



An Overview Of Natural Photo-Sensitizers And Electrolytes For Dye-Sensitized Solar Cells (DSSCs)

¹Lokesh Baloat*, ²A.S.Meena, ³Shiv Charan Meena, ⁴Dilkhush Meena

^{1,2}Assistant Professor, ³Dy. GM. Environmental Management Group (EMG), NTPC, ⁴Research Scholar

*Department of Chemistry, University of Rajasthan, Jaipur, Rajasthan-302004 (INDIA)

Abstract:

Due to their extensive investigation over the past 20 years, dye-sensitized solar cells (DSSCs) have opened up new avenues for energy research since they are more efficient, affordable, and simple to use than inorganic-based solar cells. Due to their toxicity, metal complexes in cell design and the sustainability implications of continued fast development provide the biggest problems. The dyes are taken from botanical sources, including fruits, flowers, bark, petals, roots, leaves, and beans of plants, in order to get around the issues with metal complexes. These organic dyes are widely suited for DSSC because they are nontoxic, affordable, abundant, environmentally benign, and simple to extract.

Readers can gain an understanding of how different semiconductors, solvents, light-harvesting pigments, types of electrolytes, and the addition of specific polymeric or nanomaterials to counter electrodes can affect solar cell efficiency by reading this review. Additionally, the effects that other researchers have documented on solar cell parameters, such the efficiency of DSSC, are critically studied in relation to methodology, processing temperature, and pH of the medium during synthesis.

Index Terms: *Dye Sensitized Solar Cells (DSSCs), Dyes, Electrolytes, Natural Sensitizers.*

1. INTRODUCTION

Structures known as photovoltaics are effective at converting solar energy into electrical energy, or more simply put, sunlight is transformed into electricity. These days, dye-sensitized solar cells, or DSSCs, are quite popular all over the world since they are inexpensive, easy to fabricate, and have a reduced overall cost. This idea was first put forth by Grätzel et al. and his colleagues in 1991. It was discovered that in the first DSSC, it could absorb visible light with a wavelength of about 800 nm and roughly 7% conversion efficiency. According to recent research, Mathew et al. used mesoporous semiconductor nanoelectrodes and porphyrin as sensitizers to achieve a maximum conversion efficiency of 13%.

A typical DSSC is composed of a transparent electrode that allows the sun-light to enter the system of dye and nanoparticles, a metal oxide semiconductor which having

Enough wide band gap, a dye that originates the electron for the electricity generation, a counter electrode and an electrolyte that is used as a mediator for electron transfer. In DSSCs, dye is crucial for absorbing light rays and transforming them into electrical energy. Sensitizers include complex organic dyes, natural dyes, and occasionally metal complexes or chemical dyes [1].

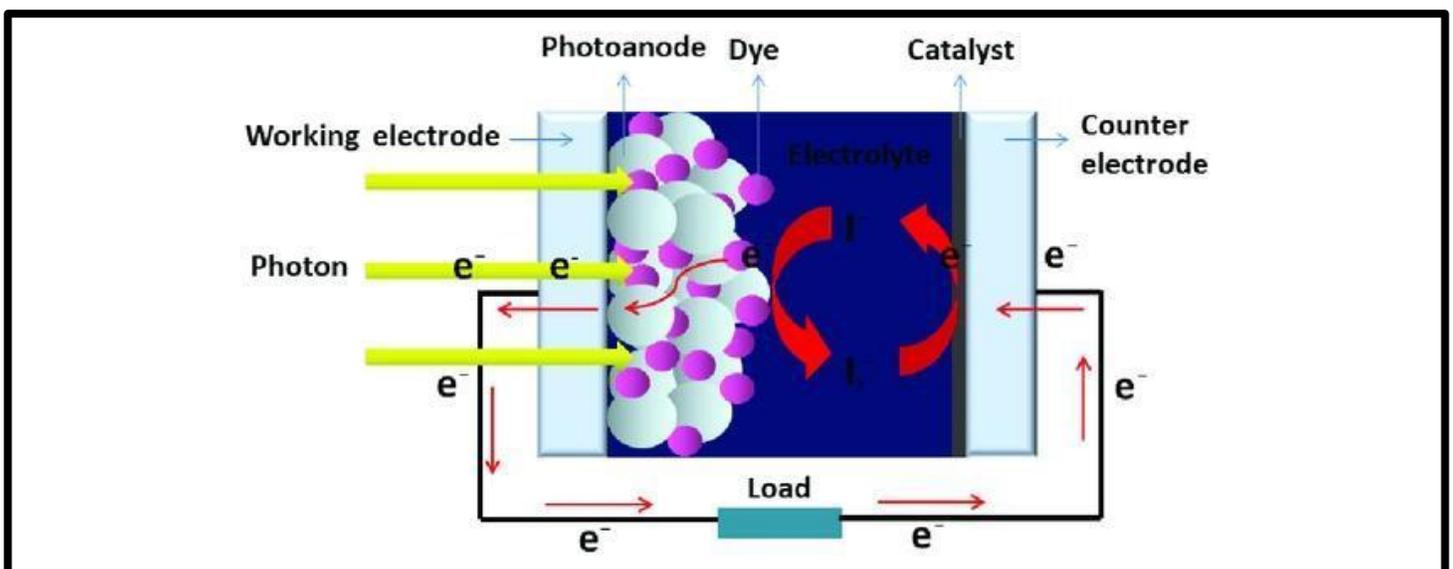
Chemical dyes, such as those based on ruthenium, are thought to be good sensitizers and are highly favored due to their exceptional capacity for massive charge absorption across a wide range of visible spectra, as well as their high conversion efficiency for metal to charge transfer and excellent electron injection to nanoparticles. Nevertheless, the use of ruthenium dyes is limited due to their toxicity, environmental effects, and high cost. Natural dyes have a number of benefits of their own, including being inexpensive, non-toxic, environmentally friendly, easily prepared with simple chemical processes, and readily available in large quantities. The metal oxide semiconductor surface was chemically absorbed by the dye. TiO_2 films are typically employed as metal oxide semiconductors due to their huge underlying surface area for light scattering absorption [2-3].

2. DSSC OPERATING PRINCIPLE

DSSC—semiconducting structure works on the principle of conversion of radiation (solar) to electrical-energy, Schematic has shown in Figure 1, DSSC comprised of various components:

- i. Transparent conducting oxide films (TCOs) which include fluorine-doped-tin-oxide (FTO) or indium-doped Tin-oxide (ITO). Although there are articles on low-cost TCOs as alternatives such as Aluminium-doped-zinc-oxide (AZO), graphene and doped-titanium-oxide (TiO_2).
- ii. In practical applications, semiconductor metal-oxide film electrodes that function as photoanodes are often made of TiO_2 nanoparticles.
- iii. Photosensitizer (dye molecules) which are anchored with the metal-oxide semiconductor to the photoanode.
- iv. Electrolyte, commonly iodide/tri-iodide based electrolytes are used as mediators between the electrodes.
- v. The counter electrode, generally platinum is mostly used as a spray on the glass substrate. Alternatively, carbon as a cheap source can also be used.

Figure-1: Schematic structure of DSSC



The operation of DSSC is progressively regenerative. No chemicals, either toxic or not, are produced or involve in the reactions. This is why DSSCs are one of the most reliable sources for the generation of electrical energy [4-6].

3. ELECTROLYTE

The most crucial and significant part of DSSCs are the electrolytes, which are in charge of internal charge-carrier transfer between the electrode and metal oxide. Through the process of its operation, the redox couple continuously regenerates both itself and the dye. Grätzel and O'Regan invented the first highly efficient dye-sensitized solar cell (DSSC) in 1991. It used an extremely simple primary liquid base electrolyte of organically produced solvent with an iodide/tri-iodide redox pair, with an efficiency of 7.1–7.9%. Combining cobalt complex with porphyrin dye co-sensitization has allowed for an efficiency of 12.3%; this combination acts as a redox couple mediating the electron and has greater potential than electrolytes based on iodine and tri-iodide. These three parameters—photovoltage, also known as open circuit voltage (V_{oc}), fill factor (FF), and photocurrent density, also known as short circuit current (J_{sc})—can be used to measure the overall efficiency of an electrolyte. The electrolyte and its interaction with the electrode interface have a significant impact on each of these parameters. Electrolytes used in dye-sealing materials (DSSCs) need to possess certain qualities. Firstly, they should be chemically and physically stable. Secondly, they should have low viscosity to reduce charge-transport resistance. Lastly, they should be an excellent solvent for redox-couple components and various types of additives. Lastly, they shouldn't cause any dissociation of the adsorbed components in the interim. The components of a standard liquid electrolyte include an ionic conductor, additives, and solvent. Although bromine (Br^-/Br_2) and hydroquinone have also been recommended as redox-electrolytes, iodine-electrolyte yields the best results. At room temperature, ionic liquids have good thermal and chemical stability as well as minimal vapor pressure, nonflammability, and high ionic conductivity. Liquid electrolytes based on organic solvents exhibit exceptional interface-contact properties and notably high ionic stability. Nevertheless, problems with solvent leakage, evaporation, and instability continue to persist, which compromise the long-term viability of DSSCs. To prevent the leakage and evaporation of liquid electrolyte a sealing material is required. Photochemical and chemical stability of sealing material is also needed against the electrolyte [7,8].

Numerous studies have been conducted on a range of electrolytes, including redox couples, ionic electrolytes, polymer electrolytes, volatile organic solvents, gel polymer electrolytes, organic–inorganic gel electrolytes, non-iodine based polymer gel electrolytes, and room temperature ionic liquid electrolytes.

Ionic electrolytes are basically salt in liquid form. Melted salts (molten phase) are called liquid-electrolytes completely comprised of ions. The MP criteria was introduced to distinguish between ionic-liquids with a low MP and low viscosity and melted salts with a high MP and high viscosity. Liquids that flow freely are called room temperature ionic liquids (RTIL). Ionic liquids have been widely used in DSSCs because of their unique properties, which include chemical and thermal stability, high conductivity, easily tunable viscosity, low vapor pressure, and negligible leakage.

When compared to ionic liquid electrolytes, the volatile organic solvent (VOS), which is most frequently employed in DSSCs, has photon to current conversion efficiency values ranging from 74% to 78%. Even while VOS exhibits increased efficiency, it also has many drawbacks, such as dubious long-term stability and durability and the ongoing requirement for a convoluted scaling procedure. Additionally, because of its low MP, VOS degrades quickly.

DSSCs achieved great development by using liquid electrolytes. However liquid electrolytes carry some issues along with it such as degradation, leakage, solvent volatilization, dye desorption, and counter electrode corrosion. To overcome these issues, one can have quasi-solid- state electrolytes. Although they are not as efficient as liquid electrolytes that can be compensated by their performance, viability, long-term stability and effective sealing capacity [9].

A semisolid condition halfway between solid and liquid states is called a quasi-solid state. Their exceptional ionic conductivity, typically exceeding $10^{-7} \text{ S cm}^{-1}$, renders them more significant. They exhibit both the diffusive (found in liquids) and cohesive (found in solids) properties at the same time. Polymer electrolytes may also be a better option to address problems with stability, durability, volatility, and degradation. Polymer electrolyte is made up of metal salts with lower energy that are dissolved in polymer matrices like ether, ester, or amide linkages. These electrolytes provide superior ionic conductivity and exceptional thermal stability in addition to resolving the leakage and sealing issues.

Compared to various electrolytes gel polymer electrolytes also offer many advantages such as good interfacial contact between electrodes, low vapor pressure, comparatively high ionic conductivity than polymer electrolytes. A lot of alternatives are being proposed to improve the demerits of electrolytes but among all the electrolytes redox couple electrolyte I^-/I^0 serves the best maximum efficiency [10].

4. NATURAL DYE PIGMENTS USED IN DSSC

A strong dye linked to semiconductor materials, a broad absorption spectrum, and the capacity to inject electrons into semiconductor materials are just a few of the conditions that the dye must meet in order to function as an outstanding dye sensitizer. Natural colors were typically taken from plant parts including fruits, flowers, leaves, and even roots. Every portion of the plant has unique pigments and colors. Thus, the recent research on natural pigments will be reviewed in this paper.

4.1. Carotenoids

Carotenoids are naturally occurring organic pigments found in various microbes and plants. Carotenoids, a form of isoprenoids that includes over 600 key members, are what give fruits and flowers their characteristic reddish-orange and yellow color as well as the reddish-orange color of their petals. Figure 2 illustrates this type of isoprenoids.

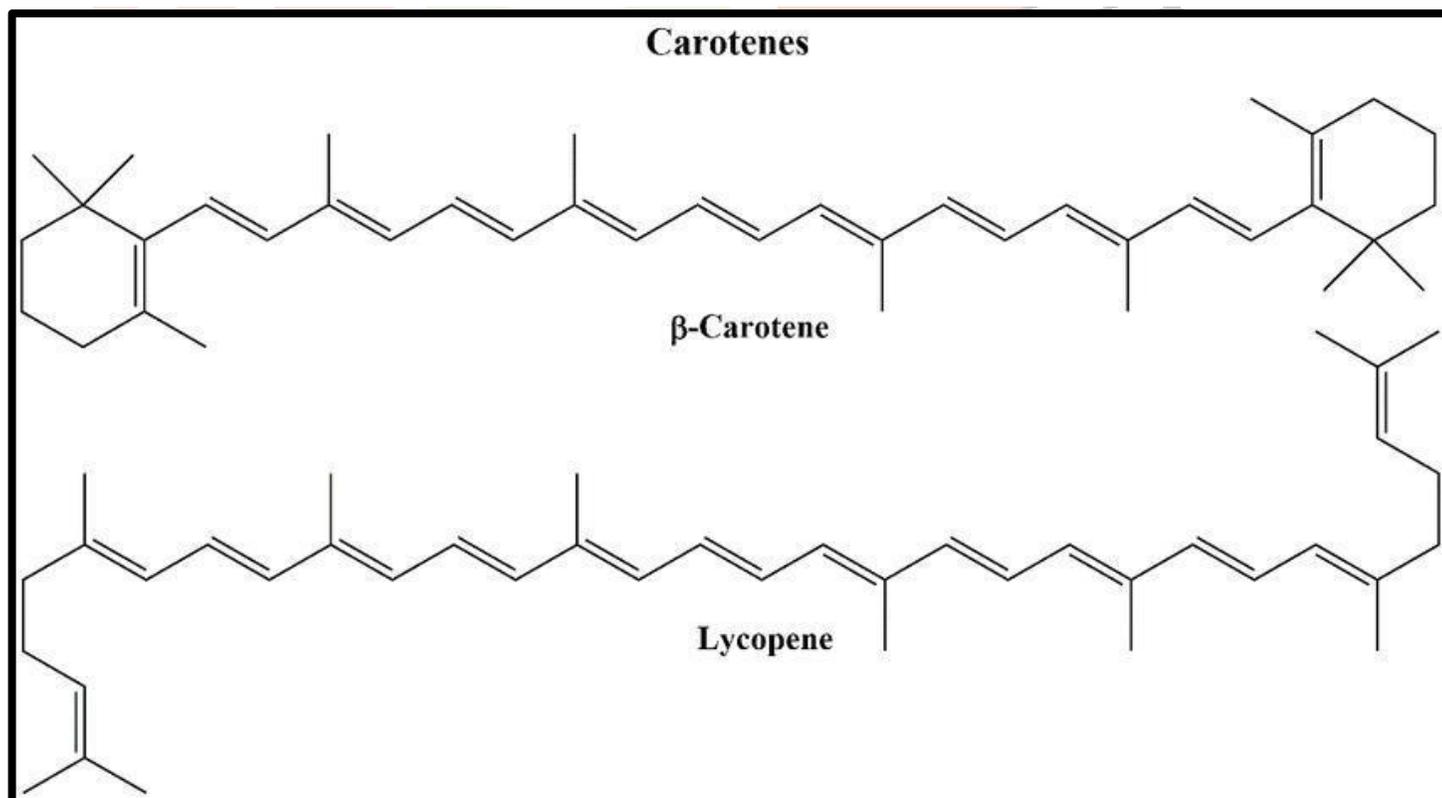


Figure-2: Structure of carotenoids.

Carotenoids are crucial for protecting photosynthesis. The C₄₀ hydrocarbon backbone, which includes structural and oxygenic modifications, makes up the majority of carotenoids. Through redox reactions, carotenoids and chlorophyll complement each other [11,12]. Since natural extracts like alcohol and biological acids aid in dye adsorption, prevent electrolyte recombination, and reduce dye accumulation, natural raw dyes are far superior to commercially refined colors. Carotenoids are excellent photosensitizers and energy harvesters. Natural crocin, carotenoids, and crocetin as a photosensitizer were all investigated by Yamazaki et al. Because crocin (0.16%) lacks a carboxylic group, crocetin-sensitive DSCs (0.56%) have a conversion competence that is more than three times higher.

4.2. Chlorophylls

Plants and microorganisms naturally produce the green pigment known as chlorophyll (Chl). Green is the color that chlorophyll receives from reflecting green wave-length after absorbing light. Their work entails accumulating solar light, converting solar energy into chemical energy, and moving electrons. DSSCs employ chlorophyll and its derivatives as a photosensitizer. Of the different kinds of chlorophyll that are accessible, chlorophyll (Chl) is the most effective at absorbing visible light. Because it is a chemical that is appealing, chlorophylls have an absorption peak at 670 nm and can function as photosensitizers in the visible spectrum. Chl having a chemical makeup The main pigment used by plants for photosynthesis is C₅₅H₇₂O₅N₄Mg.

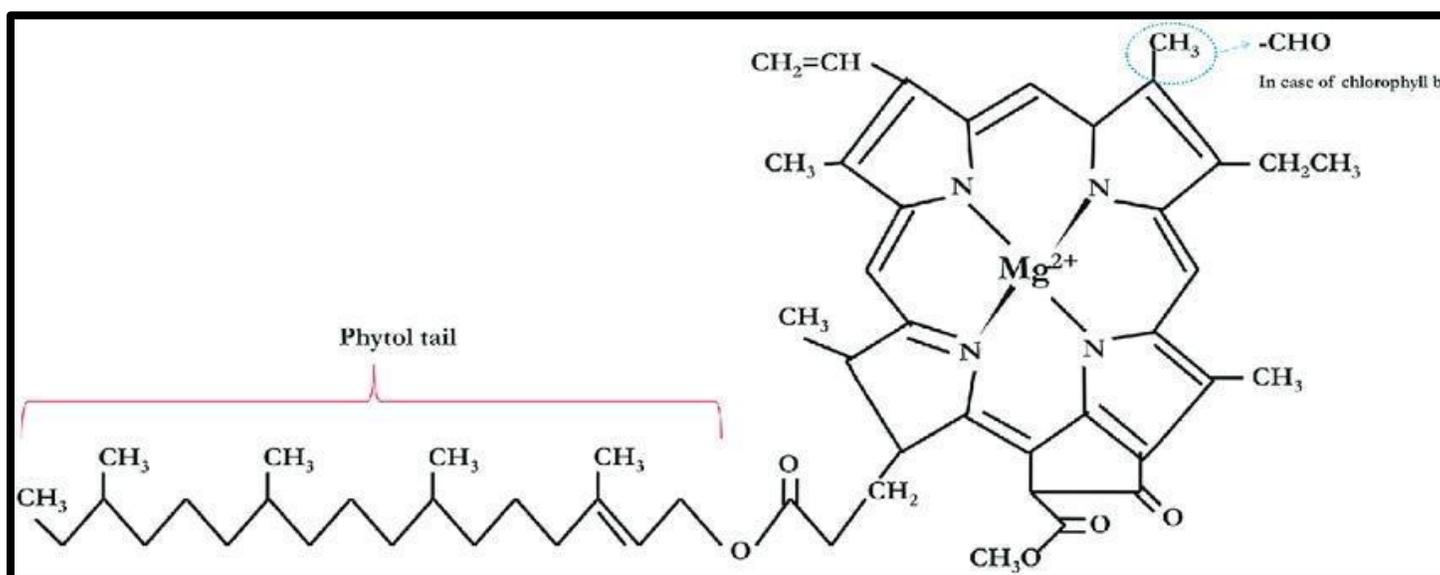


Figure-3: Structure of chlorophyll

Chlorophyll pigments have been extracted from dried plant leaves, including fig, apricot, and cream, in recent investigations. The three distinct plant leaves each performed differently for the DSSC. For figs, apricot, and cream leaves, the greatest absorption peaks were measured at 413 nm, 394 nm, and 415 nm, respectively [13,14].

4.3. Anthocyanins

Following chlorophyll, anthocyanins are an essential class of pigments that are visible to the human eye. Natural dye-based wide-band semiconductor sensitivity is frequently reported for anthocyanins. It makes up a significant category of flavonoids and is in charge of giving many different flowers, leaves, and angiosperm fruits their various colors, ranging from pink to red to violet to deep blue. The fundamental structure of anthocyanins C₃-C₆-C₃, as seen in Figure 4, is the source of the endless colors that are formed when they

chemically mix with glycosides or/and with an acyl group. Additionally, interactions with other molecules have been considered.

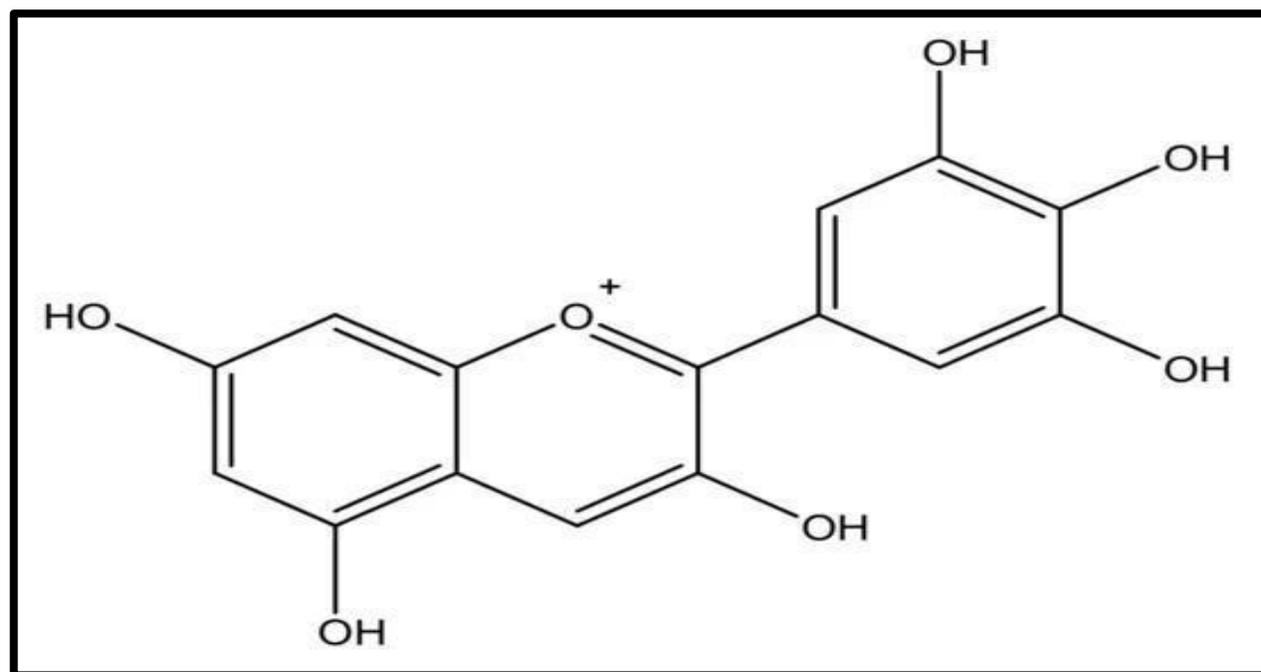


Figure-4: Structure of anthocyanins

Anthocyanins are widely dispersed throughout many plant sections, including stems, roots, and tubers. They are also present in plant seeds. All forms of anthocyanins are found in grapes, while cyanidin is found in apples, peaches, cherries, and pomegranates, and delphinidin is found in eggplants. Peonidin and cyanidin are both found in cranberries and cherry sweets. In flowers, mesophyll contains anthocyanins less frequently than epidermal cells.

The carbonate/hydroxyl groups found in anthocyanin molecules are bonded to the semiconductor surface of TiO₂ nanoparticles. This serves to stimulate and move electrons from the anthocyanin molecules to the porous TiO₂ film's conduction band. Anthocyanins have been described with 17 distinct structures, which are categorized based on the quantity of sugar molecules present, resulting in the formation of monosides, biosides, triosides, and other form [15,16].

5. CONCLUSION

A lot of study has gone into developing an environmentally friendly dye sensitizer for DSSC. Plant-based natural pigments are preferred because they are inexpensive, eco-friendly, readily available, and simple to synthesis. The most widely used natural pigments—betalain, chlorophyll, and anthocyanin—extracted from the leaves, fruits, and flowers of various plants are highlighted in this research because it has been demonstrated that these pigments are the primary factor influencing the energy conversion efficiency of

DSSC. The data comparisons indicate that the maximum energy conversion efficiency of 2.06% was obtained by betalain pigments, which were derived from purple wild sicilian prickly pear dye. This has led to betalain pigments being seen as a strong contender for the title of best natural dye sensitizer, ahead of chlorophyll and anthocyanin. Improved alternatives for porous semiconducting metal oxides and a variety of electrolytes can increase their stability and durability. TiO₂-containing polymer electrolytes can be effectively probed to get higher efficiency. To improve the DSSC's effectiveness and stability, we encourage more study to identify various natural pigments.

REFERENCES:

- [1] M.S. Chowdhury et al.,2020: An overview of solar photovoltaic panels' end-of-life material recycling.
- [2] S. Alhamed, M., Issa, A.S. and Doubal, A.W., 2012. Studying of natural dyes properties as photo-sensitizer for dye sensitized solar cells (DSSC). *Journal of Electron Devices*, 16(11), pp.1370–1383.
- [3] Calogero, G., Bartolotta, A., Di Marco, G., Di Carlo, A. and Bonaccorso, F., 2015. Vegetable-based dye-sensitized solar cells. *Chemical Society Reviews*, 44(10), pp.3244–3294.
- [4] Wu, J., Lan, Z., Hao, S., Li, P., Lin, J., Huang, M., Fang, L. and Huang, Y., 2008. Progress on the electrolytes for dye-sensitized solar Cells. *Pure and Applied Chemistry*, 80(11), pp.2241–2258.
- [5] E. Ndzibah, G. Andrea Pinilla-De La Cruz, A. Shamsuzzoha, et, al, 2022: End of life analysis of solar photovoltaic panel: roadmap for developing economies.
- [6] Sahare, S., Veldurthi, N., Singh, R., Swarnkar, A., Salunkhe, M. and Bhave, T., 2015. Enhancing the efficiency of flexible dye-sensitized Solar cells utilizing natural dye extracted from *Azadirachta indica*. *Materials Research Express*, 2(10), p.105903.
- [7] V.S. Prabhu, S. Shrivastava, K. Mukhopadhyay et, al 2021: Life Cycle Assessment of Solar Photovoltaic in India: A Circular Economy Approach, *Circ. Econ. Sustain*.
- [8] O'regan, B. and Grätzel, M., 1991. A low-cost, high-efficiency solar Cell based on dye-sensitized colloidal TiO₂ films. *Nature*, 353(6346), pp.737–740.
- [9] Zhou, H., Wu, L., Gao, Y. and Ma, T., 2011. Dye-sensitized solar Cells using 20 natural dyes as sensitizers. *Journal of Photochemistry And Photobiology A: Chemistry*, 219(2–3), pp.188–194.
- [10] Moustafa, K., Rekaby, M., El Shenawy, E. and Khattab, N., 2012. Green dyes as photosensitizers for dye-sensitized solar cells. *Journal Of Applied Sciences Research*, 8(8), pp.4393–4404.
- [11] Jasim, K.E., 2012. Natural dye-sensitized solar cell based on Nanocrystalline TiO₂. *Sains Malaysiana*, 41(8), pp.1011–1016.
- [12] Narayan, M.R., 2012. Dye sensitized solar cells based on natural Photosensitizers. *Renewable and Sustainable Energy Reviews*, 16(1), pp.208–215.
- [13] Adedokun, O., Titilope, K. and Awodugba, A.O., 2016. Review on Natural dye-sensitized solar cells (DSSCs). *International Journal of Engineering Technologies*, 2(2), pp.34–41.
- [14] Davies, K., 2009. *Annual Plant Reviews, Plant Pigments and Their Manipulation*. John Wiley & Sons. Vol. 14.
- [15] M.A. Franco, S.N. Groesser, et, al, 2021: A Systematic Literature Review of the SPV Value Chain for a Circular Economy, *Sustainability*.
- [16] Andualem, A. and Demiss, S., 2018. *Edelweiss Applied Science and Technology*, 2(1), pp.145–150.