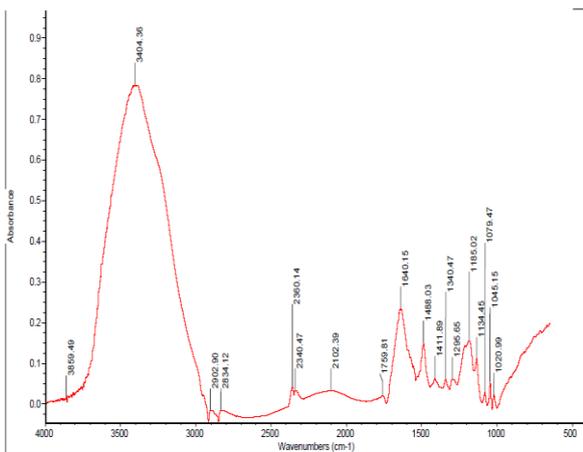


Fig. 12: FTIR spectrum of water extract of Marknut dye

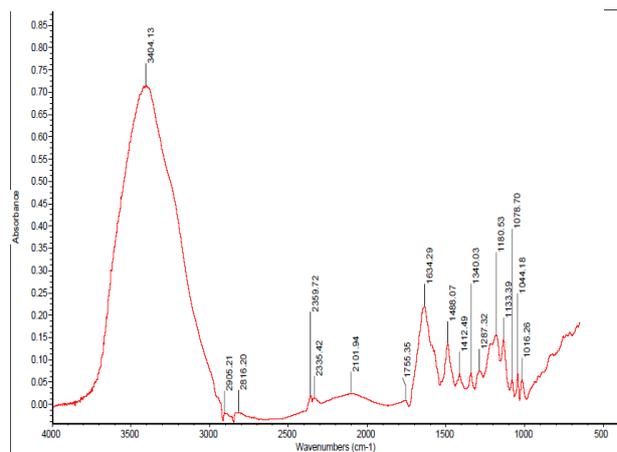


Fig. 13: FTIR spectrum of water extract of Eclipta dye

Figure 11 shows the FTIR spectral analysis of water sample of Tamarindus dye extracted from Tamarindus indica leaf rachis. In FTIR analysis, the peak at  $3382.56\text{cm}^{-1}$  represented O-H stretching vibration. The peak at  $2928.16\text{cm}^{-1}$  are attributed to the C-H stretching of Alkanes. The peak at  $1593.23$  and  $1494.42\text{cm}^{-1}$  are attributed to the C-C stretch of Aromatic groups. The peaks at wavenumber  $1324.13$ ,  $1277.30$  and  $1214.31\text{cm}^{-1}$  correspond to the C-N stretching vibration of Aromatic amines group.

The peaks at wavenumber  $1180.15$ ,  $1075.69$  and  $1049.11\text{cm}^{-1}$  corresponds to the C-O stretching vibration of Alcohol group. Amines, Alkynes,  $1^\circ$  amines, Aliphatic amines, Carboxylic acids and Alkyl halides functional groups also observed in the sample. The strong and broad bands at  $2900-3750\text{cm}^{-1}$  in Tamarindus dye sample occur due to the O-H groups of water.

Figure 12 and shows the FTIR spectral analysis of water sample of Marknut dye extracted from Semecarpus anacardium. In FTIR analysis, the peak at  $3404.36\text{cm}^{-1}$  represented O-H stretching vibration of Alcohols. The peak at  $1759.81\text{cm}^{-1}$  are attributed to the C=O stretch of Carboxylic acid group. The peaks at wavenumber  $1295.65$ ,  $1185.02$  and  $1134.45\text{cm}^{-1}$  corresponds to the C-H wag vibration of Alkyl halides.

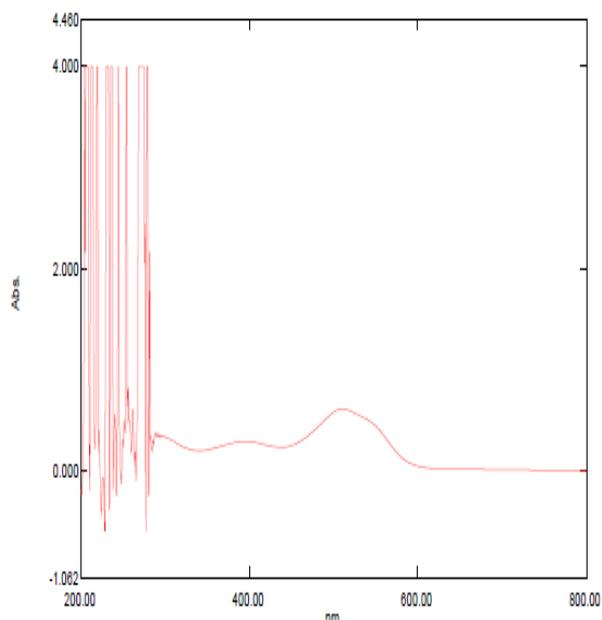


Fig. 14: UV-Vis. spectrum of water extract of Catechu dye +  $\text{TiO}_2$

The peaks at wavenumber  $1079.47$ ,  $1045.15$  and  $1020.99\text{cm}^{-1}$  corresponds to the C-N stretching of Aliphatic amines. Alkane, Aldehyde, Amine, Alkyne, Alkene, Nitro compound and Aromatic functional groups also observed in the sample.

The strong and broad bands at  $2900-3700\text{cm}^{-1}$  in both the Marknut dye sample occur due to the O-H groups of water.

Figure 13 the FTIR spectral analysis of water sample of Eclipta dye extracted from Eclipta prostrata. In FTIR analysis, the peak at  $3404.13\text{cm}^{-1}$  represented O-H stretching vibration of Alcohols. The peak at  $1755.35\text{cm}^{-1}$  are attributed to the C=O stretch of Carboxylic group. The peaks at wavenumber  $2359.72$  and  $2335.42\text{cm}^{-1}$  corresponds to the N-H stretching vibration of Amines. The peaks at wavenumber  $1287.32$ ,  $1180.53$  and  $1133.39\text{cm}^{-1}$  corresponds to the C-H wag of Alkyl halides. The peaks at wavenumber  $1078.70$ ,  $1044.18$  and  $1016.26\text{cm}^{-1}$  corresponds to the C-N stretching vibration of Aliphatic amines. Alkanes, Aldehydes, Alkynes, Alkenes, Aromatics and Nitro compounds functional groups also observed in the sample.

The strong and broad bands at  $2930-3800\text{cm}^{-1}$  in both the Eclipta dye sample occur due to the O-H groups of water.

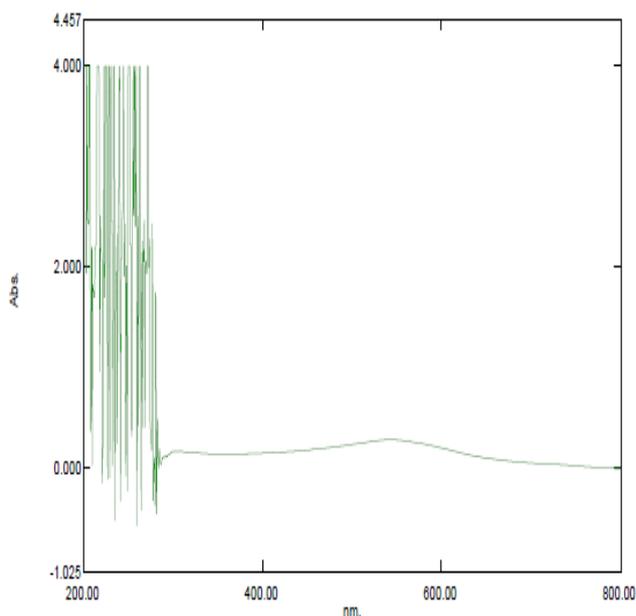


Fig. 15: UV-Vis. spectrum of water extract of Tamarindus dye +  $\text{TiO}_2$

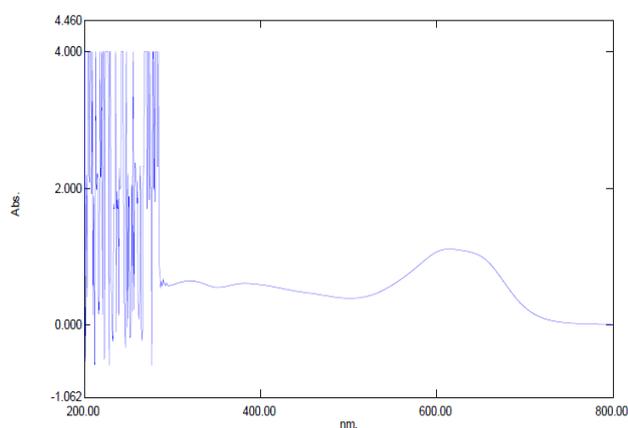


Fig.16:UV-Vis.spectrum ofwater extract of Marknut dye+ TiO<sub>2</sub>

In Figure 14, the Catechu + TiO<sub>2</sub> watersample desorbs from 200 nm to 370 nm and a strong peak absorbs at 510nm and towards the secondpeak at 390 nm and desorbsat remainingwavelengths. In Figure 14, the Tamarindus dye+ TiO<sub>2</sub> watersample desorbs from 200 nm to 290 nm and a strong peak absorbs at 543 nm and towards the second (or minor) peak at 305 nm and desorbsat remainingwavelengths. In Figure 16, the marknut dye+ TiO<sub>2</sub> watersample desorbs from 200 nm to 290 nm and a strong peak absorbs at 615 nm and towards the second and third peaks at 335 and 390 nm respectively and desorbsat remainingwavelengths.

In Figure 17, the Eclipta dye + TiO<sub>2</sub> watersample desorbs from 200 nm to 290 nm and a strong peak absorbs at 655 nm and towards the second peak at 320 nm and desorbsat remainingwavelengths. UV-Vis. spectrum of all the TiO<sub>2</sub> coated dye samples displayed broad and strong absorption bands between 510 and 655 nm which are characteristic of tannins and its derivatives or other phenolic compounds.

## V. CONCLUSION

Among various possible renewable sources ‘solar energy’ has tremendous potential to fulfil the energy demands of future generations in an environment friendly and sustainable manner. Importantly the solar energy can also power creation of other clean forms of energy such as hydrogen which is predicted to be ‘the fuel of future’ because of zero greenhouse gas emissions and high energy efficiency upon combustion. Current state of the art silicon-based photovoltaic (PV) technology is relatively expensive and therefore developing potentially cheaper PV technologies using solution processable earth abundant material systems is the need of the present time. Hence, in this research the Nanocrystalline TiO<sub>2</sub> thin films have been prepared by using doctor blade method. The prepared films were annealed at 500° C

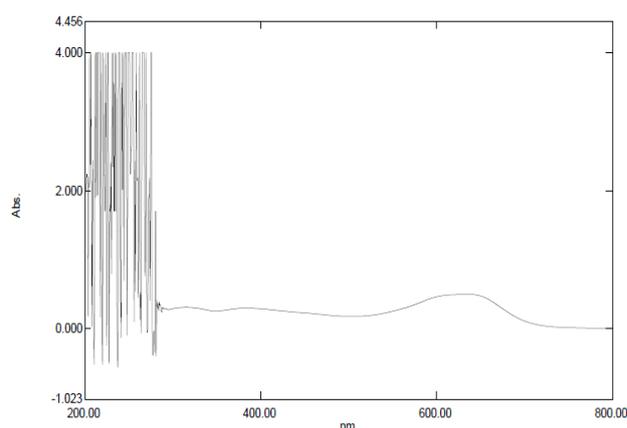


Fig.17:UV-Vis.spectrum ofwater extract of Eclipta dye + TiO<sub>2</sub>

and the structural properties were studied. TiO<sub>2</sub> nanocrystalline thin films were sensitized with natural dyes extracted from acacia catechu, leaf rachis of tamarindus indica, seed shells of semecarpusanacardium and leaves of eclipta prostrata were taken. The solar cell fabricated using TiO<sub>2</sub> film sensitized with acacia catechu dye extract exhibited a maximum power conversion efficiency of 0.83%. In future, the process must be extend towards another improvement in power conservation and efficiency.

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